EFFECTS OF CHEMICAL TREATMENTS ON HIGH PERFORMANCE POLY(P-PHENYLENE BENZOBISOXAZOLE) FIBERS

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SUMMARY: The adhesion between fiber and matrix in a composite system is a primary factor for stress transfer from matrix to fiber. Poor adhesion is generally the result of chemically inactive surface and relatively smooth surface of the reinforcement fiber. In this study, we examined the effects of chemical treatment on the surface of poly(*p*-phenylene benzobisoxazole) or PBO fibers. Kevlar fibers and carbon fibers were also studied for comparison. The changes in fiber topography and surface elemental compositions were detected using scanning electron microscopy (SEM) and electron spectroscopy for chemical analysis (ESCA). The results showed that the surface free energy varied with treatment intensity, treatment time and type of chemical treatment. The surface nitrogen-to-carbon and oxygen-to-carbon ratios were significantly increased. In addition, the surface free energy of PBO fiber was increased by 35% with methanesulfonic acid (60%, 36h) and by 14% with nitric acid (60%, 36h).

KEYWORDS: Fibers, Chemical treatment, Surface free energy, Poly(*p*-phenylene benzobisoxazole) (PBO), Electron spectroscopy for chemical analysis (ESCA)

INTRODUCTION

The adhesion between fiber and matrix in a composite system is a primary factor for stress transfer from matrix to fiber. Poor adhesion is generally the result of chemically inactive surface and/or relatively smooth surface of the reinforcement fiber. Fiber surface treatment processes provide modified fibers with improved wettability and fiber/matrix adhesion bonding through higher surface free energy, surface roughness, and polar group content on the surface of fiber [1-5].

Poly(*p*-phenylene benzobisoxazole) or PBO is a newly developed high-performance rigid-rod polymeric material with potential application as reinforcement fiber for composites. The thermal stability, stiffness, and tensile strength of PBO fiber surpasses those of other current polymers [6-12]. Fig. 1 shows the thermal behavior of several polymers using thermo-

gravimetric analysis. However, PBO fiber surface is fairly inert and the adhesion between the fiber and epoxy matrix is relatively poor. The possible surface treatment routes, including chemical treatment, plasma treatment, electrolytic oxidation, and coupling agents, still need to be investigated.

In this study, the effects of chemical treatment process on the surface of PBO fibers were examined. Kevlar fibers and carbon fibers were also studied for comparison. The changes in fiber surface topography and surface elemental compositions were detected using scanning electron microscopy (SEM) and electron spectroscopy for chemical analysis (ESCA). The results in dynamic surface free energy components would be discussed.

EXPERIMENTAL

The fiber samples were washed and dried before used in the chemical treatment process. They were washed subsequently in tetrahydrofuran (THF), methanol, and distilled water, and then dried in a vacuum oven overnight. The chemical treatment agents included methanesulfonic acid (MSA) solution and nitric acid (HNO_3) solution, both 60 wt% acid in aqueous solution. The samples were then treated for 12 h, 24 h, and 36 h at about 22 . The surface free energy was analyzed using Cahn dynamic contact angle analysis system. Five contact liquid media were used in the experiments, including n-hexadecane (N) , dimethyl sulfoxide (D), formamide (F), ethylene glycol (E) and water (W). The surface elemental compositions were determined by electron spectroscopy for chemical analysis (Physical Electronics ESCA PHI1600). The fiber surface topography was revealed by a scanning electron microscope (JEOL JSM-5410).

