

Poly(*p*-phenylene benzoxazole) Fiber Chemically Modified by the Incorporation of Sulfonate Groups

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ABSTRACT: Two kinds of modified poly(*p*-phenylene benzoxazole) (PBO), the copolymer of TPA (SPBO) and *p*-SPBO, containing ionic groups in the macromolecular chains were obtained by copolymerization from 1,3-diamino-4,6-dihydroxybenzene dihydrochloride (DAR) and terephthalic acid (TPA), with the addition of selected amounts (1.5–5.0% molar ratio over DAR) of 5-sulfoisophthalic acid monosodium salt or sulfoterephthalic acid monopotassium salt in place of the TPA, respectively, in poly(phosphoric acid) (PPA). The resultant PBO/PPA, SPBO/PPA, and *p*-SPBO/PPA lyotropic liquid-crystalline

solutions were spun into fibers by a dry-jet wet-spinning technique. Chemically modified PBO fibers with sulfonate salt pendants in the polymer chains were obtained for the first time. The surface wetting behavior and interfacial shear strength between the fiber and epoxy resin were investigated. The interference of sulfonate salt pendants on the crystalline morphology was measured. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3133–3139, 2008

Key words: copolymerization; fibers; high performance polymers; surfaces

INTRODUCTION

Poly(*p*-phenylene benzoxazole) (PBO) is one kind of rigid rod polymeric material. PBO fiber, developed by Toyobo Co., Ltd. (Osaka, Japan), shows superior tensile strength and excellent thermal stability as well as flame resistance.^{1,2} So, PBO fiber has great potential applications as reinforcement fibers for advanced composites. However, the fiber surface free energy and the interfacial adhesion between PBO fiber and matrix resins are not sufficient for practical uses. The poor surface free energy is generally the result of the chemically inactive and/or smooth surface of the PBO fibers. Therefore, several surface modification methods have been proposed, including chemical treatment, plasma treatment, corona treatment, and coupling agents.^{3–7} For example, Wu and Shyng³ studied the surface modification and interfacial adhesion of PBO fiber by methanesulfonic acid treatment and oxygen plasma treatment. The results show that the surface free energy could be significantly increased by 34%, whereas the interfacial shear strength (IFSS) was improved by 22% with the proposed methane sulfonic acid (MSA) treatment process.³ When oxygen plasma was used to treat PBO fiber, the surface element oxygen-to-carbon ratio was increased. The total surface free energy of the PBO fiber was increased by 41% with 70w oxygen plasma treatment for 5 min. The IFSS of a model

PBO/epoxy composite increased from 34.7 to 44.7 MPa after the oxygen plasma treatment for 5 min.⁴ Wang and coworkers^{6,7} also reported that corona-treated PBO fibers may give a 25.6% improvement in IFSS. Compared with surface modification, the preparation of a PBO polymer with active groups in the macromolecular chains is more advisable.

In this study, modified PBO fibers were prepared by the chemical incorporation of ionic groups into polymer chains. The wetting behavior of the obtained fiber and the IFSS between the fiber and epoxy was studied. The influence of the ionic groups on the aggregating structure of the polymer chains and the tensile strength was also investigated.

EXPERIMENTAL

Preparation of the samples

PBO was prepared by the polycondensation of 1,3-diamino-4,6-dihydroxybenzene dihydrochloride resorcinol dihydrochloride (DAR; synthesized in our laboratory) and terephthalic acid (TPA, Hyosung Co., Ltd., Seoul, Korea) in poly(phosphoric acid) (PPA). The detailed procedure was performed according to the literature.^{8,9} SPBO and *p*-SPBO were obtained by the same method with certain amounts of 5-sulfoisophthalic acid monosodium salt (Fisher Scientific, PA) and sulfoterephthalic acid monopotassium salt in place of the TPA, respectively. The molar ratios of the third monomer over DAR were 0.015, 0.03, and 0.05.

