Adhesion Property of Sulfonated Poly(arylene ether sulfone)s

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ABSTRACT: Sulfonated poly(arylene ether sulfone)s (S-PESs) were synthesized from sulfonated 4,4′-dichlorodiphenylsulfone (S-DCDPS), 4,4′-dichlorodiphenylsulfone (DC-DPS), and 4,4′-biphenol through variations in the molar ratio of S-DCDPS to DCDPS from 10/90 to 40/60. The S-PES sodium form was characterized with Fourier transform infrared, ^{1}H-NMR, thermogravimetric analysis, differential scanning calorimetry, and dynamic mechanical analysis, and the intrinsic viscosity and solubility were also evaluated. The sodium form was then subjected to acidification by immersion in 1.5M HCl for 24 h at room temperature, which was followed by washing with deionized water. The S-PES adhesive properties were measured with single laboratory shear samples with aluminum alloys, and the failure mode was investigated. The synthesized S-PESs exhibited increased glass-transition temperatures with increased S-DC-DPS/DCDPS ratios; their acid forms provided much lower glass-transition temperatures than their sodium forms. In addition, the S-PES sodium form exhibited a high intrinsic viscosity, which indicated a high molecular weight. The S-PES acid form exhibited an adhesion strength similar to that of the sodium form, and the single-lap-shear strength increased with 10% S-PES and then decreased with 20, 30, and 40% S-PES. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1211–1218, 2004

Key words: adhesion; polyelectrolytes; poly(ether sulfones)

INTRODUCTION

Because of increasing demand for fuel cells in transportation and portable electronics, proton-exchange polymer membranes for fuel cells have recently received much attention. The state-of-the-art proton-exchange membranes, which include perfluorinated polymers containing sulfonic acid moieties, such as Nafion (DuPont) and Aciplex (Asahi Chemicals), possess good chemical and physical properties, as well as high conductivity.[1] However, these membranes have several drawbacks, including high cost, a drastic reduction in conductivity at temperatures above 80°C from water loss, CO poisoning, and high methanol crossover, which limit their applications in direct methanol fuel cells.[2–5]

Consequently, there have been a number of attempts to modify polymers for proton-exchange membranes, including poly(ether sulfone)s,[6,7] poly(ether ketone)s,[8–10] polyimides,[11–13] polybenzimidazole,[14] and polyphosphazenes.[15,16] Among these polymers, poly(arylene ether sulfone)s (PESs) have received much attention because of their high thermal, oxidative, and chemical stability in fuel cell environments,[17] in addition to the fact that the starting materials for PESs are inexpensive. The sulfonation of PESs was reported by Noshay and Robeson,[18] who used a commercial PES in a postsulfonation reaction to generate sulfonic acid moieties only to the activated ortho position to the aromatic ether bond.

The low degree of sulfonation resulting from the postsulfonation method led Robeson and Matzner[19] to attempt the direct sulfonation of monomers for the first time. Later, Ueda et al.[20] further investigated the sulfonation of 4,4′-dichlorodiphenylsulfone (DCDPS), generating sulfonic acid groups on deactivated phenyl rings, but the full details were not available. Recently, Mecham et al.[21] studied the direct sulfonation of DC-DPS and reported the synthesis and characterization results in detail. This was followed by the successful synthesis of sulfonated poly(arylene ether sulfone)s (S-PESs) with a high loading of sulfonic acid groups, which possessed very good ion conductivity as well as high thermal properties and chemical stability.[22–24] In addition, sulfonated poly(arylene ether phosphine oxide) and sulfonated poly(sulfide sulfone) were also prepared.[25,26]

