Poly(arylene thioether sulfone): Synthesis, Oxidation and Membrane Properties

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Abstract: Two kinds of high glass temperature poly(arylene ether sulfone)s containing thioether and biphenyl unit (PASSs) had been developed. The polymers were prepared by a polycondensation reaction of 4,4'-bis(4-chlorophenylsulfone)biphenyl (BCPSB) and 4,4'-dimercaptodiphenyl sulfone (DMDPS) (or 4,4'-bis(4-mercaptophenylsulfone)biphenyl (BMPSB)). They showed good thermal properties such as a relatively high glass transition temperature of 263-282 oC and a 5% weight-loss temperature (T5%) of 441-445 oC. The water flux and retention rate of the resultant membranes were 0.61-2.48 L/m2h and 89.47-94.91%, respectively. Interestingly, we found that the corrosion resistance of the membranes had been largely improved with the oxidization treatment. They were even insoluble in NMP, DMSO, Concentrated H2SO4, aqua regia and so on, while the polymers without oxidation were soluble or destroyed in above solvents. In addition, we found the water flux of the oxidized membrane was also improved but the retention rate only decreased a little.

1.INTRODUCTION:

Membrane separation processes has become gradually important in the last three decades for their applications in high technology areas such as biotechnology and membrane-based energy devices. As a class of high performance engineering thermoplastic materials, poly(arylene ether sulfone)s (PAES) are found to have high glass transition temperature, thermal stability, good mechanical properties, solubility and excellent resistance to hydrolysis [1]. However, the performance of traditional PAES is not good enough for some special applications. With respect to improve or endow the polymer novel properties, the chemical structure modification or molecular design is frequently required. In order to make the membrane can be used in much more rigorous environments. Our interest is focused on the improvement of corrosion resistance and thermal properties of PAES. Poly(aryl thioether)s, such as poly(phenylene sulfide) and poly(phenylene sulfide sulfone) [2,3] are of well-known high performance engineering thermoplastics. They all have excellent thermal and corrosion resistance properties. On the basis of this consideration, we designed a kind of polymer that containing thioether, sulfonyl and diphenyl units to achieve high glass transition temperature, good corrosion resistance and film-forming properties.

4,4'-bis(4-mercaptophenylsulfone)biphenyl (BMPSB) (shown in Scheme 1)

The monomer (BMPSB) containing sulfone and thiol groups was prepared with the nucleophilic substitution reaction. The structure of BMPSB was characterized by elemental analysis, FT-IR and 1H-NMR spectrum. The FT-IR spectra of BMPSB showed characteristic absorptions near 2560, 1320, 1150 and 1075 cm^{-1} attributed to the thiol, sulfone and thio-ether groups, respectively. The 1H-NMR spectrum of BMPSB consisting of one single peak at 3.391 ppm and four double signals at 7.500-8.019 ppm which due to the thiol and benzene protons, respectively. The ratio of the corresponding integral curves was also about 1:2:2:2:2. That is consistent with the calculated results.

The chemical structure characterizations indicating the monomers are synthesized as shown in **Scheme 1**.
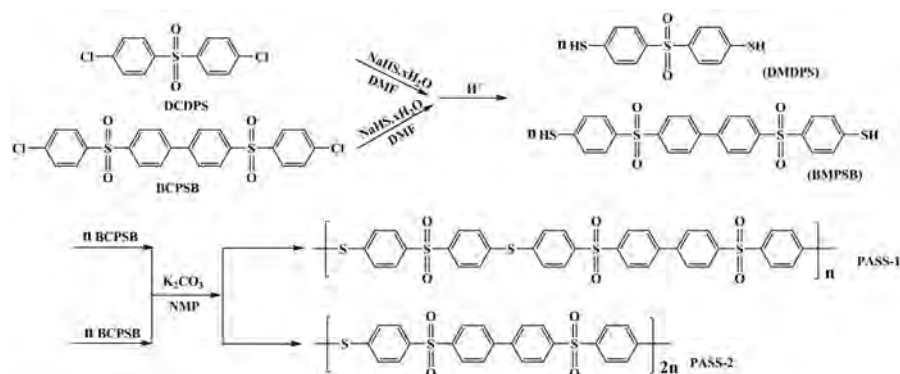
**Scheme 1. Synthesis routes of monomers and PASSs.**

