

Preparation and Properties of Novel Boric Acid Modified Poly(aryl ether sulfone) Membranes

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ABSTRACT: In this article, boric acid-modified poly(aryl ether sulfone) (PES-B) membranes were prepared by solution blending, solution casting, evaporation, and programmed temperature curing method for the first time. The chemical modification of poly(aryl ether sulfone) was accomplished by the curing of poly(aryl ether sulfone) with pendent phenyl hydroxide (PES-OH) under the function of boric acid. The reaction mechanisms and the effects of boric acid content were thoroughly investigated. Processing conditions and structures of PES-B were determined by FT-IR spectra. It has been found that the B(OH)₃/PES composite membranes were completely cured after treatment at 300°C for 4 h. When boric acid content was over 4.7%, PES-B membranes presented phase separation and full cross-linking structures. DSC measurements demonstrated that the addition of boric acid had influenced the glass transition temperature of PES-B, which provided the proof of the appearance of cross-linking network structure. TGA results confirmed that the thermal stability of the prepared PES-B composites was improved. Furthermore, the cross-linked composite membranes exhibited excellent mechanical property and solvent resistance. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40860.

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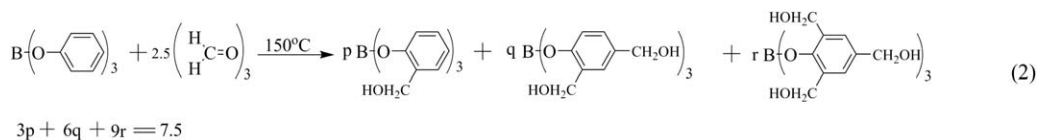
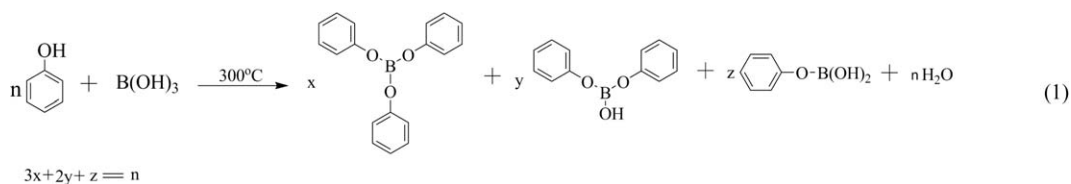
INTRODUCTION

Poly(aryl ether sulfone)s (PES)s is an important class of high-performance engineering plastics owing to their excellent thermo-mechanical stability and chemical resistance. It has been widely used in various industrial applications, such as electronics, machinery, automobile, food, and medical equipments, paints and so on.^{1–3} However, because of their amorphous nature, poly(aryl ether sulfone)s is readily soluble in common solvents such as *N*-methylpyrrolidone (NMP), *N,N*-Dimethylacetamide (DMAc), chloroform, and tetrahydrofuran (THF). This limits their application. To obtain materials with better solvent resistance and thermal stability, the functional groups which could proceed with cross-linking reactions have been introduced into these polymers. In previous studies, extensive promising approaches are described for cross-linking poly(aryl ether sulfone). Nolte et al.⁴ combined diamines to SO₃H groups using carbodiimide as a dehydrating agent, forming sulfonamide bridges. Ren et al.⁵ fabricated a series of cross-linking (sulfonated PES with 4-amino-phenyl pendant group)/SiO₂ hybrid membranes by the sol-gel method. In fact, these processes are difficult. Pak et al.⁶ have prepared poly(aryl ether sulfone)s with pendent aryl amines on the backbone, which were further modified by maleic anhydride to afford pendent maleimides, and then thermally cross-

linked. In contrast to amine-terminated polysulfones,^{7–9} the pendent amines are no longer restricted to be only on polymer chain ends, and molecular weight of the pendent amino polysulfones can be controlled independently of the concentration of the amines. The above advantages made it a better method.

Boric acid has been well established as flame retardants and cross-linking agents for some considerable time.^{10–12} The effectiveness of boric acid as cross-linking agents in various materials has been researched. Boric acid enhanced flame retardance while maintaining mechanical properties of the materials.^{13–18} In addition, boron could exert its flame retardant action on polymeric materials at a temperature well below the normal pyrolysis temperature of these materials.