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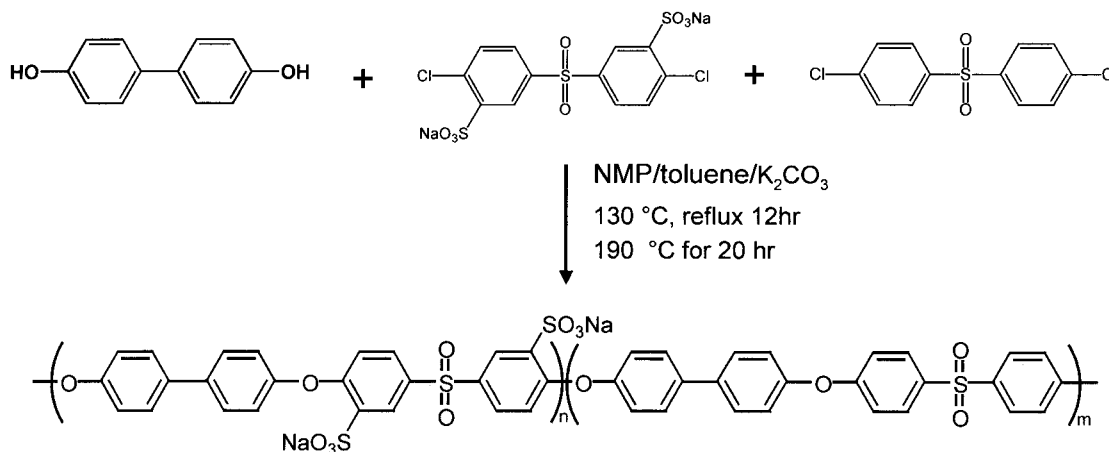
Scheme 1 Synthesis of S-PES.

Because the properties of S-PESs, including the ion conductivity, have proven to be good enough for proton-exchange membrane fuel cells, it may be valuable to investigate the adhesion property of S-PESs, given that the adhesion between the proton-exchange membrane and the cathode or anode is a critical factor in fuel cell performance. In this study, therefore, the sulfonated 4,4'-dichlorodiphenylsulfone (S-DCDPS) monomer was prepared as reported previously[21] and used to prepare PESs with 4,4-dichlorodiphenylsulfone (DCDPS) and 4,4'-biphenol. The resulting polymers were characterized with Fourier transform infrared (FTIR), NMR, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA), and their intrinsic viscosity and solubility were also measured. Then, the bonding conditions, such as the bonding temperature, pressure, and time, were optimized because these polymers possessed such high glass-transition temperatures (T_g's) that at times they degraded before flow occurred to give good adhesion. The adhesion property of S-PESs was investigated as a function of the degree of sulfonation via single-lap-shear tests, and the results from their sodium form and acid form were compared. In addition, the failure modes and the degradation of adhesives were also investigated as functions of the bonding conditions, degree of sulfonation, and type of acid group (sodium or acid form).

EXPERIMENTAL

Materials

4,4'-Dichlorodiphenyl sulfone (DCDPS) and 4,4'-bipenol (BP) from Aldrich were purified by recrystallization from toluene and deoxygenated acetone, respectively. DCDPS was then subjected to sulfonation with fuming sulfuric acid, as reported previously.[21] All other reagents, including fuming sulfuric acid and

potassium carbonate, were obtained from Aldrich and used as received. N-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation after being stirred overnight with phosphorus pentoxide, whereas N,N-dimethylacetamide (DMAc) and toluene were purified by vacuum distillation.

Synthesis and characterization of S-PES

S-PES was synthesized via an aromatic nucleophilic substitution reaction with S-DCDPS, DCDPS, and BP in the presence of potassium carbonate in NMP with toluene as an azeotroping agent (Scheme 1). The polymerization was carried out in a 100-mL, three-necked, round-bottom flask fitted with a mechanical stirrer, a nitrogen inlet, and a Dean–Stark trap with a reflux condenser. The molar ratio of S-DCDPS to DC-DPS was 10/90, 20/80, 30/70, or 40/60. A detailed synthesis of 10% S-PES, containing 10% S-DCDPS and 90% DCDPS, is described next.

First, 20 mmol (3.7242 g) of BP and 1.15 equiv of potassium carbonate were added to a flask. NMP (20 mL) was then charged into the flask, and toluene was added as an azeotroping agent (14 mL). The reaction mixture was refluxed at 130°C for 12 h under a nitrogen flow and cooled to room temperature (RT). Next, 2 mmol of S-DCDPS (1.0500 g) and 18 mmol of DCDPS (5.2052 g) were added, followed by NMP (20 mL). The mixture was heated slowly to 190°C and allowed to react for 20 h; it was then cooled to RT. The polymer solution was diluted with DMAc, filtered to remove the sodium, and precipitated into isopropanol.