2. EXPERIMENTAL

2.1 Synthesis and chemical structure of polymers (BH-*trans*-BFCD and BH-*cis*-BFCD)

The polycondensation reaction was carried out by nucleophilic substitution polymerization using potassium carbonate as the catalyst. The reaction temperature was about 180-200 °C. From the FT-IR spectra of polymers exhibited the characteristic stretching absorption of sulfone and thioether near 1315, 1150 and 1070 cm^{-1}, respectively. Comparing with the spectrum of monomer (BMPSB), the characteristic absorption around 2560 cm^{-1} (-SH) disappeared. The ^{1}H-NMR spectrum of PASS-1. The signals of protons on bezene ring were in the range of 7.407-8.086 ppm. Four groups of peaks appeared in the ^{1}H-NMR spectra. The calculated result should have six group peaks and the ratio of corresponding integral curves was 1:1:1:1:1:1, but the chemical shift of H1 and H2, H3 and H4 was so approximate that it could not be separated. The ratio of corresponding integral curves was (H1+H2):(H3+H4):H5:H6=2:2:1:1. Combined with the FT-IR and elemental analysis results suggest that the polymerization proceeds as descript in **Scheme 1**. The structures of PASS-2 were also characterized by NMR FT-IR spectra and elemental analysis.

2.2 Thermal Properties of Polymers

The thermal properties of polymers were evaluated by TGA and DSC measurements. The glass transition temperature (T_gs) of the polymers was estimated by DSC. As shown in **Figure 1**, the T_g of the resultant polymers were 263 and 282 °C, respectively. They were 40-60 °C higher than that of poly(phenylene sulfide sulfone) (T_g: 207~222 °C), polyether sulfone (T_g: ~230 °C) and PVDF (T_g: ~40 °C). Compared with PES and PVDF, they can be used in higher temperature environment. In particular, PASS-2 has about 19 °C higher T_g than that of PASS-1 because of the much more content rigid structure of biphenyl unit. Also from the DSC curves we had not find the endothermic melting peak of polymers. That suggests the amorphous nature of the polymers. As shown in **Figure 2**, the initial degradation temperatures of PPSS, PASS-1 and PASS-2 in nitrogen ($T_{5\%}$) were 431, 441 and 445 °C, respectively. They provided about 40.8%, 42.6%, 43.9% char yield at 800 °C in nitrogen. The TGA data indicated that these polymers had good thermo-stability. Also we found that PASS-2 had the highest thermal stability among these three kinds of polymers. The main reason was that PASS-2 had much higher content of sulfone and biphenyl units in the polymer main chain than that of PPSS and PASS-1.The thermal decomposition curves also revealed the degradation process of PPSS, PASS-1 and PASS-2 was one step.
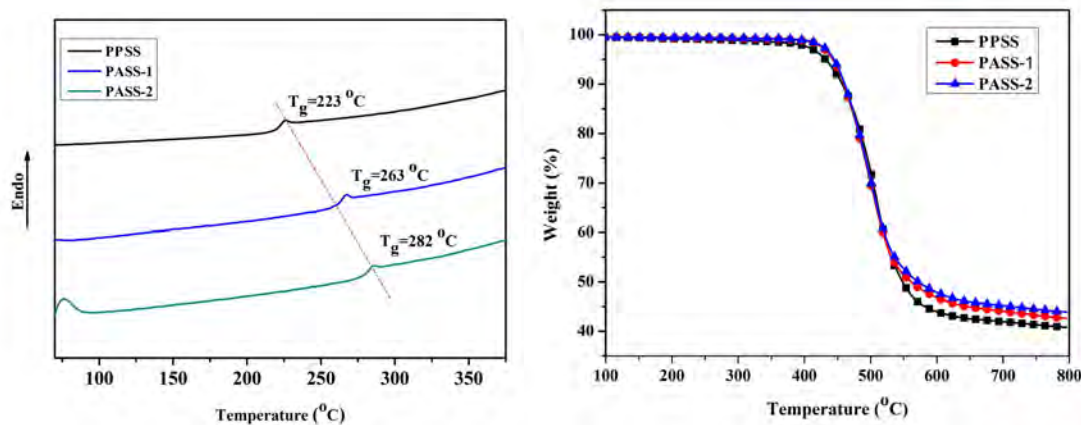
Figure 1 DSC curves of PPSS and PASSs   **Figure 2** TGA curves of PPSS and PASSs