Hirohata et al.^{19,20} have reported a solid-state preparation method for BPR [Eqs. (1) and (2)]. They suggested that a mixture of mono-, di-, and tri-phenyl substituted boric acid were prepared by altering the molar ratio of phenol to boric acid. However, no structural characterization for the prepared resins was reported in their study. But thermal characterization of the hardened prepared resin showed that the BPR had more outstanding resistance against thermo-oxidative degradation than the hardened regular and halogenated PR.^{15,20}



In this article, we investigated the role of boric acid penetrated into the PES membranes after the B(OH)₃/PES composites were manufactured by solution blending and casting membrane method. First, processing conditions were determined by FT-IR. Secondly, the structure and morphology of the B(OH)₃/PES composite membranes were researched. At last, curing behaviors, thermal stabilities, and mechanical interfacial properties of B(OH)₃/PES composite membranes were studied. The purpose of this article was to develop an effective synthetic strategy to obtain high performance PES membranes which owned improved solvent resistance and thermal stability.

EXPERIMENTAL

Materials

(3-methoxy)phenyl-hydroquinone (3-CH₃OPHQ) was synthesized in our lab through a two-step coupling-reduction reaction.²¹ Bis(4-chlorophenyl) sulfone and Boric acid (99.5%) was respectively obtained from Energy Chemical, China and Sinopharm Chemical Reagent, China. Tetramethylene sulfone (TMS) was purified by vacuum distillation. Dimethylsulfoxide (DMSO), pyridine, toluene, ethanol were purchased from Beijing Chemical Reagent, China. Dimethylsulfoxide (DMSO) was dried by CaH₂. K₂CO₃ (Sinopharm Chemical Reagent, China) was dried at 120°C for 24 h before polymerization.

Measurements

Typical mechanical properties were tested by SHIMADZU AG-1 universal testing machine. The molecular weight of the sample was determined by gel permeation chromatography (GPC, PL-GPC 220, Polymer Laboratories, USA). FT-IR spectra were measured on a Bruker Victor22 Fourier-transform infrared spectrometer. ¹H NMR experiments were carried out on a Bruker 510 spectrometer (500 MHz for ¹H) using DMSO-d₆ and CDCl₃ as solvent. The morphology of the membranes was analyzed by scanning electron microscope (SEM) (SHIMADZU SSX-550, Japan). The phase structures of the membranes were identified by wide-angle X-ray diffraction (WAXD). The WAXD measurements were performed on a Siemens D5005XRD diffractometer. Differential scanning calorimeter (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument at a heating rate of 20°C·min⁻¹ from 100°C to 300°C under nitrogen. Thermo-gravimetric analysis (TGA) was performed on a Perkin Elmer Pyris 1 TGA analyzer at 10°C·min⁻¹ under nitrogen.

Synthesis

Synthesis of Poly(aryl ether sulfone) with (3-hydroxy)Phenyl Group (PES-OH). The PES-OCH₃ and PES-OH were synthesized using the same procedure as our previous work.^{21,22} (The number-average molecular weight of the PES-OCH₃ is 7.2 × 10⁴ with a distribution of 1.32 determined by GPC. The number-average molecular weight of the PES-OH is 8.3 × 10⁴ with a distribution of 1.43 determined by GPC.)