The resulting powdery polymer was isolated, washed with deionized water to remove the residual sodium, and dried in vacuo at 120°C for 12 h. The product was dried for an additional 12 h at 180°C in a vacuum oven; this provided the sodium form of S-PES. Polymer films, which were prepared through the dissolution of the
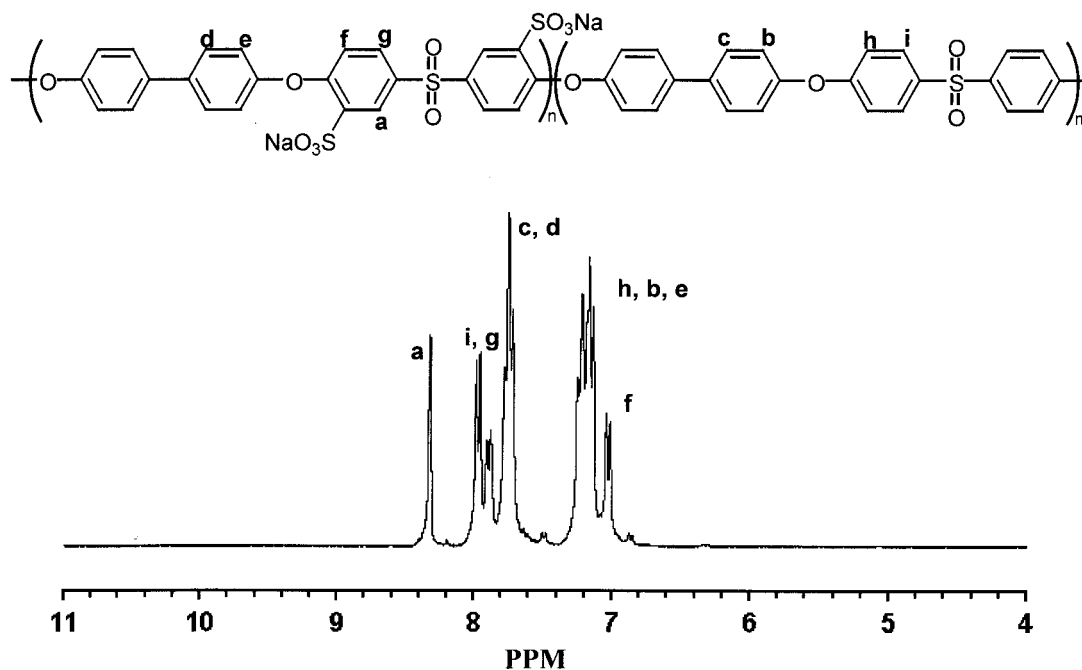
Figure 1 ^{1}H-NMR spectrum of S-PES (solvent = dimethyl sulfoxide-d_6).

polymer in DMAc, solution casting, and drying under an IR lamp, were used for characterization and adhesion studies. Portions of these films were also immersed in sulfuric acid (1.5M) for 24 h at RT to afford their acid forms, which were then immersed in deionized water for 3 h. The process was repeated three times.

Characterization of S-PES

The polymers were characterized with FTIR (IR 2000, PerkinElmer, Torrance, CA) and ^{1}H-NMR (JNM-LA 300 WB FT-NMR, JEOL, Tokyo, Japan), whereas the intrinsic viscosities were measured in NMP at 25°C

with a Cannon-Ubbelohde viscometer. The T_g values were measured with DSC (model 2010, TA, New Castle, DE) at 10°C/min and with DMA (model 983, TA) at 5°C/min with a 10 mm × 7 mm × 0.05 mm sample in the resonance mode. The thermal stability of the polymers was recorded by TGA (model 2050, TA) at 10°C/min in air. Solubility measurements were also carried out through the immersion of the polymer films (0.1 g) in 10 mL of a solvent, such as NMP, DMAc, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), chloroform, acetone, methanol, and water, at RT for 24 h.
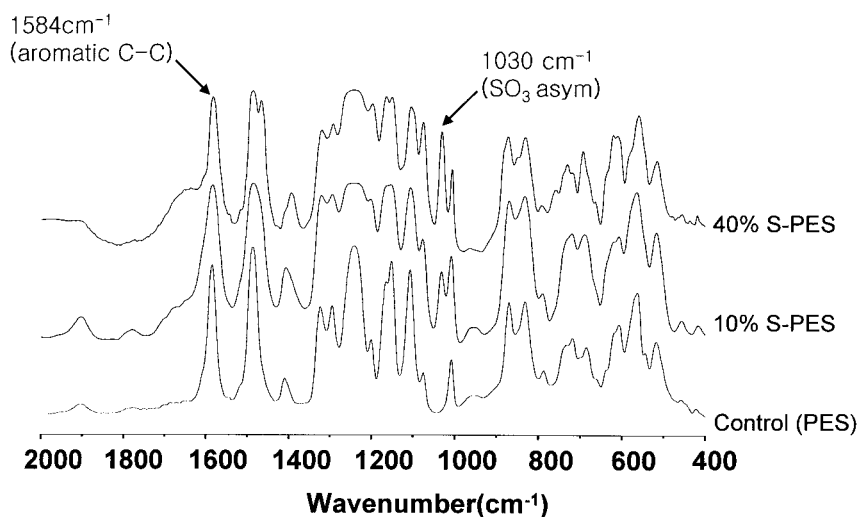

Figure 2 FTIR spectra of S-PES.