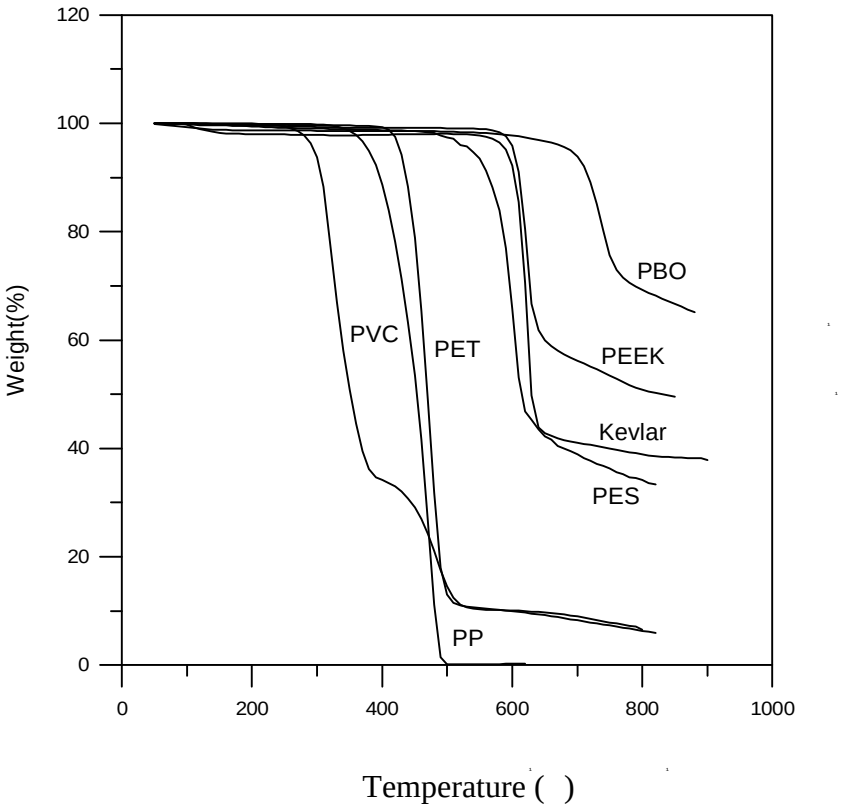

Fig. 1: Thermal stability of various polymers

RESULTS AND DISCUSSION

Table 1 showed the measured contact angles of PBO fiber samples with the five contact media. The standard deviations were also given in parentheses. The calculated surface free energy components were listed in Table 2. In general, they increased with increasing treatment time (Fig. 2). However, the polar component (γ^p) of surface free energy increased more than the dispersive component (γ^d), especially in the MSA system, indicating a much stronger chemical interaction.

Table 1: Measured contact angles of PBO fibers

	N	D	F	E	W
PBO	36.0 (2.0)	33.8 (4.3)	54.7 (4.3)	41.8 (2.6)	51.7 (5.2)
MSA					
12h	31.9 (1.1)	21.4 (1.2)	45.8 (1.6)	39.6 (2.0)	43.7 (2.1)
24h	25.1 (1.0)	17.5 (1.1)	36.0 (1.8)	33.2 (1.3)	30.4 (2.4)
36h	15.3 (0.7)	12.9 (1.0)	25.8 (1.2)	15.4 (1.2)	27.5 (1.9)
HNO_3					
12h	34.8 (2.9)	30.9 (0.5)	50.6 (1.5)	34.8 (1.5)	42.9 (0.9)
24h	29.7 (1.1)	28.1 (1.0)	44.4 (2.3)	30.6 (0.8)	48.8 (1.0)
36h	25.5 (1.4)	22.7 (1.3)	36.5 (0.3)	31.9 (1.3)	44.6 (1.8)

Table 2: Calculated surface free energy components of PBO fibers (mJ/)

Free Energy	↑	↓	γ^d	γ^p	$\gamma=\gamma^d+\gamma^p$
PBO	4.18	5.08	17.5	25.8	43.3
MSA					
12H	4.28	5.49	18.3	30.1	48.4
24H	4.26	6.13	18.2	37.6	55.8
36H	4.48	6.2	20.1	38.4	58.5
HNO_3					
12H	4.1	5.6	16.8	31.4	48.2
24H	4.4	5.2	19.4	27.1	46.5
36H	4.5	5.4	20.3	29.2	49.5

γ^d = dispersion (nonpolar)