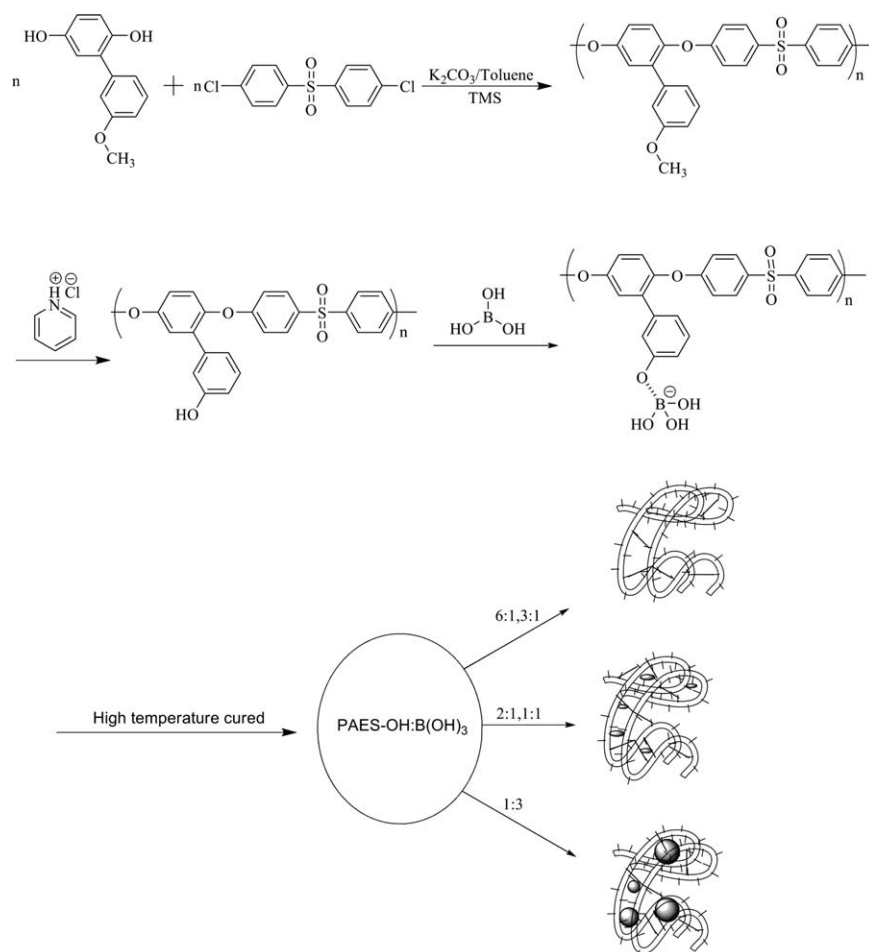
Preparation of B(OH)₃/PES Composite Membranes. PES-OH membrane and the B(OH)₃/PES composite membranes were prepared by solution casting and evaporation method. The pure polymer membrane named as PES-OH was cast from 12% (w/v) solution directly, and then kept at 60°C for 24 h, 80°C for 12 h, 100°C for 2 h, 120°C for 2 h and 150°C for 6 h step-by-step under the aegis of high purity nitrogen. After cooling to 80°C, the membranes were vacuumized, followed by heating at 80°C, 100°C, 120°C, and 150°C for 6 h, respectively. However, for the composite membranes, more processes were needed. Firstly, the PES-OH was dissolved in DMSO at room temperature to prepare a 12% (w/v) solution. Secondly, 1/6 equivalent, 1/3 equivalent, 1/2 equivalent, 1 equivalent, and 3 equivalent B(OH)₃ (2.4, 4.7, 6.9, 12.9, and 30.8 wt %) was, respectively, added into the homogeneous solution, which were named as PES-B-1, PES-B-2, PES-B-3, PES-B-4, PES-B-5, respectively. The composite membranes were obtained by solution casting methods as same as the PES-OH membrane after stirring for 24 h.

Preparation of Boric Acid-Modified Poly(aryl ether sulfone) Membranes. The membranes were cured by different temperature, they were treated at 150°C for 4 h, 180°C for 4 h, 220°C for 2 h, 260°C for 4 h and 300°C for 4 h to enhance thermal activation of the cross-linking reaction between PES-OH and B(OH)₃. The thickness of membranes was in the range 70–100 μm.

RESULTS AND DISCUSSION

Preparation of Boric Acid-Modified Poly(aryl ether sulfone) Membranes and Mechanisms of the Chemical Cross-Linking Reaction

PES-OCH₃ and PES-OH were synthesized according to our previously reported work.¹⁹ PES-OCH₃ was obtained by an aromatic nucleophilic substitution polycondensation, as shown in Scheme 1. And then, PES-OCH₃ was converted into PES-OH with high yield through demethylation reaction in molten



Scheme 1. Preparation of boric acid modified poly(aryl ether sulfone) membranes

pyridine hydrochloride (Scheme 1). Boric acid modified poly(aryl ether sulfone)s was prepared by solution blending, solution casting, evaporation and high temperature curing method.

The $^1\text{H-NMR}$ spectra were used to confirm the occurrence of the demethylation reaction and were shown in Figure 1. When

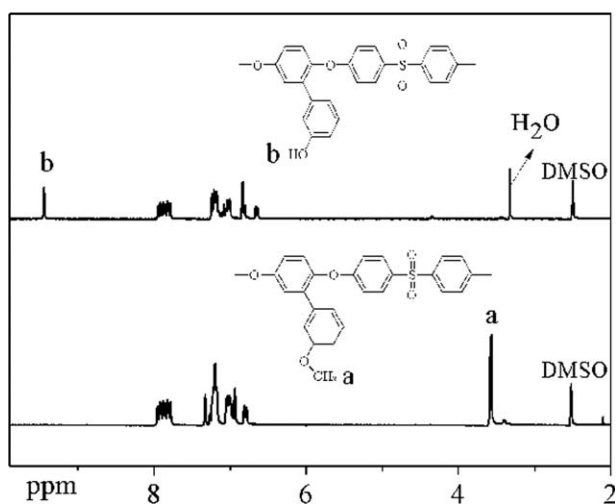


Figure 1. $^1\text{H-NMR}$ of PES- OCH_3 and PES-OH.