The polymerization solutions were directly spun into fibers via a dry-jet wet-spinning technique in

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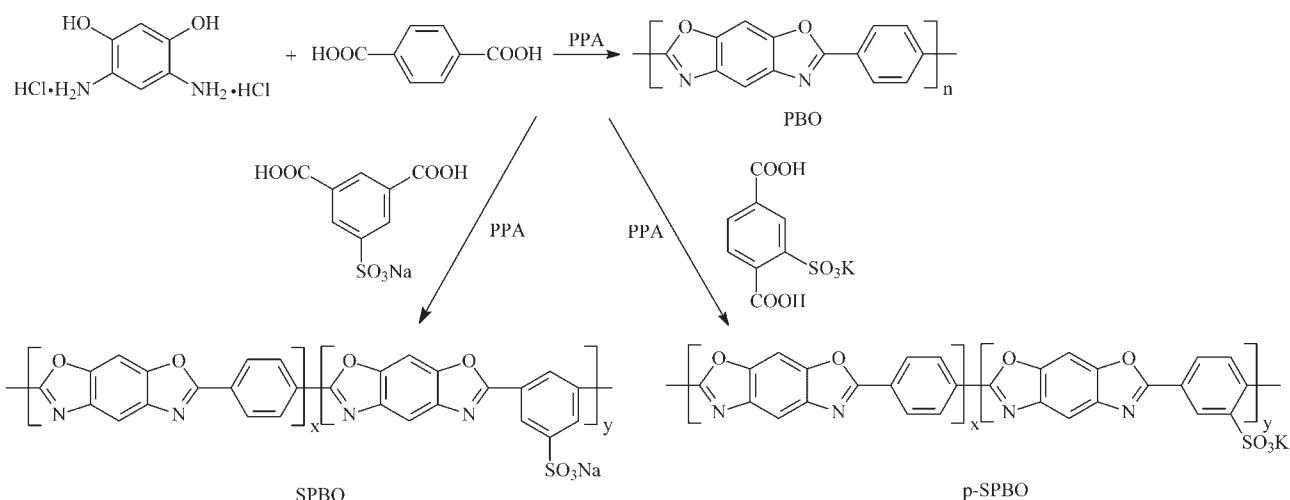


Figure 1 Polymerization of PBO and the modified PBO polymers.

our laboratory. Fiber spinning was performed at 170°C through an 18-hole spinneret with a hole size of 0.25 mm. An air gap with proper length was applied before the coagulation bath, which contained water at room temperature. The fiber was taken up at a speed of 70–100 m/min, washed completely in running water, and then dried at 100°C *in vacuo*.

Characterization

The surface wetting behavior of PBO and the modified PBO fiber was analyzed from the measured contact angles between the fiber surface and two test liquids, water and ethanol, with an OCA40 micro dynamic contact angle analysis system (Dataphysics Instruments Co., Ltd., Filderstadt, Germany) and with a JF99A powder wetting process measurement (Powereach, Co., Ltd., Shanghai, China). The IFSS between the fiber and epoxy resin was determined by a microbond fiber pullout test. The surface morphology of the pulled-out fiber from the epoxy was observed by a JSM-5600LV scanning electron microscope (JEOL DATUM Ltd., Tokyo, Japan).

X-ray diffraction measurements were performed on a Rigaku D/max-2550PC X-ray diffractometer (Rigaku Co., Tokyo, Japan) with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$), with a step size of 0.02° and a step time of 0.12 s. Average crystal sizes for the diffraction planes in the case of the polymer were estimated from the measured widths of the diffraction peaks with the use of Scherrer's formula.

RESULTS AND DISCUSSION

Synthesis of PBO, SPBO, and *p*-SPBO and preparation of the fibers

PBO polymer was prepared by the polymerization of 4,6-diamino-1,3-benzenediol and TPA. Because of

the high instability of 4,6-diamino-1,3-benzenediol, usually 4,6-diamino-1,3-benzenediol dihydrochloride is received as a reactive monomer. So, dehydrochlorination will take place before polymerization, as illustrated in Figure 1.

