

EVAPORATION-INDUCED SURFACE MODIFICATION OF PBO FIBER AND INVESTIGATION ITS UV RESISTANCE

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ABSTRACT

Poly(p-phenylene benzobisoxazole) (PBO) fibers were modified with evaporation-induced surface modification method. Through this method, the PEI (Polyetherimide) chains with the encapsulated nano-TiO₂ were firmly adsorbed on the fiber surface. Surface morphologies of the fibers were examined using scanning electron microscopy (SEM). Surface chemical composition of PBO fibers were analysed by Energy Dispersive X-ray spectrometry (EDX). Thermogravimetry (TG) and single filament tensile strength (TS) were also characterized. The results indicate that the evaporation-induced surface modification enhanced surface roughness and changed surface morphologies of PBO fibers by absorption of PEI chains with the encapsulated nano-TiO₂. And it improved the poor interfacial adhesion and UV resistance of PBO fibers.

1 INTRODUCTION

Poly(p-phenylene benzobisoxazole) (PBO) fiber with excellent properties, such as high tensile strength, high modulus, high thermal stability and light weight, was widely used as reinforcements of advanced composites aerospace, marine and automobile industries.[1, 2] However, due to its chemical inactivity and surface smooth, PBO fiber has a poor interfacial adhesion with matrix resin, which greatly restricts its applications [3-5]. Great efforts have been made towards the improvement of the interfacial adhesion between PBO fiber and matrix resin including chemical treatment [3, 4, 6], plasma treatment, electrolytic treatment, enzymatic surface treatment, coupling agents and surface grafting treatment.

In this work, in order to endow PBO fiber with better UV resistance and better interfacial adhesion, we prepared dilute solution containing PEI coated nano-TiO₂ and free PEI chains, and then immersed PBO fiber in the solution; finally put the impregnated PBO fiber in fume hood for solvent evaporation. We called this process evaporation-induced surface modification method.

2 EXPERIMENTAL PROCEDURES

2.1 Fabrication of Nano-TiO₂ treatment solution

The Nano-TiO₂ (STR-100N, SAKAI, Japan) treatment solution was performed on TiO₂ nanoparticles in NMP (KANTO, Japan) at a concentration of 0.1wt.% (nanoparticles: solvent). Following ultrasonication in an ice bath for 20 min, γ -MPS (100wt.% of the TiO₂ nanoparticles) was added and then stirred for 6h at ambient temperature. PEI particles (100wt.% of the TiO₂ nanoparticles, Acros Organics, USA) were added to the mixture and stirred at 70 °C for 2h. Subsequently, nano-TiO₂ treatment solution was obtained.

2.2 Evaporation-induced surface modification of PBO fiber

A bundle of untreated PBO fibers (HM, Toyobo, Japan) was immersed in NMP solvent and ultrasonic vibrated for 15 min. Then put the infiltrated PBO fibers into the nano-TiO₂ treatment solution as fabricated in section 2.1. After ultrasonic vibration in an ice bath for different time (10min, 20min, 30min), PBO fibers were dipped for 24 hours. Finally put pretreated PBO fibers on the Teflon plate in fume hood at ambient temperature for evaporation a week. Then we obtained the treated-PBO fiber as shown in Table 1.

Sample	Ultrasonic vibration in NMP solvent/min	Ultrasonic vibration in nano-TiO ₂ treatment solution/min
PBO-10	15	10
PBO-20	15	20
PBO-30	15	30

Table 1: Formulation process of treated PBO fibers.

2.3 Characterization

Surface morphologies of the fibers were examined using scanning electron microscopy (JSM-6010LA, JEOL, Japan). Surface chemical composition of PBO fibers were analyzed by Energy Dispersive X-ray spectrometry (JSM-6010LA, JEOL, Japan). Thermogravimetry (Thermo plus TG-8120, RIGAKU, Japan) was also characterized. The adhesive durability of the modified components was evaluated by ultrasonic exposure test, which was carried out in water for 30 min with an ultrasonicator (300W, 38kHz, US-106, SND Co., Ltd, Japan).

The samples were subjected to UV-irradiation (365 nm) using a high-pressure mercury lamp (100 W, HLR100T-2, SEN Light CORP, Japan). The intensity of incident light (40 mW/cm^2) was measured using an Ultraviolet Radiometer UIT-201 (USHIO, Japan). Single filament tensile strength (TS) before and after UV irradiation was carried out using a EZ-SX 50N tensile tester (Shimadu, Japan), 35 specimens at least were tested.