$-\text{OCH}_3$ groups transferred into $-\text{OH}$ groups, a strong signal at 3.56 ppm corresponding to the protons of $-\text{OCH}_3$ disappeared and an additional strong signal at 9.45 ppm corresponding to the protons of $-\text{OH}$ appeared. This proved that the $-\text{OCH}_3$ groups had transformed into $-\text{OH}$ groups completely. GPC results showed that high molecular weight polymers were prepared. These results suggested that no obvious degradations occurred via demethylation.²⁰

FT-IR spectra were used to determine the processing conditions and characterize the structures of boric acid modified poly(aryl ether sulfone)s. The PES-OH and $\text{B(OH)}_3/\text{PES}$ composite samples were dissolved in DMSO (The concentration of PES-OH was same) and then coated as a thin film on a potassium bromide plate. When the solvent in the film was completely evaporated in vacuum, the potassium bromide plate was scanned by the FT-IR instrument. PES-B-4 was taken as an example to study the processing conditions. The plates were placed in a heated oven with variational temperature of 180°C, 220°C, 260°C, and 300°C. During the curing reaction at these temperatures, the plate was repeatedly withdrawn at regular time intervals (30 min) for analysis. The chemical structure changes during the cross-linking process were monitored by FT-IR and were shown in Figure 2. Based on the invariable content of sulfonyl groups in the process of thermo-curing, transmittance of

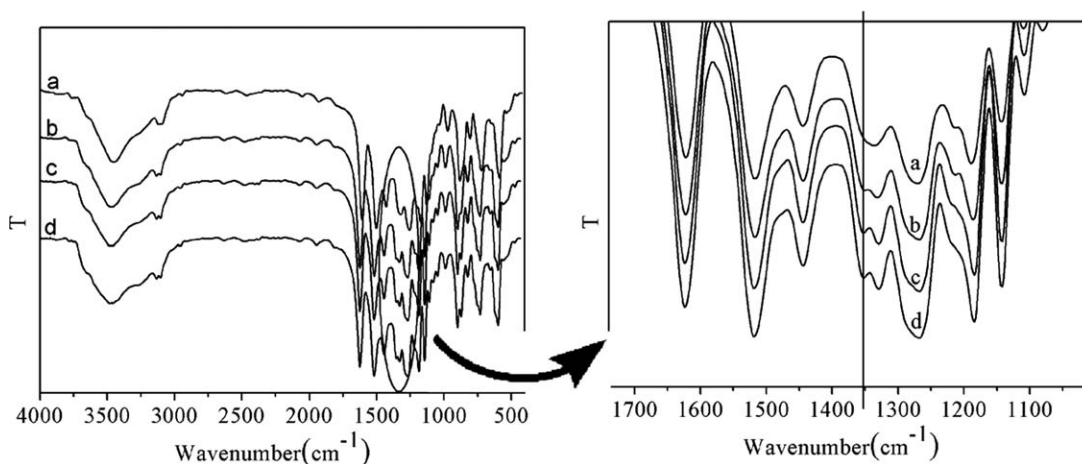


Figure 2. FT-IR spectra of PES-B-4 a, at 180°C for 4 h; b, at 220°C for 2 h; c, at 260°C for 4 h; d, at 300°C for 4 h.

Table I. FT-IR Values of B(OH)₃/PES Composite Membranes Cured Isothermally at Different Temperature for Various Periods of Time

Temperature (°C)/time (h)	Transmittance of sulfonyl groups/ T_1	Transmittance of borate ester groups/ T_2	T_2/T_1	Step differentials
180/4	0.33363	0.42397	1.27	0.12
220/2	0.33363	0.38386	1.15	0.11
260/4	0.33363	0.34699	1.04	0.04
300/4	0.33363	0.33201	1.00	-

sulfonyl groups was chosen at the same value. The intensities of the characteristic peaks of borate ester groups at 1350 cm⁻¹ increased with the increase of temperature, as shown in Table I. Meanwhile, the differentials of T_2/T_1 were reductive. This indicated that the B(OH)₃/PES composite membranes had been completely cured after treatment at 300°C for 4 h.

FT-IR spectra were also used to characterize the structures of boric acid modified poly(aryl ether sulfone) membranes, as shown in Figure 3. The spectra had absorption peaks of borate

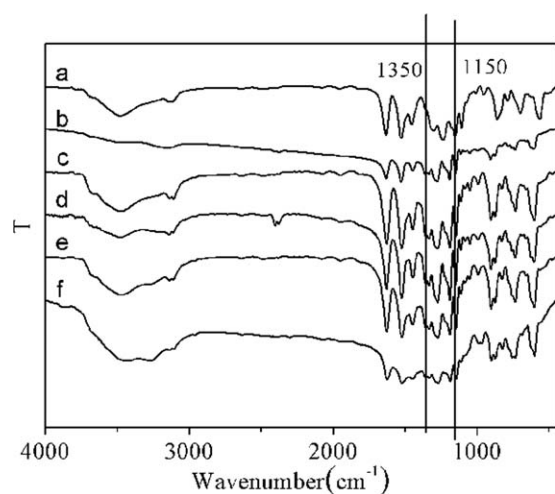


Figure 3. FT-IR spectra of a, PES-OH; b, PES-B-1; c, PES-B-2; d, PES-B-3; e, PES-B-4; f, PES-B-5.