It is very common for much foam to form with the development of dehydrochloride in the reactor. This foam formation must be limited because solid monomer particles (e.g., TPA particles) could adhere in the frame of the stirrer and the inner wall of the reactor together with the foam, especially at high monomer concentrations, which would destroy the strictly chemical stoichiometric quantity of the two monomers. To control the level of foaming, a lower temperature or periodic cooling to 15°C was applied to the reactive mixture by Wolf et al.⁹ Dehydrochlorination takes a very long time in this way. In our study, a novel technique was invented. That is, the dehydrochlorination took place at high pressure ($3\text{--}5 \times 10^5 \text{ Pa}$), as shown in Figure 2. Foaming could be effectively limited in this way, and the dehydrochlorination could be processed at higher temperatures within a shorter time.

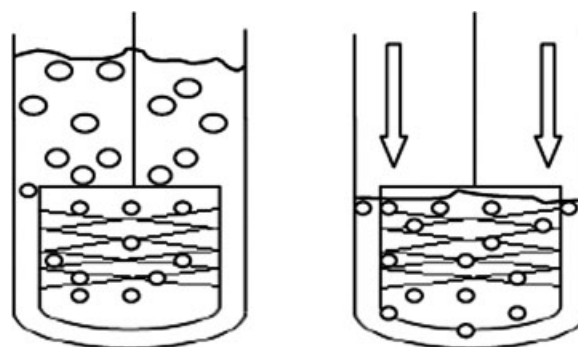


Figure 2 Dehydrochlorination in the atmosphere (left) and at a high pressure (right).

TABLE I
Comparison of the Different Methods of Dehydrochlorination

Dehydrochlorination method	Temperature (°C)	Time needed for the complete loss of HCl (h)	Total time of prepolymerization (h)
Atmosphere	30–60–70–90	80–100	140
High pressure	12	20–30	60

It was easy to realize this technique in practice. A pressure-controlling valve was installed in the reactor. When the pressure in the reactor exceeded the pressure limit of the valve, the valve opened and let the HCl gas escaped gradually. With the escape of the gas, the pressure decreased, and the valve closed again below a certain value of pressure.

The advantage of this technique are distinct. First, the dehydrochlorination proceeds at a higher temperature, and the time for the complete loss of hydrogen chloride is shortened greatly, which favors polymerization efficiency. Table I shows the comparison of dehydrochlorination by different methods.

The second advantage is a guarantee of the stoichiometric amount ratio of reactants and the stability of polymerization, which is essential for obtaining high-molecular-weight PBO polymer at all times.

We applied this technique to prepare the PBO prepolymer, and we used a twin-screw extruder (PSHJ-35-32L/D, JiangYin Xinda Plastics Machinery Co., Ltd., Jiangsu, China) to accomplish the polycondensation of the prepolymer and liquid-crystal spinning at the same time.

An illustration of the reactive-extrusion liquid-crystalline spinning is given in Figure 3. High-performance PBO fiber was obtained in this way.

Chemical composition of the modified PBO

The chemical structures of PBO, SPBO, and *p*-SPBO are shown in Figure 1. The FTIR spectra (Fig. 4) of

PBO and SPBO showed all of the specific absorption peaks of PBO except the one at 625 cm^{-1} , which corresponded to C—S bond absorption.

Contact-angle measurements

Table II shows the measured contact angles between the fiber and water/alcohol; the change in the contact angles with time is also presented in Figures 5 and 6. It was obvious that the contact angles of SPBO and *p*-SPBO with water and ethyl alcohol were smaller than those of PBO with either liquid. The wetting process of water and ethyl alcohol on the SPBO fiber was faster than on the PBO fiber; the same process for *p*-SPBO is not shown to avoid repetition. Also, the wetting process of ethyl alcohol on *p*-SPBO 5% was too fast for us to take a clear photograph for calculation of the contact angle at 0 ms.