3 RESULTS AND DISCUSSION

3.1 SEM observation

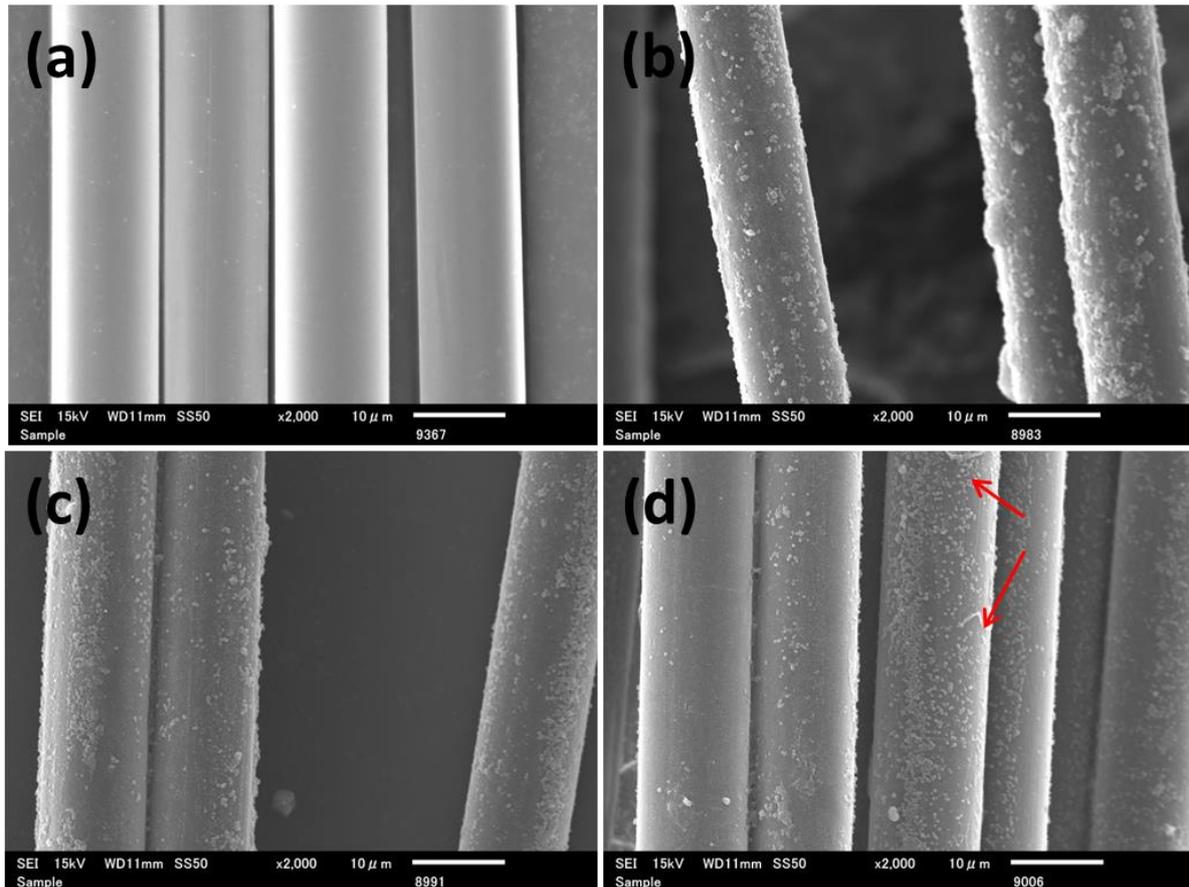


Fig. 1. SEM micrographs of PBO fibers: (a) untreated; (b) PBO-10; (c) PBO-20; (d) PBO-30.

The adhesion properties of the interface between the fiber and the resin were affected significantly by the fiber surface morphology. The surface morphology was observed using SEM and the results are shown in Fig. 1. It is evident from the figure that the surface of untreated PBO fiber is neat and smooth (Fig. 1a). Fig. 1b~d were PBO fibers treated with different ultrasonic vibration time in nano-TiO₂ treatment solution. As we can see from Fig. 1b, besides uniformly distributed nano-TiO₂ and PEI nanospheres, there were many micro clusters due to the aggregation of nanoparticles. nano-TiO₂ and PEI nano microspheres both were uniformly distributed on the fiber surface as shown in Fig. 1d, but the cortex of PBO fiber was damaged after 30 min ultrasonic vibration time in nano-TiO₂ treatment solution. And we can see micro-fibrils on the fiber surface marked with the red arrows. Fig. 1c was PBO fiber with 20 min ultrasonic vibration in nano-TiO₂ treatment solution. As shown in Fig. 1c, there were many PEI nanospheres with average diameter at 400 nm; under which is the coating with uniformly distributed nano-TiO₂.