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TABLE I
Characteristics of S-PESs

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Degree of sulfonation (%)	Sodium form					Acid form	
	$[\eta]$ (dL/g)[a]	T_g (°C)[b]	T_g (°C)[c]	T_d (°C)[d]	Weight remaining (wt %)[e]	T_g (°C)[f]	T_d (°C)[g]
Control	0.92	223	232	508	0	223	508
10% S-PES	0.93	237	253	497	4	230	441
20% S-PES	0.98	260	283	495	6	242	384
30% S-PES	1.03	—	331	489	11	256	356
40% S-PES	1.17	—	377	480	13	264	345

[a] Intrinsic viscosity measured at 25°C in NMP.
[b] By DSC, second heat, 10°C/min.
[c] By DMA, 5°C/min, resonance mode.
[d] By TGA, decomposition temperature, 5% weight loss temperature.
[e] By TGA at 800, 10°C/m in air.
[f] By DSC, second heat, 10°C/min.
[g] By TGA, 5 wt % loss in air.

Adhesive property of S-PESs

The adhesive properties of sulfonated poly(arylene ether)s were measured with single-lap-shear specimens prepared from Al 2024 alloys (25.4 mm × 101.6 mm) according to ASTM D 1002. Al coupons were etched according to ASTM D 2651-79 through immersion in the specified solution [30 parts water, 10 parts sulfuric acid (specific gravity = 1.84), and 1 part sodium dichromate by weight] for 10 min at 68 ± 3°C. The specimens were then rinsed with distilled water and cleaned in an ultrasonic bath at 65.5°C for 10 min. After the specimens were dried in air and in a vacuum oven at 60°C for 20 min, they were coated with a 10 wt % polymer solution in DMAc and dried at 140°C for 1 h and at 180°C for 10 min. All pretreated Al coupons were stored in a desiccator until they were needed. The adhesives were prepared via solution casting with DMAc, and the resulting films were cut into 30 mm × 15 mm specimens.

Single-lap-shear samples were prepared with a bonding jig, which was designed to have a bonded area of 12.5 mm × 25.4 mm. Two Al coupons were stacked together with the adhesive sandwiched between the layers. The bonding temperature was optimized through the variation of the temperature from 280 to 340°C under a fixed holding time of 30 min and a pressure of 2 MPa with 10 and 30% sodium forms of S-PES. After the samples were heated to 200°C under contact pressure at a heating rate of 7°C/min, a pressure of 2 MPa was applied, and the samples were further heated to 280, 300, 320, or 340°C at a heating rate of 7°C/min. After being held for 30 min, the samples were allowed to cool to RT under pressure. The optimized bonding temperature, along with a holding time of 30 min and a pressure of 2 MPa, was used to evaluate the adhesion of sodium and acid forms of S-PESs. The adhesion strengths were measured with an Instron 5567 (Canton, MA) at a crosshead speed of 1.25 mm/min at RT. At least three specimens were tested, and the results were averaged. To understand the adhesion behavior of S-PES, we examined the failure surfaces and the color of the adhesives with the naked eye, and we estimated the flow behavior by inspecting the adhesives after bonding.