Wetting rate

The schematically explanation of the JF99A powder wetting process measurement is given in Figure 7. The fiber was cut into powder form and filled in the glass tube. When the fiber powder filled glass tube contacted the liquid, the wetting took place. The pressure in the glass tube rose. The change in the pressure difference square, which could explain the wetting rate, with time could be read from the

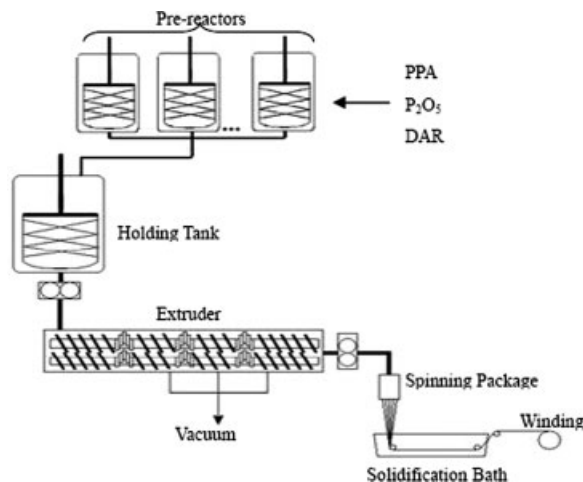


Figure 3 Illustration of reactive-extrusion liquid-crystalline spinning (dry-jet wet spinning).

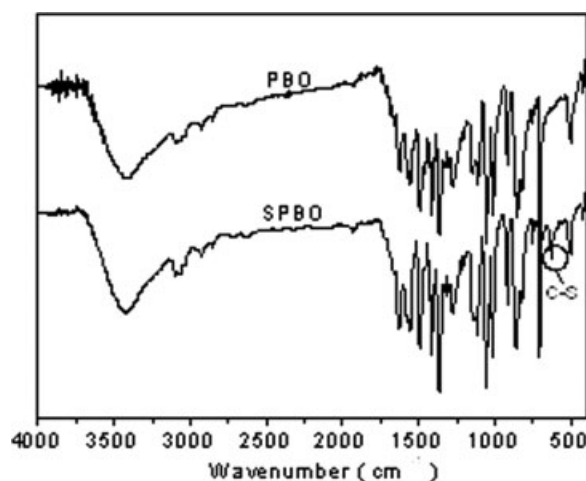


Figure 4 FTIR spectra of PBO and SPBO.

TABLE II
Contact Angles (at 0 ms) of the Test Liquids
on the Fiber Surface

Sample	Water	Ethyl alcohol
PBO	71.4	37.2
SPBO 1.5%	66.3	30.6
SPBO 3.0%	64.3	23.1
<i>p</i> -SPBO 1.5%	66.2	27.2
<i>p</i> -SPBO 3.0%	65.1	25.8
<i>p</i> -SPBO 5.0%	61.9	—

equipment, as shown in Figure 8(a,b). It was clear that the pressure difference square increased greatly.

IFSS

The IFSS between the fiber and epoxy resin was determined by a microbond pull-out test. The IFSS

was improved through the incorporation of ionic groups ($-\text{NaSO}_3$ and $-\text{KSO}_3$), and generally, the IFSS increased with increasing content of ionic groups (Fig. 9). We confirmed that the incorporation of ionic groups in a small amount was effective for improving the IFSS, and the specific interaction between the SPBO macromolecules and epoxy was established, although the mechanism of the specific interaction will require further explanation in the future.

Surface morphologies of the pulled-out fiber

The improvement of the IFSS was observed by scanning electron microscopy. The scanning electron micrographs of the fiber surface after the microbond pull-out test are given in Figure 10. There was still epoxy resin remaining on the SPBO fiber surface after the epoxy droplet was sheared. Otherwise, little