γ^p = polar

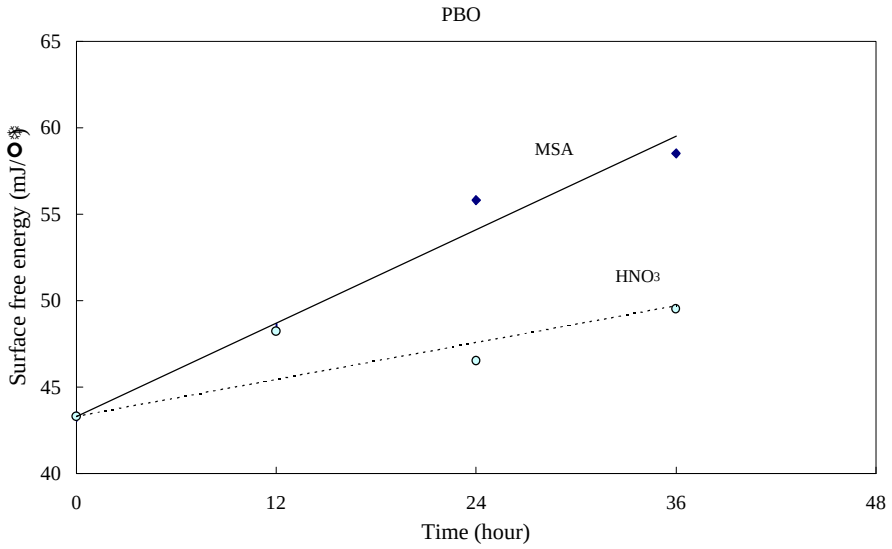

Fig. 2: Effect of treatment time on total surface free energy of PBO fibers

The treatment processes introduced polar groups onto fiber surface and roughened the surface of fibers, which increased the total contact surface area. ESCA results of PBO fiber samples were also shown in Table 3. The sampling depth was around 5 nm and the surface composition could be very different from the bulk composition. The theoretical values were calculated based on chemical formula of PBO. The surface nitrogen-to-carbon and oxygen-to-carbon ratios were increased significantly using various treatment processes. In addition, the surface free energy of PBO fiber was increased up to 35% by MSA (60 wt%) for 36 h. The increase was 14% by HNO_3 (60 wt%) for the same treatment time.

Table 3: Surface elemental compositions of PBO fibers

Type of Surface Treatment	Atomic Percent (%)				Atomic Ratio	
	C	O	N	S	N/C	O/C
Theoretical	71.80	13.66	11.96	-	0.166	0.190
Control	79.18	16.95	3.86	-	0.049	0.214
MSA	73.86	20.28	4.77	1.08	0.065	0.275
HNO_3	76.05	17.19	6.75	-	0.089	0.226
O_2-plasma	73.09	22.59	4.32	-	0.059	0.309

Similar experiments were also carried out using Kevlar fibers (Fig. 3) and carbon fibers (Fig. 4). In Kevlar fibers, the total surface free energy was increased up to 32% (MSA) and 27% (HNO_3). In Carbon fibers, the total surface free energy was increased up to 38% (MSA) and 42% (HNO_3).