3.2 EDS analysis

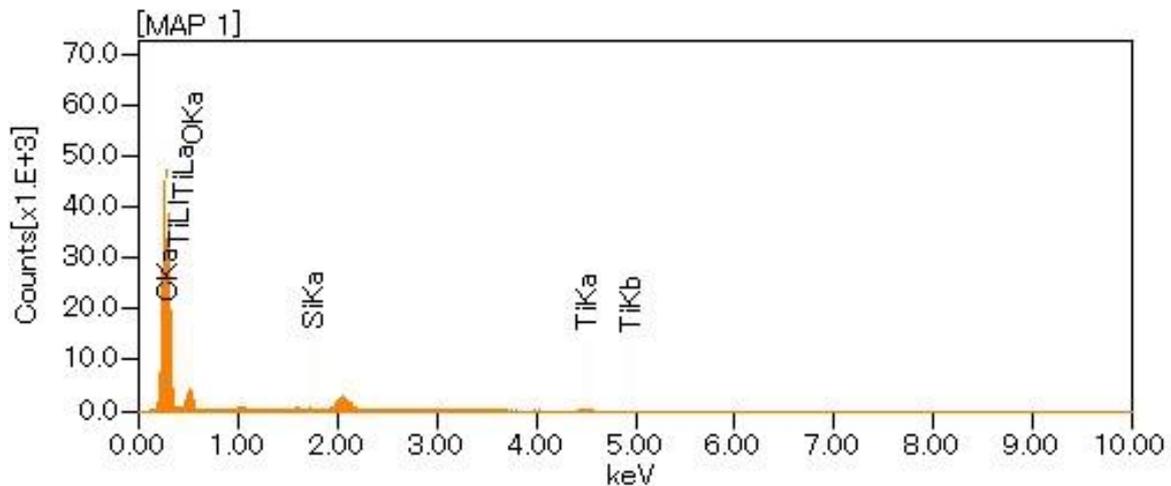


Fig. 2. EDS of PBO-20 surface

Fig. 2 shows EDS analysis of PBO-20 surface, in addition to C and O elements we also found Si and Ti elements in the Energy Dispersive Spectroscopy. Si element was derived from γ -MPS which reacted with hydroxyl groups on nano-TiO₂ particles surface; And Ti element belonged to nano-TiO₂ particles. Both Si and Ti elements were come from the modified nano-TiO₂ particles. From these two element analysis we can find that the modified nano-TiO₂ particles we prepared were absorbed on the PBO surface. In addition, the corresponding elements and contents in the EDS analysis were listed in Table 2. Compared to the C and O elements, the content of Si or Ti element was very small.

Elements	Weight (%)	Atom (%)
C	80.42	84.91
O	18.72	14.84
Si	0.12	0.06
Ti	0.74	0.20
Total	100.00	100.00