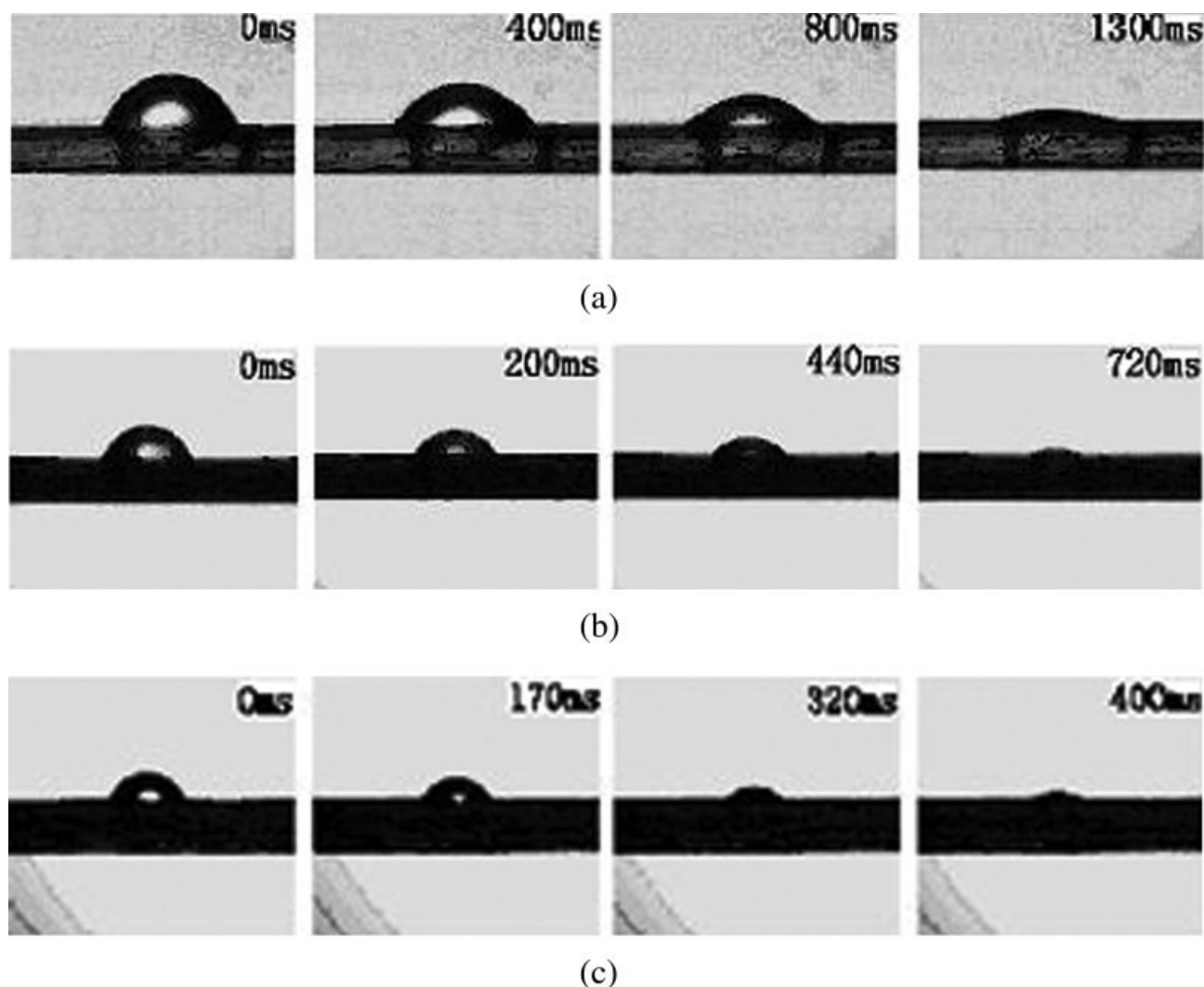


Figure 5 Wetting of water on (a) PBO, (b) SPBO 1.5%, and (c) SPBO 3.0% fibers.