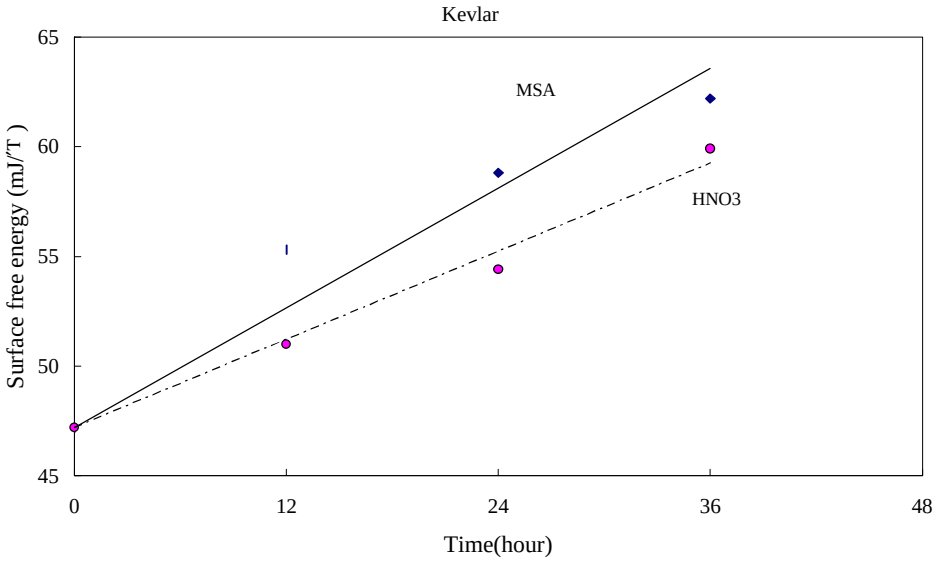

Fig. 3: Total surface free energy of Kevlar fibers

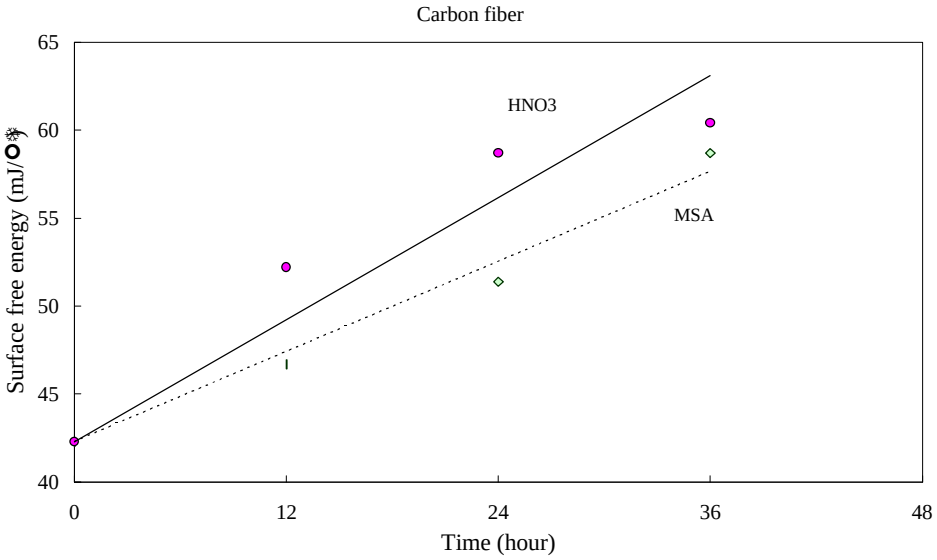

Fig. 4: Total surface free energy of carbon fibers

In addition, SEM micrographs of PBO fibers were shown in Fig. 5. MSA seemed to have interacted with PBO fiber surface molecules and roughened the surface, which could increase the total contact surface area.

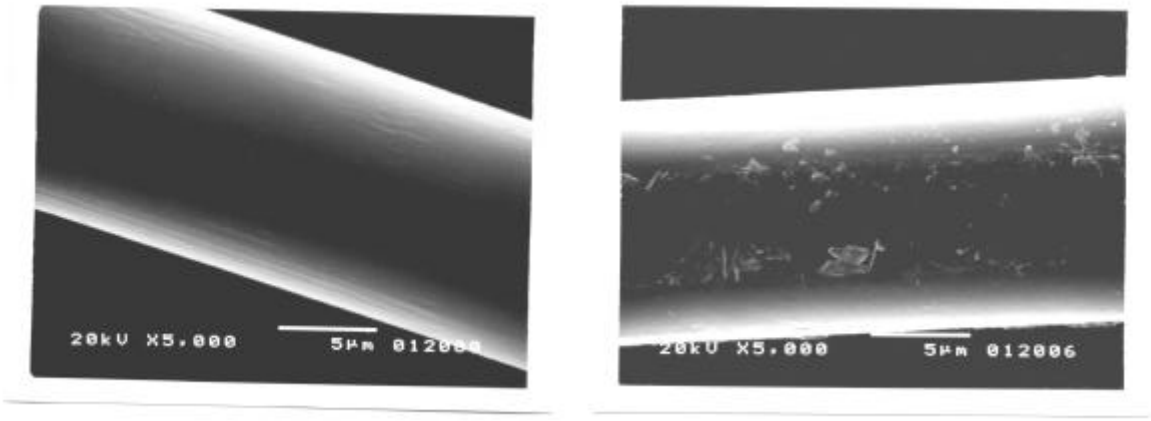

Fig. 4: SEM micrographs of PBO fibers: before (left) and after (right) MSA treatment

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