2.3 Oxidation of PASSs membranes

FT-IR analysis was used to study the chemical group changes of the oxidation reaction. Comparing with the spectra of untreated PASS-1 membrane, the spectra of oxidized PASS-1 and PASS-2 membranes (PASS-1O and PASS-2O) showed significantly absorption increasement near 1320 cm^{-1} and 1150 cm^{-1} (attributed to the vibration of sulfone group: -SO$_2$-), at the same time we found the absorption decreasement near 1073 cm^{-1} (attributed to the vibration of thioether unit: -S-). The FT-IR result suggests that the content of sulfone group has increased, while the thioether content has decreased with the oxidation reaction. It indicates that the thioether group on the membrane surface of PASS-1 has been converted to sulfone (-SO$_2$-) units with the oxidation treatment. X-ray photoelectron spectroscopy (XPS) was used to characterize the valenece and content changes of the chemical elements with the oxidation treatment. As shown in **Figure 3**, un-oxidized PASSs exhibited two sulfur peaks, which suggested that the S atom in the polymer main chain had two kinds of valence states (-SO$_2$-: ~167.5 eV and -S-: 163.5 eV). We found that the sulfur peak near 163.5 eV attributed to thioether moiety almost disappeared after oxidation treatment, while the peak near 167.5 eV got more large than that of un-oxidized sample. We also fond a new peak near 165-166 eV with the oxidation reaction. It may be attributed to the little amount of sulfoxide (-SO-) group. It revealed the thioether was converted into sulfoxide and sulfone group with the oxidation process. With the treatment of oxidation, the content of oxygen was raised from 18.81-16.16% to 22.82-18.20%. It also indicated the thioether was converted to sulfone unit with the treatment. That was agreed with the results of FT-IR analysis.
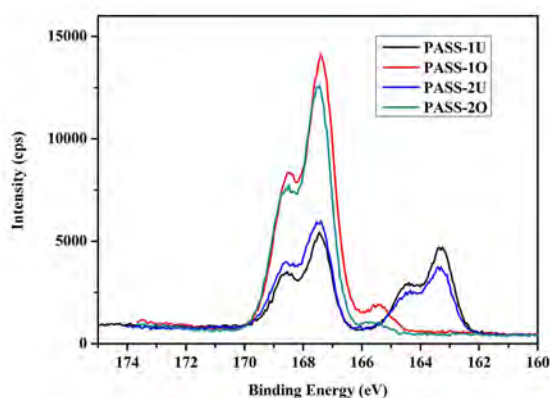
Figure 3 X-ray photoelectron spectroscopy (XPS) of sulfur in PASSs

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(unoxidized and oxidized).

## 2.4 Corrosion resistance properties of oxidized PASSs membranes

The corrosion resistance of PASS-1U (untreated), PASS-1O (oxidized) PASS-2U (untreated) and PASS-2O (oxidized) are summarized in **Table 1**. Comparing with PASS-1U and PASS-2U, PASS-1O and PASS-2O showed a relatively excellent corrosion resistance. PASS-1U and PASS-2U dissolved in some strong polar solvents such as DMF, DMAC, NMP, concentrated sulfuric acid and so on. While PASS-1O and PASS-2O absolutely had no changes after keeping for about 6 months in NaOH (2 M), NMP, concentrated sulfuric acid and even aqua regia (as shown in **Figure 4**). The main reason was that the thioether bonds in the polymer backbone were almost oxidized to sulfone groups [4] (as described in **Figure 5**) with the mixture of $H_2O_2/CH_3COOH/H_2SO_4$ (small amout) under moderate condition. The aromatic ring planes lie essentially orthogonal to a plane defined by the bridging C-S-C groups in $\left[\!\!\begin{array}{c}\overset{O}{\underset{O}{\overset{\|}{S}}}\!-\!Ar\!-\!\overset{O}{\underset{O}{\overset{\|}{S}}}\!-\!Ar\!-\!\overset{O}{\underset{O}{\overset{\|}{S}}}\!-\!Ar\end{array}\!\!\right]_n$, and the diaryl sulfone units adopt near-perfect open-book conformations and the molecules crystallize with the aromatic rings of laterally adjacent chains essentially parallel as shown in **Figure 5**. This results was similar with the earlier reports about that the poly(1,4-phenylenesulfone) is highly crystalline and insoluble [5].