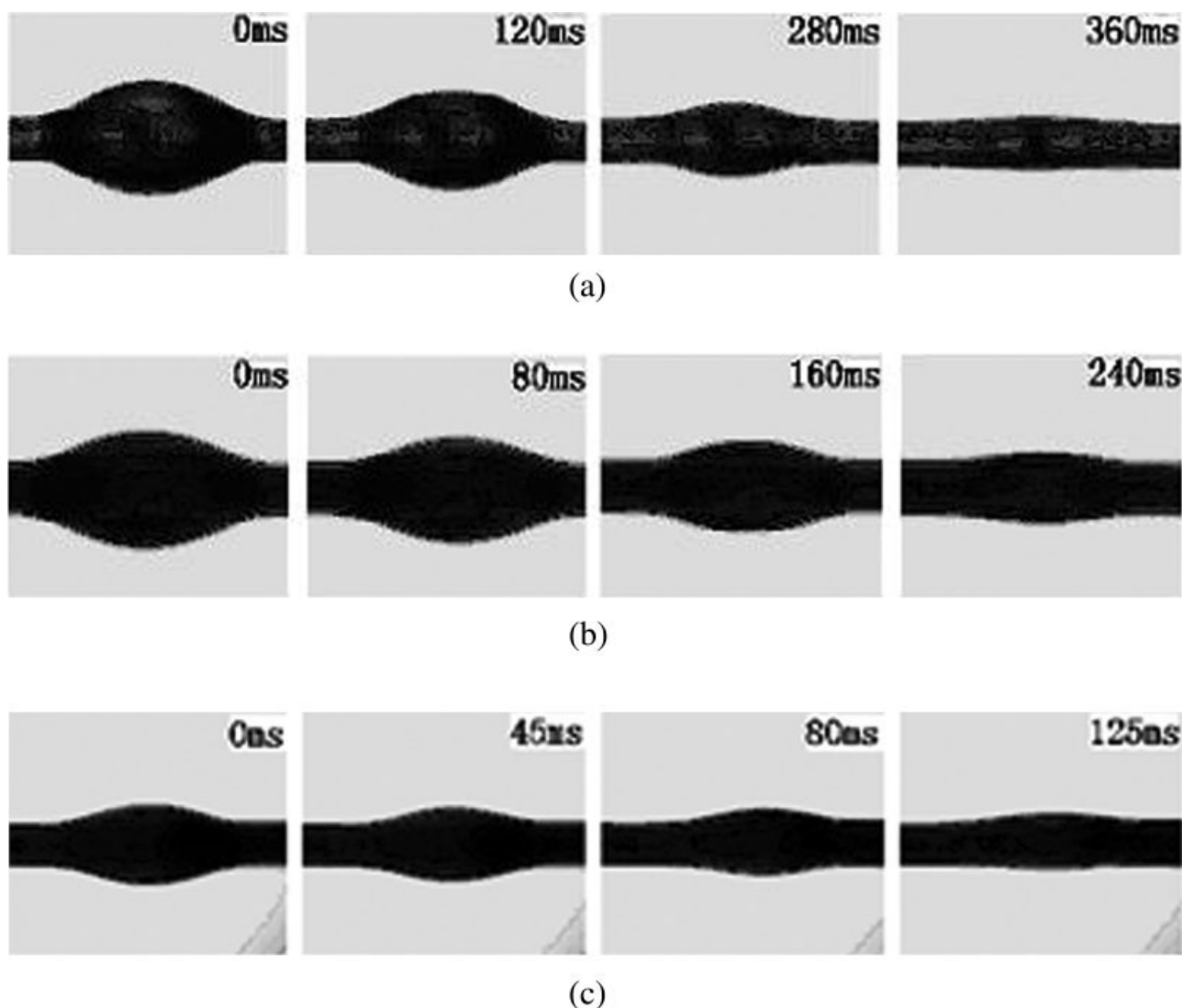


Figure 6 Wetting process of alcohol on (a) PBO, (b) SPBO 1.5%, and (c) SPBO 3.0% fibers.

epoxy resin adhered on the PBO fiber surface. We inferred that the failure mode for the composites changed from fiber/matrix interface adhesive to partly cohesive failure.