ester groups at 1350 cm⁻¹ and absorption peaks of sulfonyl groups at 1150 cm⁻¹. Meanwhile, the characteristic peaks of the benzene ring can be found at 1500, 1600, and 3030 cm⁻¹.^{2,3}

Solubility and Mechanical Properties of Boric Acid-Modified Poly(aryl ether sulfone) Membranes

The solubility behavior of the membranes in some solvents was tested. It is well known that the conventional PES could be dissolved in most known organic solvents, and PES-OH had good solubility.^{9,22} However, boric acid-modified poly(aryl ether sulfone) membranes were not soluble at room temperature in aprotic polar solvents such as NMP, DMAc, and DMF as well as in the less polar solvents such as chloroform and tetrahydrofuran. The bad solubility of composite membranes could be attributed to the introduction of B(OH)₃, which led to the formation of cross-linking network structure.

The mechanical properties of the composite membranes cast from DMSO were summarized in Table II. The PES-OH membrane was transparent and had tensile strengths of 71.8 MPa, Young's moduli of 2.03 GPa, and elongations at break of 8%. The results indicated that it was a strong and flexible material. As the content of boric acid increased, both tensile strengths and elongation at break of the composite membranes increased at first and then decreased. Originally, because of the cross-linking network structure which formed by esterification reaction between PES-OH and B(OH)₃, PES-B-1, PES-B-2, and PES-B-3 showed more excellent performance than PES-OH, especially PES-B-2. When content of B(OH)₃ exceeded 7%, B(OH)₃ could not react with PES-OH completely, leading to the occurrence of

Table II. Mechanical Properties of PES-OH Membrane and Boric Acid-Modified Poly(aryl ether sulfone) Membranes

Polymer	Tensile strength (MPa)	Young's modulus (Gpa)	Elongation at break (%)
PES-OH	71.8	2.03	8
PES-B-1	86.8	2.08	9
PES-B-2	78.8	2.24	14
PES-B-3	76.9	2.54	14
PES-B-4	65.6	2.61	11
PES-B-5	58.7	2.20	7

phase separation. Then the chain mobility and free volume of the polymer decreased,²⁴ resulting in a steep decline of the mechanical properties of PES-B-4 and PES-B-5. However, these materials still had excellent mechanical properties.

Morphology of Boric Acid-Modified Poly(aryl ether sulfone) Membranes

The microstructures could influence properties of membranes. SEM and WAXD were the characteristic means of morphology. The internal morphology of the membranes was studied by SEM, as shown in Figure 4. Before testing, all of the samples were fractured in liquid nitrogen. Figure 1(a–c) showed that boric acid was dispersed in the PES continuous phase. Figure

1(d–f) showed evident microphase separations, which might be attributed to unreacted boric acid. Owing to the amorphous nature of the poly(aryl ether sulfone)s, all the membranes showed amorphous wide-angle X-ray diffraction (WAXD) patterns in Figure 5. The patterns in Figure 5(a–c) exhibited only diffraction peaks corresponding to PES. However, PES-B-3, PES-B-4, PES-B-5 showed well-defined diffraction peaks at about 14.8° and 28.0°, corresponding to the most intense of known reflections of B(OH)₃ crystals respectively.^{25–27} Their crystallographic properties can be attributed to the incorporation of unreacted boric acid. The results were in accord with the SEM analysis.

Thermal Degradation and Stability of Boric Acid-Modified Poly(aryl ether sulfone) Membranes

Thermal property is one of the most important factors on the usage of materials. The glass-transition temperature (T_g) curves of PES-OH and PES-Bs were shown in Figure 6. The T_g of PES-OH, PES-B-1 and PES-B-2 were 204°C, 231°C and 250°C respectively. This indicated that T_g s of composite membranes increased with the increase of B(OH)₃ content. The PES-B-3, PES-B-4, and PES-B-5 did not show apparent glass-transition temperature before 300°C. It could be attributed to the curing reaction between phenolic hydroxyl groups of PES-OH and B(OH)₃, which limited the movement of main chain completely.