RESULTS AND DISCUSSION

Characteristics of S-PESs

In ^{1}H-NMR spectra, six groups of proton peaks were observed, as reported previously.[23] As shown in Figure 1, the most deshielded proton was the one be-

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TABLE II
Solubility of S-PESs (Sodium Form)

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Degree of sulfonation (%)	NMP	DMAc	DMSO	THF	CHCl$_3$	Acetone	Methanol	Water
Control	S	S	S	S	S	P	I	I
10% S-PES	S	S	S	P	S	I	I	I
20% S-PES	S	S	S	P	P	I	I	I
30% S-PES	S	S	S	I	I	I	I	SW
40% S-PES	S	S	S	I	I	I	I	SW

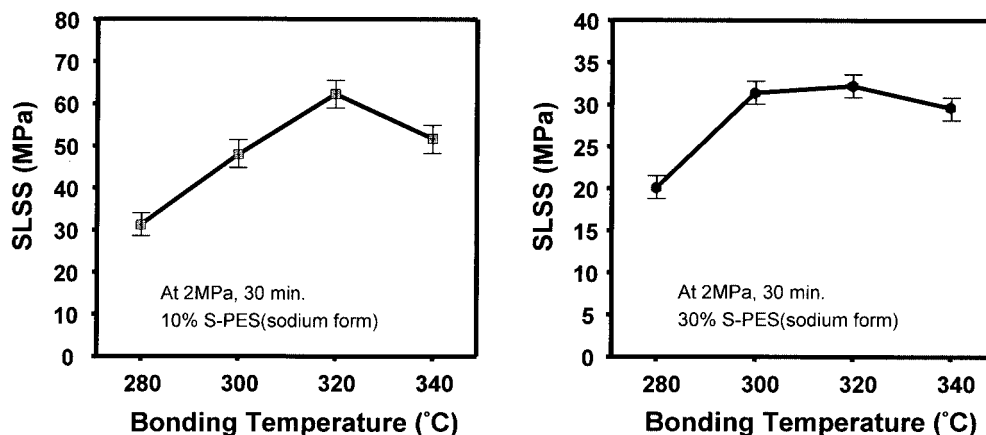S = soluble; P = partially soluble; I = insoluble; SW = swollen.

Figure 3 Optimization of the bonding temperature at 30 min and 2 MPa with 10 and 30% S-PES (sodium form).

tween SO_2 and SO_3Na because of the strong electron-withdrawing nature of these moieties, and it was thus assigned to the peak at 7.323 ppm, followed by protons g and i next to SO_2, which were assigned to the peaks that appeared at 7.881 and 7.985 ppm, respectively. The next deshielded protons were c and d on the biphenyl unit. The most shielded proton f was next to the electron-donating ether group, followed by h, b, and e, given the electron-donating effect of the ether group and electron-withdrawing SO_2 and SO_3Na. The successful synthesis of S-PESs was also confirmed by FTIR, which showed the symmetric and asymmetric stretching of the sodium sulfonate group at 1030 and 1096 cm^{-1}, respectively (Fig. 2). The intensity of these peaks increased as the molar percentage of S-DCDPS increased, as reported by Wang et al.[23] In addition, the characteristic aromatic C—C and C—O—C peaks at 1584 and 1215 cm^{-1} from PESs were also observed, along with the SO_2 peak (asymmetric) at 1150 cm^{-1}.

T_g of the control PES by DSC was 223°C, whereas the S-PES acid form had T_g's of 230, 242, 256, and 264°C for 10, 20, 30, and 40% S-DCDPS, respectively, which indicated increased intermolecular interactions of sulfonic acid groups, as shown in Table I. These values were slightly lower than those reported by Wang et al.,[23] possibly because of the relatively high

water absorption evidenced by the TGA results. On the other hand, the S-PES sodium form exhibited T_g's of 237 and 260°C with 10 and 20% S-DCDPS, respectively, but no clear T_g was detected with 30 and 40% S-DCDPS, likely because of the strong intermolecular interactions of the ionic groups. Therefore, the S-PES sodium form was analyzed by DMA, and this resulted in clear T_g's in a much higher range than those obtained from the S-PES acid form for all the polymers. This indicated that intermolecular interactions were much stronger in the sodium form than in the acid form. In the thermal stability tests, the S-PES acid form was only stable up to 340–440°C (Table I); the control PES and PES sodium form exhibited good thermal stability up to 480°C or higher. The poor thermal stability of the S-PES acid form was attributed to the easy degradation of the sulfonic acid groups. Moreover, the degradation temperature decreased as the loading of S-DCDPS increased.