Table 2: The corresponding elements and contents of treated PBO-20 surface

3.3 TG analysis

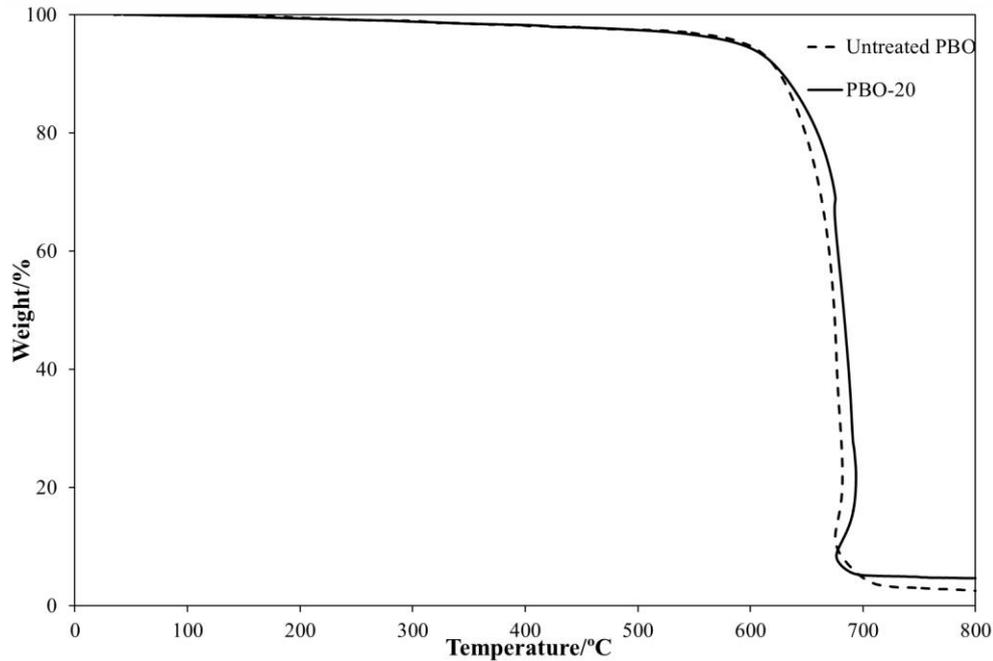


Fig. 3. TG curves of PBO fibers: untreated PBO and PBO-20.

The thermal stability of untreated and modified PBO fibers is studied by TG, as depicted in Fig. 3. The results indicated that all samples exhibit excellent thermal stability. For untreated PBO fiber, the weight loss before 300 °C corresponds to elimination of water and residual solvent, and the obvious weight loss between 600 °C and 800 °C was due to the decomposition of PBO fiber [2]. Compared to untreated PBO fiber, there was more weight loss in the TG curve of PBO-20 from 500 °C to 600 °C. It was due to the decomposition of PEI, which was the component of the surface coating and the nanospheres distributed on PBO-20 fiber surface. However, the curve of untreated PBO fiber dropped faster than that of PBO-20 after 600 °C until the curve become flat. It was because of the coating of inorganic nanoparticles on the fiber surface, which improved the thermal stability of PBO-20.

3.4 Adhesive durability

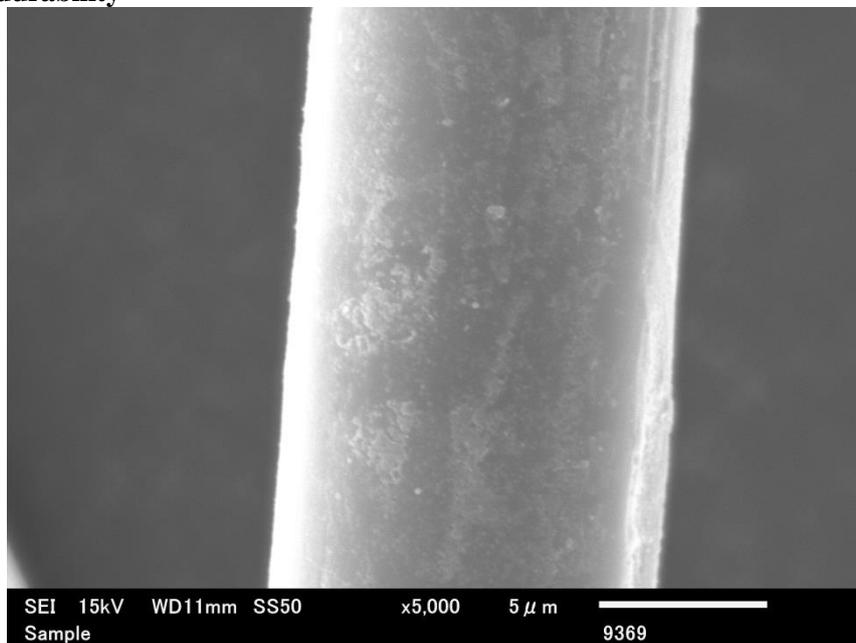


Fig. 4. SEM image of PBO-20 after ultrasonic exposure for 30 min.

The adhesive durability of nanoparticle on the modified fiber surface has been a very difficult problem. Here the adhesive durability of modification coating on PBO fiber surface was evaluated by ultrasonic exposure test as shown in Fig. 4. Contrast Fig. 1c and Fig. 4, we can find that the nanospheres basically all cleaned out. That was because the contact area between the nanospheres and the coating or the fiber surface was relatively small. They were easier to fall off under the action of external force after ultrasonic exposure for 30 min. But we can see that there were still uniform nano-TiO₂ in most area of the fiber surface. This indicated that nanoparticles absorbed on the PBO fiber surface using evaporation-induced surface modification method had some adhesive durability.