Table 1 Corrosion resistance behavior of PASSs.

Solvents	Polymers			
	PASS-1U	PASS-1O	PASS-2U	PASS-2O
concentrated sulfuric acid	++	-	++	-
formic acid	-	-	-	-
NMP	++	-	++	-
DMF	++	-	++	-
DMAC	++	-	++	-
pyridine	+-	-	-	-
acetone	-	-	-	-
chloroform	+-	-	+-	-
DMSO	++	-	+	-
1, 4-Dioxane	-	-	-	-
toluene	-	-	-	-
cyclohexanone	-	-	-	-
Phenol+tetrachloroethane	++	-	++	-

● ++: soluble at room temperature; +: soluble at solvents boiling point; +-: swelling with heating; -: insoluble with heating.

a   b

c   d
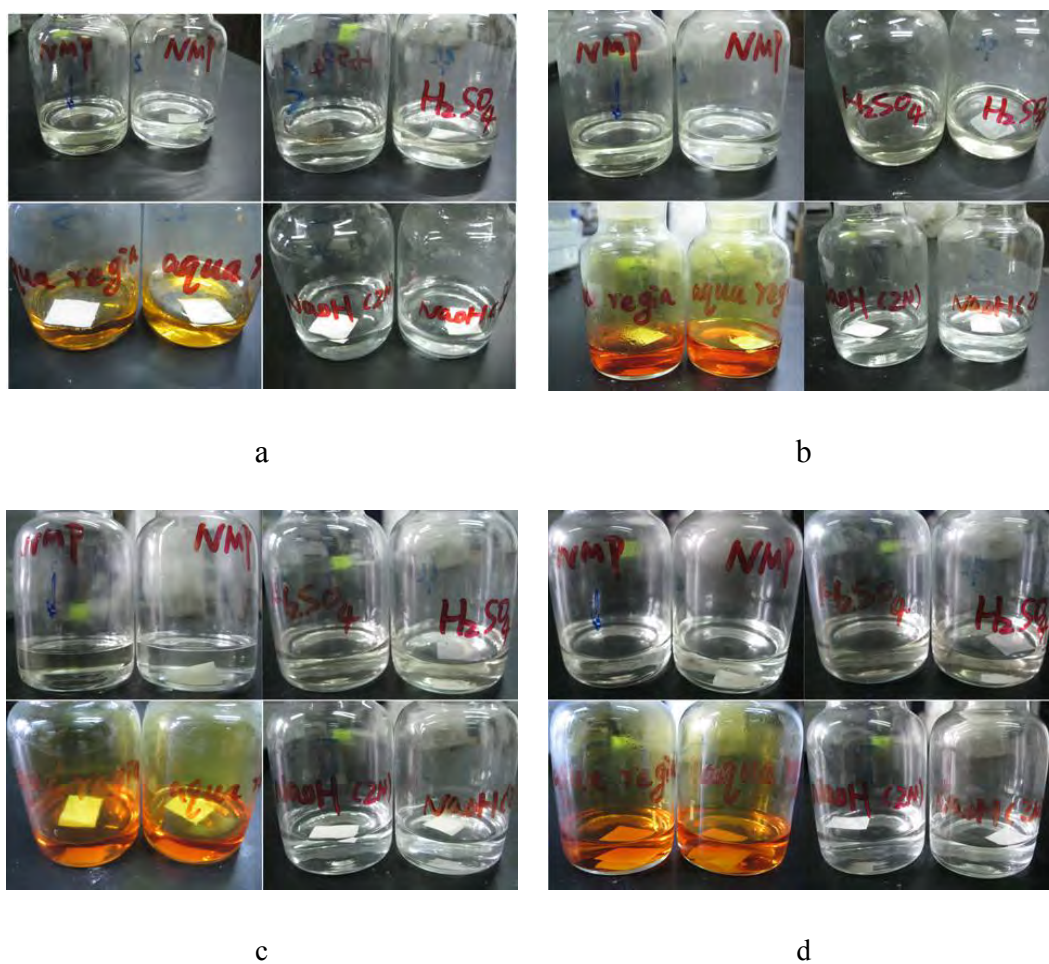
Figure 4. The images of PASS-1 membrane (unoxidized-the left sample, oxidized-the right sample) kept for different time (a. 5 min, b. 24 h, c. 15 d, d. 180 d) in solvents (NMP, concentrated sulfuric acid, aqua regia, NaOH).
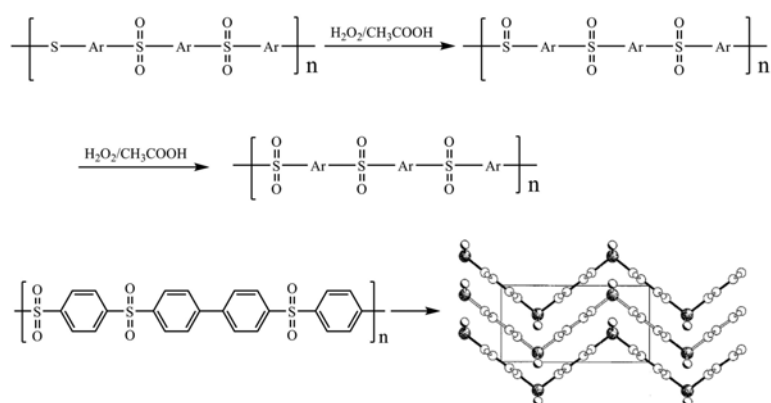