The control PES was soluble in NMP, DMAc, DMSO, chloroform, and THF. However, the S-PES sodium form was completely soluble in NMP, DMAc, and DMSO, with 10 and 20% S-PES partially soluble in tetrahydrofuran and chloroform (Table II). The S-PES sodium form containing 30 or 40% S-DCDPS remained insoluble in tetrahydrofuran and chloroform, but it

TABLE III
Bonding-Temperature Optimization with 10 and 30% S-PESs

Bonding temperature (°C)	10% S-PES (sodium form)				30% S-PES (sodium form)			
	SLSS (MPa)	Flow	Color	Failure mode	SLSS (MPa)	Flow	Color	Failure mode
280	31.3 ± 3.5	P	LB	I	20.3 ± 3.2	P	LB	I
300	48.5 ± 4.3	P	LB	I	31.7 ± 3.3	P	LB	I
320	62.7 ± 5.5	G	LB	C	32.3 ± 4.7	G	DB	C
340	51.1 ± 5.3	G	DB	C	29.1 ± 3.9	G	BL	C

Flow: E = excellent; G = good; P = poor. Color of adhesive after bonding: LB = light brown; DB = dark brown; BL = black. Failure mode: C = cohesive; M = mixed; I = interfacial.

exhibited swelling in water because of the sulfonic acid moieties. The poor solubility exhibited by the S-PES sodium form in organic solvents and their swelling in water could be attributed to the strong ionic interaction of sulfonic acid moieties. Because all the S-PES sodium form samples prepared in this study were soluble in NMP, the intrinsic viscosity was measured in NMP at 25°C. The S-PES sodium form exhibited intrinsic viscosities of 0.93–1.17 dL/g, which indicated relatively high-molecular-weight polymers. As noted, the intrinsic viscosity increased as the sulfonic acid moiety increased because of the increased intermolecular interaction. Our values were similar to the viscosity values reported by Wang et al.[22] but slightly lower than their results from subsequent studies.[23] Our results and earlier results by Wang et al. were possibly caused by slightly lower polymer molecular weights than those from their later report.

Bonding-temperature optimization

To achieve the maximum adhesive bond strength, the bonding temperature was optimized with 10 and 30% S-PES (sodium form) under a bonding pressure of 2 MPa and a holding time of 30 min. As the bonding temperature increased, the adhesive bond strength of 10% S-PES increased sharply from 31.3 (280°C) to 48.5 (300°C) and 62.7 MPa (320°C) and then decreased to 51.1 MPa (340°C), whereas 30% S-PES exhibited bonding strengths of 20.3 (280°C), 31.7 (300°C), 32.3 (320°C), and 29.1 MPa (340°C), as shown in Figure 3. The increased adhesion with bonding temperatures of 300 and 320°C can be explained by enhanced flow, whereas decreased adhesion at 340°C was caused by the degradation of the adhesive at that temperature. In addition, lower adhesion with 30% S-PES was attributed to poorer flow resulting from higher ionic interactions, with respect to 10% S-PES. As expected, interfacial failure was observed from samples prepared at 280 and 300°C, whereas cohesive failure was observed from samples prepared at 320 and 340°C with 10 and 30% S-PES.

An analysis of the adhesives showed good flow at 320 and 340°C, but there was poor flow from bonding at 280 and 300°C (Table III); this was expected from the T_g values of the S-PES sodium form. Moreover, the light brown color of the 10% S-PES sodium form did not change at bonding temperatures of 280, 300, and 320°C but turned dark brown at 340°C; this indicated the degradation of 10% S-PES and thus explained the low adhesion despite the good flow and cohesive failure. However, 30% S-PES showed no color change or a slight change at bonding temperatures of 280 and 300°C, in contrast to dark brown (at 320°C) or black (at 340°C). This demonstrated that much greater degradation occurred in 30% S-PES at 320 and 340°C, again
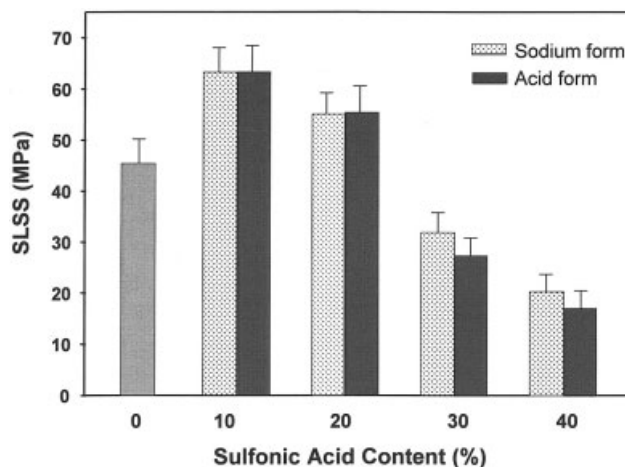

Figure 4 Comparison of the SLSS values of the sodium and acid forms of S-PES.

explaining the low adhesion obtained at 340°C. On the basis of the optimization results, 320°C was chosen as the bonding temperature for this study.