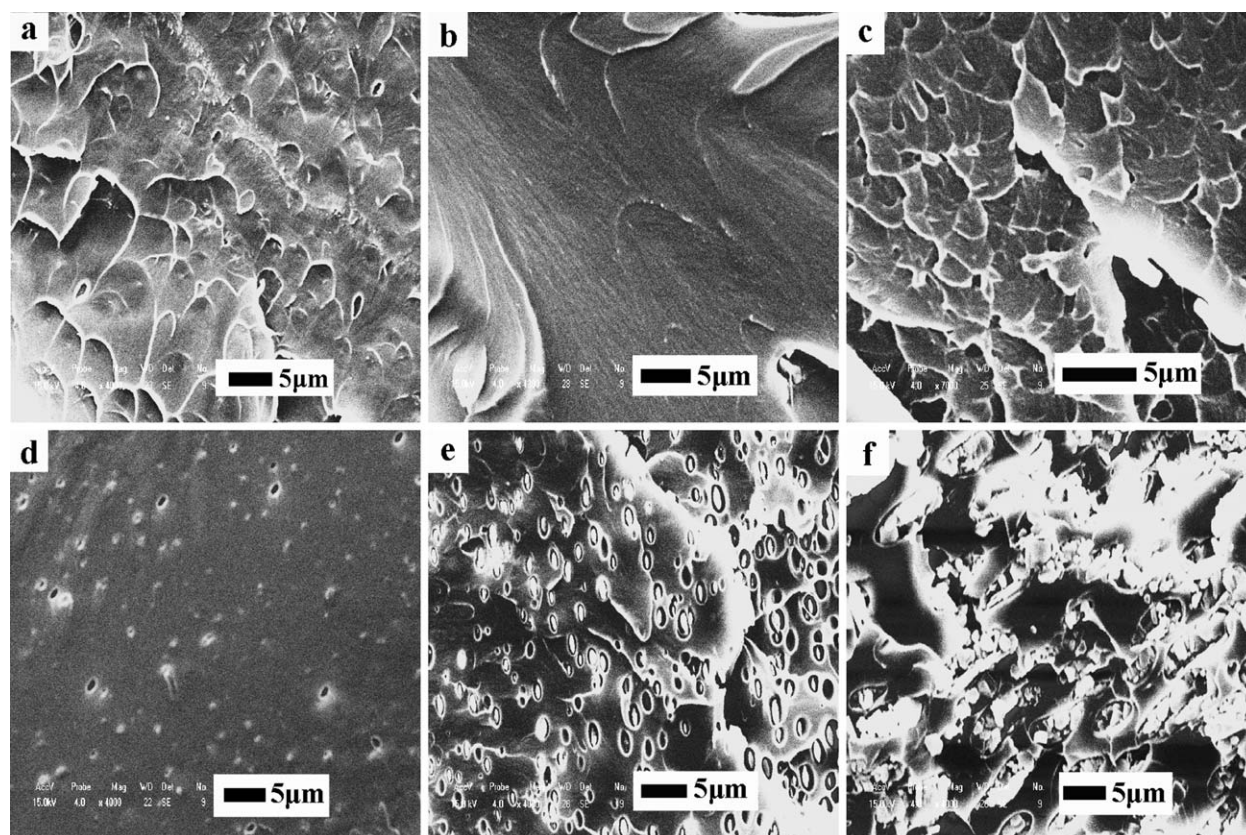


Figure 4. SEM micrographs of a, PES-OH; b, PES-B-1; c, PES-B-2; d, PES-B-3; e, PES-B-4; f, PES-B-5.

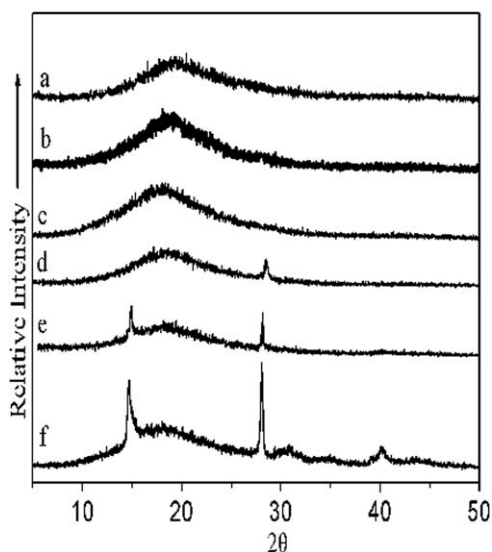


Figure 5. WAXD spectra of a, PES-OH; b, PES-B-1; c, PES-B-2; d, PES-B-3; e, PES-B-4; f, PES-B-5.