**Figure 5.** The oxidation reaction mechanism and three-dimensional diagrammatic sketch.

2.5 Flux and Permeation of oxidized PASSs membranes

The flux of PASSs was tested with deionized water in a dead-end ultrafiltration (UF) cell under 0.1 MPa. Each membrane was initially pre-pressurized with deionized water for 2 h at 0.2 MPa. As shown in **Figure 6**, The flux of PASS-1 and PASS-2 were 0.61-2.02 and 0.74-2.48 L/m^2, respectively. We found that the flux value decreased with the resin concentration increased. It was consitent with the regularity of the water flux

of seperation membrane. Also we found the pure PASSs had minor flux than commercial products such as PVDF, PES and so on, we will improve its water flux property next. Interestingly, we found that the flux of PASS-1 and PASS-2 became more large than that of untreated samples (PASS-1O: 1.06-2.52 L/m^2, PASS-2O: 1.25-3.56 L/m^2) after oxidation treatment. Whereas the retention rate (bovine serum albumin) decreased a little in a reasonable range as shown in **Figure 7**. In order to investigate this phenonmenon, the SEM and AFM was carried to observe the section and suface of the membranes. As shown in **Figure 8**, the oxidized and un-oxidized membranes exhibited similar asymmetric structure: a dense top layer, a porous finger-like and sponge-like sub layer. From the AFM images (**Figure 9**), we found that the microporous on the oxidized membranes suface became much more obvious than that of un-oxidized samples.The main reason is that the polymer chain is tend to appear local order structure with the oxidation treatment as demonstrated in **Figure 5**. The surface of the membrane begun to shrink, then the microporous structure got more and more clear. We also further studied the changes of flux and retention rate before and after oxidization with the contact angle experiment. As shown in **Figure 10**, the contact angle became smaller with the oxidation treatment. It suggested the hydrophilicity of the membrane got better after oxidation treatment. And that was beneficial for the contamination resistance of the membranes. It could be concluded that both the surface structure and hydrophilicity of the membrane before and after oxidation affected the flux and retention rate results.
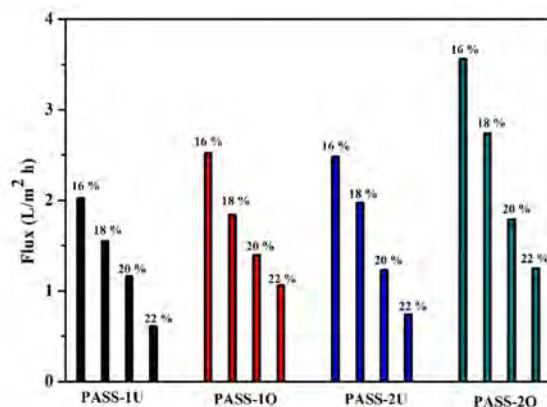
Figure 6. Flux of PASSs membrane before and after oxidation.
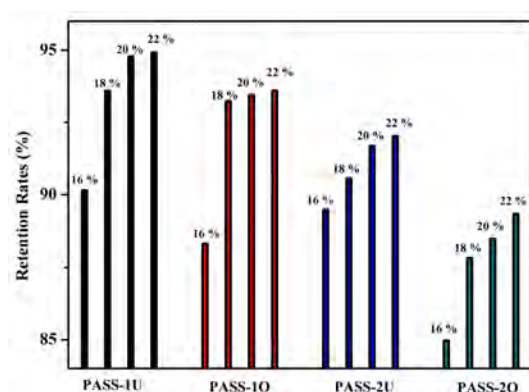
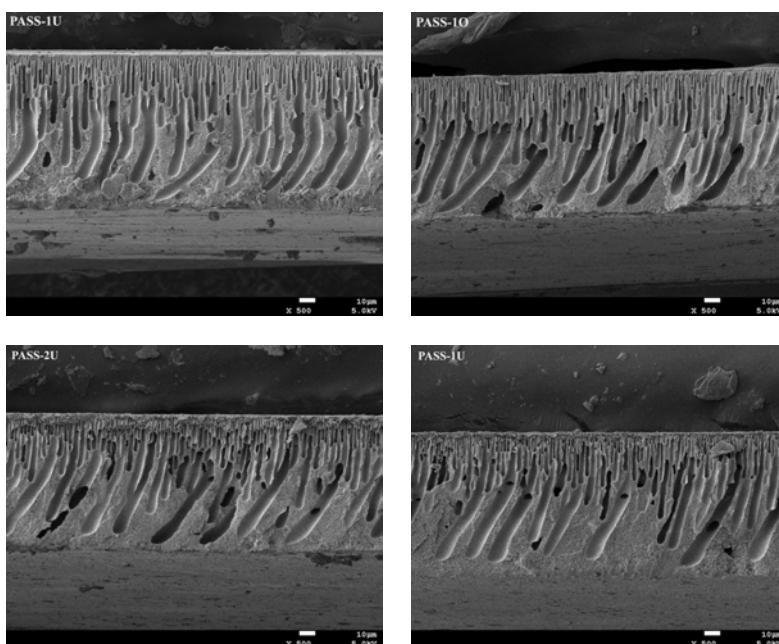**Figure 7**. Retention rate (bovine serum albumin) of PASSs membrane before and after oxidation.