3.5 Mechanical properties

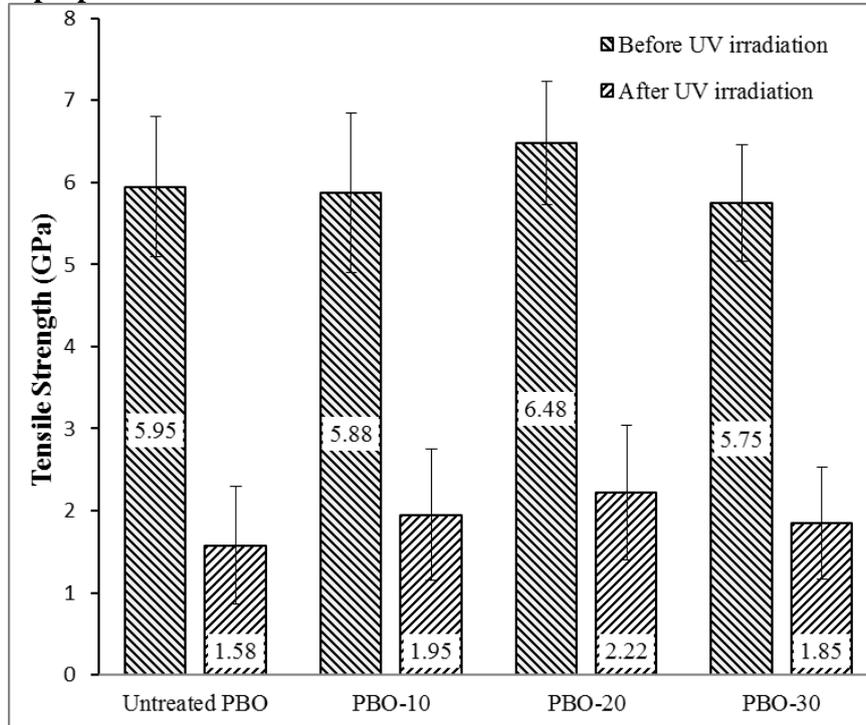


Fig. 5. Single fiber tensile strength of PBO fibers before and after UV irradiation.

The single fiber tensile strength of PBO fibers before and after UV irradiation is presented in Fig. 5. Compared to 5.95 GPa of untreated PBO fiber, the tensile strength of PBO-20 was increased to 6.48 GPa. That was because after solvent was completely evaporated, the nano-TiO₂ particles with PEI chains uniformly distributed on the fiber surface and then formed the thin uniform coating. Kitigawa [7] demonstrate that PBO fiber is formed from microfibrils and contain many capillary-like microvoids, which exist between microfibrils. And there is void-free region in the very surface of the fiber. Because of this special core-shell structure, even small damages to the PBO fiber's cortex may bring about disproportionately large effects to its fiber strength. The thin uniform coating worked like a protective coating, so the structure of the cortex is hard to be destroyed in the process of drawing. But as we can see from Fig. 5 the tensile strength of PBO-10 decreased to 5.88 GPa. That must be because the agglomeration of nano particles, the coating could not completely and uniformly covered the fiber surface. And the ultrasonic vibration process would make fibrillation which damaged the fiber. This phenomenon was clearly shown in the Fig. 1c. The lowest tensile strength (5.75 GPa) of PBO-30 was also verified by this view. Although the surface had a uniform protective coating, the PBO-20 fiber had been damaged by ultrasonic vibration and produced microfibrils.

After UV irradiation (40 mW/cm²) for about 30h, the tensile strength of PBO samples was obviously decreased as shown in Fig. 5. The tensile strength of untreated PBO fiber decreased to 1.58 GPa, only 26.6% of the original strength. The tensile strength of the treated PBO fibers was also decreased, but obviously better than untreated PBO fiber. Due to the coating with uniform nano-TiO₂ particles which have good absorption and scattering of UV light, the tensile strength after 30h UV

irradiation of PBO-20 was 2.22 GPa, which was 40.5% higher than that of the untreated. But with the long time ultrasonic vibration process, the tensile strength after 30h UV irradiation of PBO-30 was just 1.85 GPa, which was 17.1% higher than that of the untreated.

4 CONCLUSIONS

In summary, a uniform coating with nano-TiO₂ particles was absorbed on PBO fiber surface by evaporation-induced surface modification method. The SEM and EDS analysis shown that nano-TiO₂ particles were uniformly distributed on the fiber surface. Meanwhile, the uniform coating with nano-TiO₂ particles had some adhesive durability. Furthermore, the single fiber tensile strength of treated PBO fiber increased both before and after UV irradiation. This method is simple and reversible, and shows great promise for surface modification of smooth and chemically inert surface.

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