To investigate thermal degradation and stability, thermogravimetric weight loss of PES-OH and PES-Bs were studied. The resulting curves were shown in Figure 7 and the resulting data were summarized in Table III. As shown in Figure 4, PES-OH exhibited two distinct thermal degradation steps. The first weight loss step was at about 260°C, which associated with loss of the phenolic hydroxyl groups; the second weight loss was observed at about 480°C, which was due to main chain degradation. However, PES-B had only one obvious step, which was assigned to the degradation of the main chain. The temperatures at 5% weight loss (T_5) of composite membranes were over 460°C, demonstrating the excellent thermal stability of PES-B. It also observed that carbon residue level at 800°C was increased with the increasing content of $B(OH)_3$. Furthermore, due to the curing reaction between phenolic hydroxyl groups of PES-OH and $B(OH)_3$, thermal stability of the composites were improved

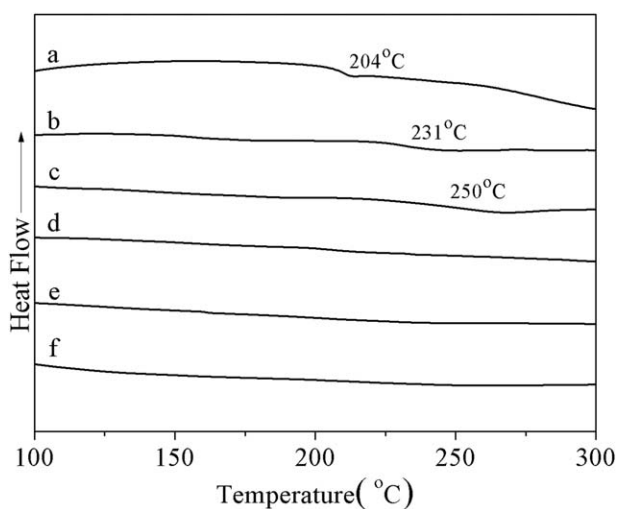


Figure 6. DSC curves of a, PES-OH; b, PES-B-1; c, PES-B-2; d, PES-B-3; e, PES-B-4; f, PES-B-5.

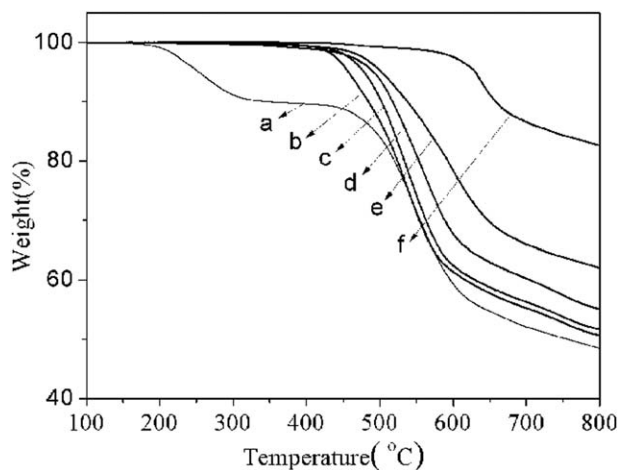


Figure 7. TGA curves under N_2 of a, PES-OH; b, PES-B-1; c, PES-B-2; d, PES-B-3; e, PES-B-4; f, PES-B-5.

with the increasing content of $B(OH)_3$. In a word, $B(OH)_3$ played an important role in improving thermal stability of composite membranes.

CONCLUSIONS

In this article, boric acid-modified poly(aryl ether sulfone) (PES-B) membranes were obtained, and the effect of $B(OH)_3$ content on the curing behaviors, thermal stability, and mechanical interfacial properties of $B(OH)_3$ /PES blends was studied. During the boric acid-modified poly(aryl ether sulfone) membranes formed from $B(OH)_3$ /PES-OH composites at high temperature via curing process, phenol borate linkage was formed. The data indicated that the crosslinking component effectively improved the properties of the composite membranes. TGA results showed that thermal stability of the composites was improved with the increasing content of $B(OH)_3$, which indicated that the boron-containing PES had good heat oxidative resistance and thermal stability. Besides, the products exhibited good mechanical property and solvent resistance. All in all, based on these excellent performances, the boron-containing PES is potential in heat-resistant adhesives, coating materials and neutron absorber and shielding material, etc.

Table III. Thermal Properties of PES-OH and Composites

Polymer	Decomposition temperature (°C)		Residue at 800°C (wt %)	Carbon residue level (wt %)
	T_5^a	T_{10}^a		
PES-OH	254	346	48.4	48.4
PES-B-1	460	485	50.6	49.2
PES-B-2	479	502	51.6	49.5
PES-B-3	492	518	55.1	51.1
PES-B-4	503	538	62.1	56.0
PES-B-5	535	658	82.6	62.6

^a Temperature at which 5 and 10% weight loss was recorded by TGA at heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ in a N_2 atmosphere.