Adhesion properties of the sodium form of S-PESs

The S-PES sodium form exhibited adhesion strengths of 62.7, 55.1, 32.3, and 20.5 MPa with 10, 20, 30, and 40% S-PES, respectively; the adhesion strength was 45.4 MPa for biphenyl-based control PES, as shown in Figure 4. The adhesion strength increased with 10% S-PES, possibly because of the ionic interactions of sulfonic acid groups, which were high enough to result in good interactions with Al adherends but low enough to allow good flow in comparison with that of the control samples. However, adhesion decreased as the ionic concentration further increased to 20, 30, and 40% S-PES, and this was attributed to reduced flow from increased ionic interactions. Consequently, the flow behavior of S-PES was estimated from the adhesives after bonding (Table IV). As expected, 10 and 20% S-PESs (sodium form) exhibited a good consolidation of two layers of film, and this indicated good flow. In comparison, 30 and 40% S-PES showed poor consolidation as a result of an increased ionic concentration and thus increased ionic interaction.

The flow behavior can be directly correlated to the failure mode—cohesive failure with 10 and 20% S-PES, which showed approximately half of the adhesive on each adherend, and interfacial failure with 30 and 40% S-PES—although the exact failure mode had to be investigated by surface analysis techniques such as X-ray photoelectron spectroscopy. In addition, the color change in the S-PES adhesives after bonding was dependent on the ionic concentration: light brown in 10 and 20% S-PES, dark brown in 30% S-PES, and

TABLE IV
Adhesion Behavior of S-PESs

Degree of sulfonation (%)	Sodium form				Acid form			
	SLSS (MPa)	Flow	Color	Failure mode	SLSS (MPa)	Flow	Color	Failure mode
Control	45.4 ± 5.3	E	LB	C	—	—	—	—
10% S-PES	62.7 ± 5.5	E	LB	C	63.3 ± 5.8	G	LB	C
20% S-PES	55.1 ± 4.8	G	LB	C	55.5 ± 5.2	G	BR	C
30% S-PES	32.3 ± 4.7	P	BR	I	28.3 ± 3.2	P	DB	M
40% S-PES	20.5 ± 3.4	P	DB	I	18.3 ± 3.4	P	BL	M

Flow: E = excellent; G = good; P = poor. Color of adhesive after bonding: LB = light brown; DB = dark brown; BL = black. Failure mode: C = cohesive; M = mixed; I = interfacial.

black in 40% S-PES (Table IV). This behavior resulted from decreasing thermal stability with increasing ionic concentration, and this was also observed in TGA. Therefore, decreasing adhesion with increasing ionic concentration can be said to result from less flow and more thermal degradation with increasing ionic concentration.

Adhesion properties of the acid form of S-PES

The single-lap-shear strengths (SLSSs) of the S-PES acid form were 63.3, 55.5, 28.3, and 18.3 MPa with 10, 20, 30, and 40% S-PES, respectively (Fig. 4). Again, increased adhesion with 10% S-PES, with respect to the control sample, could be attributed to increasing ionic interactions resulting from sulfonic acid groups, whereas decreasing adhesion with 20, 30, and 40% S-PES could be explained by lowered flow properties and decreased thermal stability with increasing ionic interactions. As shown in Table IV, acid form samples with 10 and 20% S-PES exhibited cohesive failure, whereas 30 and 40% acid form S-PESs showed mixed failure. All S-PES acid form samples provided good flow, as evidenced by the good consolidation of adhesives upon bonding; this could be attributed to the poor thermal stability of the S-PES acid form.

The S-PES acid form exhibited an adhesion strength similar to that of the S-PES sodium form, despite the lower T_g values, possibly because of the lower thermal stability of the S-PES acid form (320–340°C in air). As shown in Table IV, the S-PES acid form turned light brown (10%), brown (20%), dark brown (30%), or black (40%) upon bonding; the S-PES sodium form turned light brown (10, 20%), brown (30%), and dark brown (40%). This demonstrated the poorer thermal stability of the S-PES acid form. Therefore, that the adhesion strength obtained from the S-PES acid form was similar to that of the S-PES sodium form could be attributed to the higher thermal degradation of the former despite the good flow; this was also supported by the TGA results.