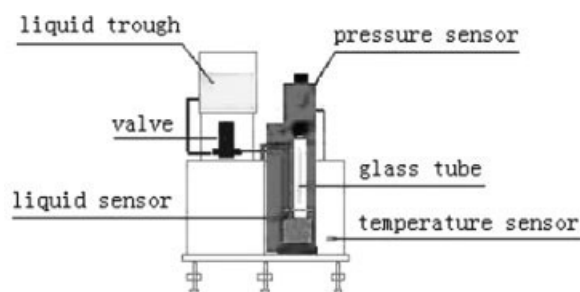


Figure 7 Schematic diagram of the JF99A powder wetting process measurement.

Crystalline structure

The average crystal size of PBO was larger than that of SPBO and *p*-SPBO, as shown in Table III. In our study, the average crystal size of PBO was smaller than the reported value.¹⁰ The main reason was that the PBO fiber was an as-spun fiber without heat treatment. The small crystal size meant a relatively low regional order of macromolecular packing, which could be ascribed to the interference of the sulfonate salt units in the macromolecular chains. At the same time, the PBO modified by the incorporation of sulfoterephthalic acid monopotassium salt had a less negative influence on the ordered aggregation of polymer chains compared to that modified with 5-sulfoisophthalic acid monosodium salt, as the average crystal size of *p*-SPBO was larger than that of SPBO at the same content of sulfonate groups. Thus, we expected that the mechanical properties of

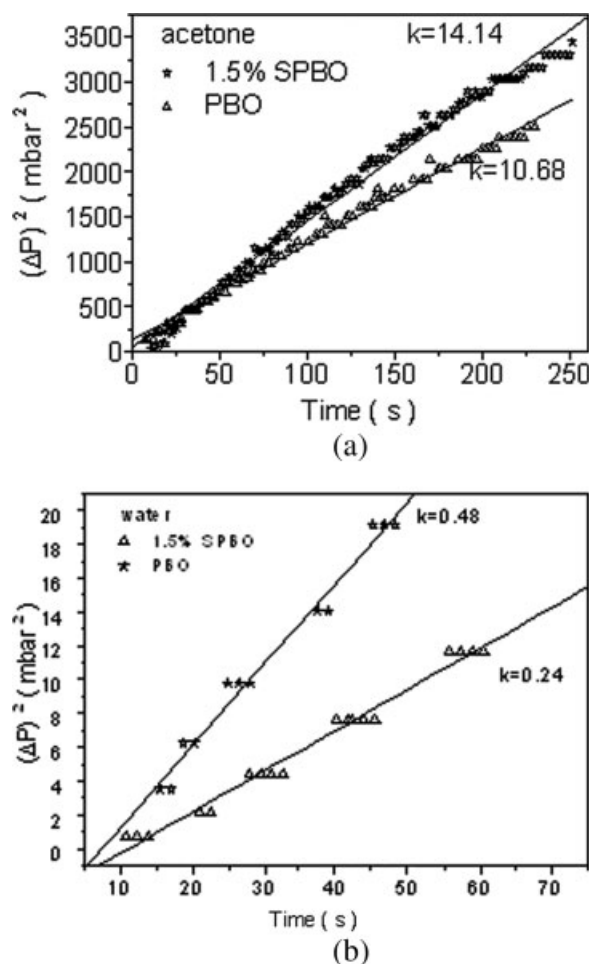


Figure 8 Change in the pressure difference square (ΔP^2) versus time during wetting.

the *p*-SPBO fiber would be better than those of the SPBO fiber.

Tensile strength

As mentioned previously, the *p*-SPBO fiber displayed a higher tensile strength than the SPBO