Figure 8. SEM images of cross-section of PASSs membrane (18 wt%) before and after oxidation.
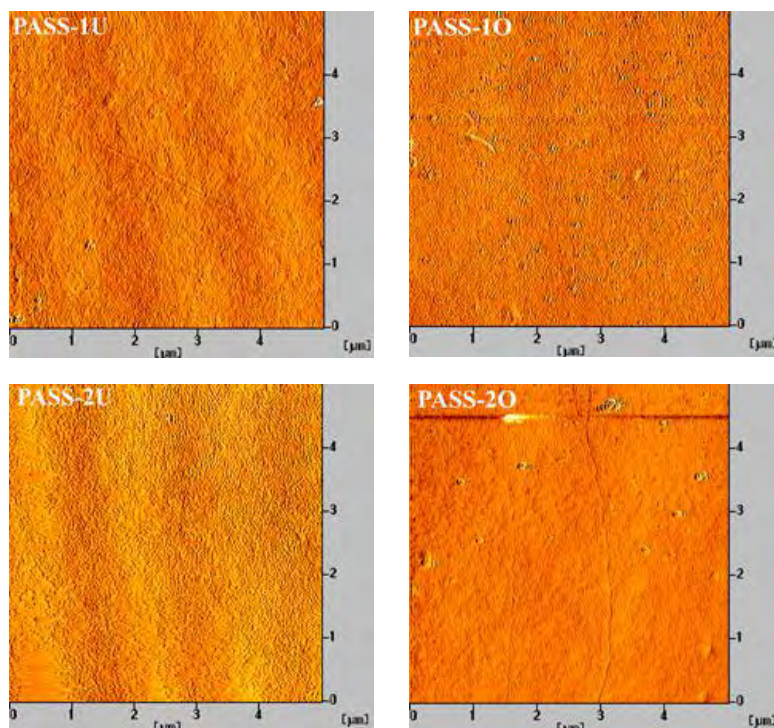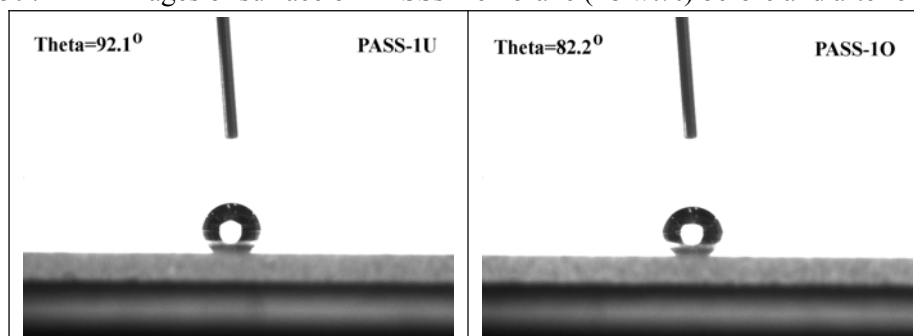

Figure 9. AFM images of surface of PASSs membrane (18 wt%) before and after oxidation.
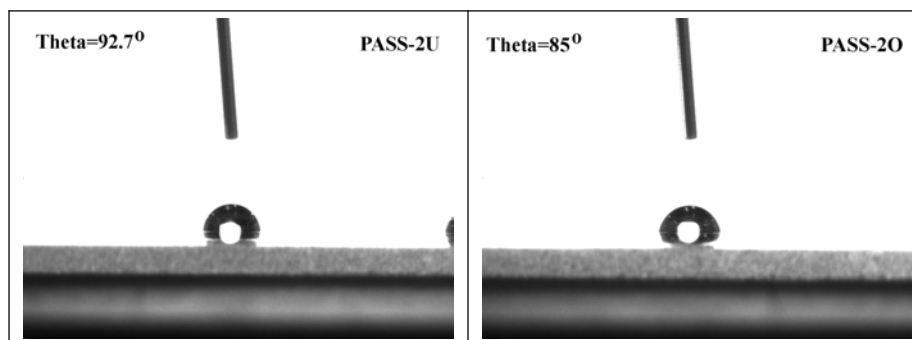
Figure 10. Contact angle of PASSs membrane (18 wt%) before and after oxidation

3. CONCLUSIONS

Two kinds of aromatic dithiol (BMPSB and DMDPS) monomers containing sulfone unit and high sulfur content were synthesized in one step. They were conducted to react with BCPSB by nucleophilic polycondensation to prepare poly(arylene ether sulfone)s containg thioether units (PASSs) with higher glass transition temperture and excellent thermal stability than that of commercial products such as PVDF and PES. The resultant polymers can dissolve in strong polar solvents such as NMP and supply a separation membrane with flux of 0.61-2.48 L/m^{2}h, retention rate of 88.32-94.91 %. Interestingly, we found that the thioether in the polymer main chain can be oxidized with a moderate condition. The corrosion resistance of these membranes after oxidation is largely improved. The oxidized samples are even not insoluble in concentrated sulfuric acid, NMP, aqua regia and so on. This approach provides a convenient method for preparation of chemically and thermally stable poly(arylene ether sulfone)s polymers with excellent corrosion resistance. Thus, the PASSs can be good candidates as membrane materials for industrial filtration especially in some harsh environments (high operating temperature and corrosion condition), although the pure water flux need improvement.

References

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