REFERENCES

1. Chang, Y.; Lee, H. H.; Kim, S. H.; Jo, T. S.; Bae, C. *Macromolecules* **2013**, *46*, 1754.
2. Zhang, Q.; Li, S. H.; Zhang, S. B. *Chem. Commun.* **2010**, *46*, 7495.
3. Wang, Z. G.; Chen, T. L.; Xu, J. P. *Macromolecules* **2001**, *34*, 9015.
4. Nolte, R.; Ledjeff, K.; Bauer, M.; Mülhaupt, R. *J. Membr. Sci.* **1993**, *83*, 211.
5. Ren, J. N.; Zhang, S. L.; Liu, Y.; Wang, Y.; Pang, J. H.; Wang, Q. H.; Wang, G. B. *J. Membr. Sci.* **2013**, *434*, 161.
6. Pak, S. J.; Lyle, G. D.; Mercier, R.; McGrath, J. E. *Polymer* **1993**, *34*, 885.
7. Hedrick, J. L.; Yilgor, I.; Jurek, M.; Hedrick, J. C.; Wilkes, G. L.; McGrath, J. E. *Polymer* **1991**, *32*, 2020.
8. Hedrick, J. L.; Yilgör, I.; Wilkes, G. L.; McGrath, J. E. *Polym. Bull.* **1985**, *13*, 201.
9. Lyle, G. D.; Senger, J. S.; Chen, D. H.; Kilic, S.; Wu, S. D.; Mohanty, D. K.; McGrath, J. E. *Polymer* **1989**, *30*, 978.
10. Armitage, P.; Ebdon, J. R.; Hunt, B. J.; Jones, M. S.; Thorpe, F. G.. *Polym. Degrad. Stabil.* **1996**, *54*, 387.
11. Wang, D. C.; Chang, G. W.; Chen, Y. *Polym. Degrad. Stabil.* **2008**, *93*, 125.
12. Martín, C.; Ronda, J. C.; Cádiz, V. *Polym. Degrad. Stabil.* **2006**, *91*, 747.
13. Gao, J. G.; Liu, Y. F.; Yang, L. T. *Polym. Degrad. Stabil.* **1999**, *63*, 19.
14. Gao, J. G.; Liu, Y. F.; Wang, F. L. *Eur. Polym. J.* **2001**, *37*, 207.
15. Abdalla, M. O.; Ludwick, A.; Mitchell, T. *Polymer* **2003**, *44*, 7353.
16. Pitts, A. In *Flame Retardancy of Polymeric Materials*; Kuryla, W. C.; Papa, A. J., Eds.; Marcel Dekker: New York, **1973**; Vol. 1, Chapter 2.
17. Shen, K.; Griffin, T. In *ACS Symposium Series*; ACS: Washington, DC, **1990**; Vol. 245, Chapter 12.
18. Ross, V. F.; Edwards, J. O. In *The Chemistry of Boron and Its Compounds*, Murettterties, E. L., Ed; Wiley: New York, **1956**; Chapter 3.
19. Hirohata, T.; Misaki, T.; Yoshii, M. *J. Soc. Mater. Sci. Jpn.* **1987**, *36*, 185.
20. Hirohata, T.; Misaki, T.; Komodo, S.; Yoshii, M. *J. Soc. Mater. Sci. Jpn.* **1989**, *38*, 1098.
21. Yue, X. G.; Zhang, H. B.; Chen, W. H.; Wang, Y. S.; Zhang, S. L.; Wang, G. B.; Jiang, Z. H. *Polymer* **2007**, *48*, 4715.
22. Liu, Z.; Liu, B. J.; Li, L.; Zhang, Y. N.; Jiang, Z. H. *Macromol. Res.* **2013**, *21*, 608.
23. Liu, Y. F.; Gao, J. G.; Zhang, R. Z. *Polym. Degrad. Stabil.* **2002**, *77*, 495.
24. Misra, R. D. K.; Hadal, R.; Duncan, S. J. *Acta Mater.* **2004**, *52*, 4363.
25. Petrovic, Z. S.; Javni, I.; Waddon, A.; Bánegyí, G. *J. Appl. Polym. Sci.* **2000**, *76*, 133.
26. Gurr, G. E.; Montgomery, P. W.; Knutson, C. D.; Gorres, B. T. *Acta Cryst.* **1970**, *26*, 906.
27. Sinha, A.; Mahata, T.; Sharma, B. P. *J. Nucl. Mater.* **2002**, *301*, 165.