CONCLUSIONS

S-PESs were successfully prepared from S-DCDPS, DCDPS, and BP. T_g of S-PESs increased with the S-DCDPS content, whereas the thermal stability and solubility decreased, because of increased intermolecular interactions from ionic bonds. The adhesion strength of S-PESs (acid and sodium forms) increased with 10% S-PES, in comparison with the control sample, but decreased further with 20, 30, and 40% S-PESs; this was attributed to increased intermolecular interactions, which in turn resulted in poor flow and decreased thermal stability of S-PESs. Failure-mode analysis revealed that cohesive failure with 10 and 20% S-PES, but mixed or interfacial failure was present with 30 and 40% S-PES; this demonstrated reduced flow and poor thermal stability for S-PESs with increasing S-DCDPS content. The flow behavior and thermal degradation observed for the adhesives after bonding became worse as the ionic concentration increased.

References

1. Savadogo, O. J New Mater Electrochem Syst 1998, 1, 47.
2. Sumner, J. J.; Creager, S. E.; Ma, J. J.; DesMarteau, D. D. J Electrochem Soc 1998, 145, 107.
3. Kauanen, P. S.; Skou, E. J Appl Electrochem 1996, 26, 909.
4. Jia, N.; Lefebvre, M. C.; Halfrad, J.; Qi, Z.; Pickup, P. G. Electrochem Solid-State Lett 2000, 3, 529.
5. Malhotra, S.; Datta, R. J Electrochem Soc 1997, 144, 1498.
6. Genova-Dimitrova, P.; Baradie, B.; Foscallo, D.; Poinsignon, C.; Sanchez, J. Y. J Membr Sci 2001, 185, 59.
7. Lufrano, F.; Squadrito, O.; Patti, A.; Passalacqua, B. J Appl Polym Sci 2000, 77, 1250.
8. Bailly, C.; Williams, D. J.; Karasz, F. E.; MacKnight, W. J. Polymer 1987, 28, 1009.
9. Zaidi, S. M. J.; Mikahailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S. J Membr Sci 2000, 172, 17.
10. Alberti, G.; Casciola, M.; Massinelli, L.; Bauer, B. J Membr Sci 2001, 185, 73.

11. Cornet, N.; Diat, O.; Gebel, G.; Jousse, F.; Marsacp, D.; Mercier, R.; Pineri, M. J New Mater Electrochem Syst 2000, 3, 33.

12. Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. Polymer 2001, 42, 359.

13. Hong, Y. T.; Einsla, B.; Kim, Y.; McGrath, J. E. Polym Prep 2002, 43, 666.

14. Jones, D.; Roziere, J. J Membr Sci 2001, 185, 41.

15. Allcock, H. R.; Hofmann, M. A.; Ambler, C. M.; Lvov, S. N.; Zhou, X. Y.; Chalkova, E.; Weston, J. J Membr Sci 2002, 210, 47.

16. Tang, H.; Pintauro, P. N. J Appl Polym Sci 2001, 79, 49.

17. Cotter, C. J. Engineering Plastics: A Handbook of Polyarylethers; Gordon & Breach: London, 1995.

18. Noshay, A.; Robeson, L. M. J Appl Polym Sci 1976, 20, 1885.

19. Robeson, L. M.; Matzner, M. (to Union Carbide). U.S. Pat. 4,380,598 (1983).

20. Ueda, M.; Toyota, H.; Ochi, T.; Sugiyama, J. I.; Yonetake, K.; Masuko, T.; Teramoto, T. J Polym Sci Part A: Polym Chem 1993, 31, 85.

21. Mecham, J. B.; Wang, F.; Glass, T. E.; Xu, J.; Wilkes, G. L.; McGrath, J. E. Polym Mater: Sci Eng 2001, 84, 105.

22. Wang, F.; Mecham, J.; Harrison, W.; McGrath, J. E. Polym Prepr 2000, 41, 237.

23. Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mecham, J.; Zawodzinski, T. A.; McGrath, J. E. Macromol Symp 2001, 175, 387.

24. Wang, F.; Hickner, M.; Ji, Q.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. J Membr Sci 2002, 197, 231.

25. Shobha, H. K.; Smalley, G. R.; Sankarapandian, M.; McGrath, J. E. Polym Prepr 2000, 41, 180.

26. Wiles, K. B.; Bhanu, V. A.; Wang, F.; McGrath, J. E. Polym Prepr 2002, 43, 993.