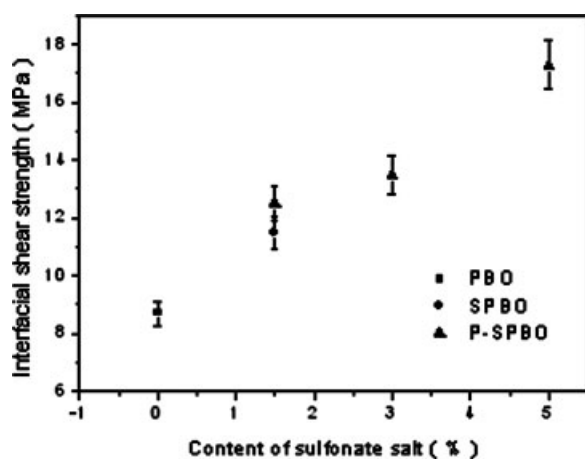
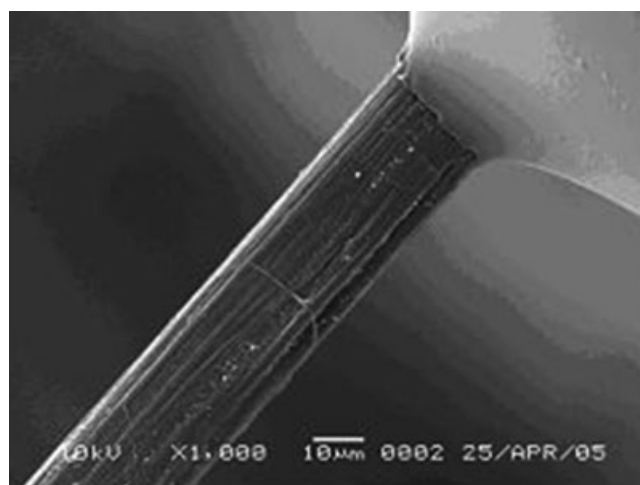
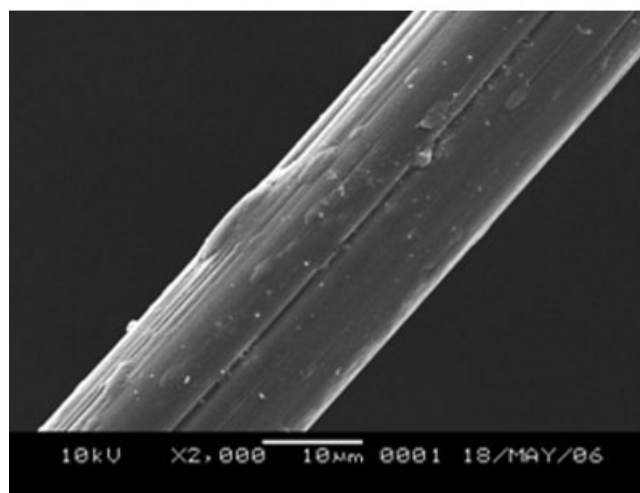


Figure 9 IFSS versus the content of sulfonate groups.



(a)



(b)

Figure 10 Micrographs of the pulled-out fiber surface.

fiber at the same sulfonate salt content, as listed in Table IV.

CONCLUSIONS

Chemically modified PBO fiber was prepared by the incorporation a small amount of ionic groups to polymer chains. The wetting behavior of the modi-

TABLE III
Average Crystal Size (L) of PBO and the Modified PBO Fibers

Sample	$L_{(200)}$ (\AA)	$L_{(010)}$ (\AA)	$L_{(210)}$ (\AA)
PBO	46.9	29.6	38.9
SPBO 1.5%	30.3	25.7	28.4
SPBO 3.0%	27.1	23.5	25.9
<i>p</i> -SPBO 1.5%	40.7	26.4	32.2
<i>p</i> -SPBO 3%	37.5	23.3	29.8
<i>p</i> -SPBO 5%	34.9	23.1	28.9

TABLE IV
Tensile Strength of the Obtained Fibers

Sample	Intrinsic viscosity (dL/g)	Tensile strength (GPa)
PBO	24.5	4.4
SPBO 1.5%	17.4	2.5
SPBO 3.0%	8.9	1.6
<i>p</i> -SPBO 1.5%	21.3	3.3
<i>p</i> -SPBO 3%	18.9	2.5
<i>p</i> -SPBO 5%	18.7	1.7

fied PBO fiber was improved, and the IFSS between the fiber and epoxy increased with increasing content of ionic groups. Comparatively, the incorporation of sulfoterephthalic salt to polymer chains showed a less negative influence on the macromolecular ordered packing and the tensile strength than that of sulfoisophthalic salt.

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