Polyphenylethersulfone adhesive for EPDM elastomer-to-stainless steel joints in a hydrothermal environment

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Hot-melt polyphenylethersulfone (PES) adhesive was used to link ethylene-propylenediene terpolymer (EPDM) elastomer, which can protect geothermal drill pipes, to a stainless steel (SS) substrate. These joints then were exposed for up to 70 days in steam at 200 °C to evaluate the durability of the bond. Although the preparation and modification of EPDM and SS surfaces played an important role in ensuring a strong bond in the EPDM-to-SS adhesive joint system, the susceptibility of the PES adhesive to hydrothermal oxidation led to conformational transformation of its sulfone group into a fragmental sulfonic acid derivative during the exposure. Moreover, a prolonged exposure time caused the decomposition of polyphenylethersulfonic acid derivative, forming two additional derivatives, aryl radical and H_2SO_4. Hot H_2SO_4 favorably reacted with Fe in the SS to yield a water-soluble $Fe_2(SO_4)_3$ reaction product. This reaction product generated at the interfaces between PES and SS caused a decrease in peel strength. In fact, the loss of adhesion occurred in the SS adjacent to the PES. © *1998 Kluwer Academic Publishers*

1. Introduction

Ethylene-propylene-diene terpolymer (EPDM) elastomers are known to possess great hydrothermal stability at temperatures up to 200 °C, chemical inertness to carbon dioxide and hydrogen sulfide, and a good resistance to abrasion. Such excellent properties urged the elastomer users in the geothermal drilling-tool industries to evaluate its potential usefulness as sealing material such as packers and O-rings for sealed drill bits [1]. However, in applying EPDM as a dynamic packer sealing to protect drill pipes or casings in geothermal well, one problem encountered was the lack of adhesion between the EPDM and the metal; it was very difficult to maintain the linkage of EPDM to the drill pipe with conventional adhesives, such as epoxy resin, polyurethane, polyamide, polyimide, polychorprene, and phenol-formaldehyde resin. Most of EPDM-to-pipe adhesive bonding systems failed after a short period of exposure to a wet, harsh geothermal environment at 200 °C, thereby causing delamination and disbondment of the EPDM elastomer from the metal substrates [2]. The reason for the failure of these adhesive bonding systems was due mainly to the hydrothermal degradation of the adhesives themselves, and their poor bonding behavior to either EPDM or metal side. In fact, the loss of adhesion after exposure was observed to take place in the adhesive layer and at the interfaces between the adhesive and adherend. Thus, there needs to develop hydrothermally stable adhesives and coupling technologies for them to enhance bond durability

at the interfaces between the adhesive and the EPDM or metal, ensuring that the EPDM would remain in place over the drill pipe's surfaces for a long-exposure period in steam at 200 °C.

Polyphenylethersulfone (PES), a family of high-performance engineering thermoplastics, is very attractive to use as a hot melt coupling adhesive to link EPDM to the metal substrates because of its deflection temperature of 203 °C under a pressure of 1.8 MPa, its high glass transition temperature (T_g) of $\sim$ 230 °C, processing temperature in the region of 320 to 390 °C, and excellent chemical resistance [3]. The objective of the current study was therefore focused on investigating the usefulness of PES as a coupling adhesive in maintaining an intact EPDM/metal joint in steam at 200 °C under a hydrothermal pressure of 1.64 MPa. The factors to be investigated included the thermal characteristics of PES, such as glass transition temperature, melting point, and thermal decomposition temperature, the changes in bond strength as a function of exposure time, the identification of interfacial reaction products, and the bond failure mechanisms of EPDM/PES/ metal joints.

2. Experimental
2.1. Materials

The metallic substrate used was commercial AIST 304 stainless steel (SS). EPDM elastomer was supplied by Uniroyal Chemical Company. The PES powder used as hot melt adhesive was provided by Imperical Chemical

Industries (ICI); it was mixed with isopropyl alcohol to make a slurry consisting of 45 wt % PES powder and 55 wt % isopropyl alcohol.

2.2. Measurements

Information was obtained on the thermal properties of bulk PES polymers in air or in a 99.9% N_2 environment using the combined techniques of thermogravimetric analysis (TGA), and differential thermal analysis (DSC). The properties studied included the thermal decomposition temperature and the melting point. The chemical composition and states on the bond-failure side at interfaces of the PES/substrate joint systems before and after exposure in steam at 200 °C were investigated by examining the binding energies (BE) deduced from X-ray photoelectron spectroscopy (XPS). The atomic concentrations for the respective chemical elements were estimated by comparing the XPS peak areas, which can be obtained from differential cross-sections for core-level excitation. To set a scale in the high-resolution XPS spectra, the binding energy was calibrated with the C_{1s} of the principal hydrocarbon-type carbon peak fixed at 285.0 eV as an internal reference. A curve deconvolution technique, using a DuPont curve resolver, revealed the respective chemical components from the high-resolution spectra of each element. To gain information on the hydrothermal stability of the EPDM elastomer-to-SS plate adhesive joints, the peel strength of these systems were measured at a separation angle of ~ 180° and cross-head speed of 10 mm/min. The test specimens consisted of one piece of EPDM elastomer, $25 \times 100 \times 3$ mm, bonded for 40 mm at one end to an adhesive slurry-coated rigid SS plate, 25×80 mm, with the unbounded portions of each member lying face to face. To melt the PES adhesive, the specimens were heated for 2 hours in an oven at 300 °C under the loading of 13.8 kPa. After a cooling to room temperature, these joint specimens were exposed for up to 70 days in 200 °C steam.

3. Results and discussion
3.1. Thermal properties of bulk PES polymers

A thermal analysis, combining TGA and DTA, revealed the decomposition characteristics during pyrolysis of "as-received" PES powders in air or in N_2 gas (Fig. 1). The TGA curve for PES in N_2 (dashed line) showed that pyrolytic decomposition starts near 550 °C, and is followed by a weight loss of ~ 40% between 550 and 650 °C. This reduction is reflected directly on the DTA endothermic peak at 640 °C. Beyond 650 °C, weight loss occurs gradually. Although the temperature of onset of decomposition was almost the same as that in N_2, the major distinctive feature of the TGA curve for the sample pyrolysed in air was that there were two decomposition stages: the first began around 550 °C and the second occurred between ~ 600–720 °C. These decompositions correspond to the DTA peaks at 640 and 725 °C. In addition, a large weight loss of > 90% occurred at ~ 710 °C. This loss in air was more than
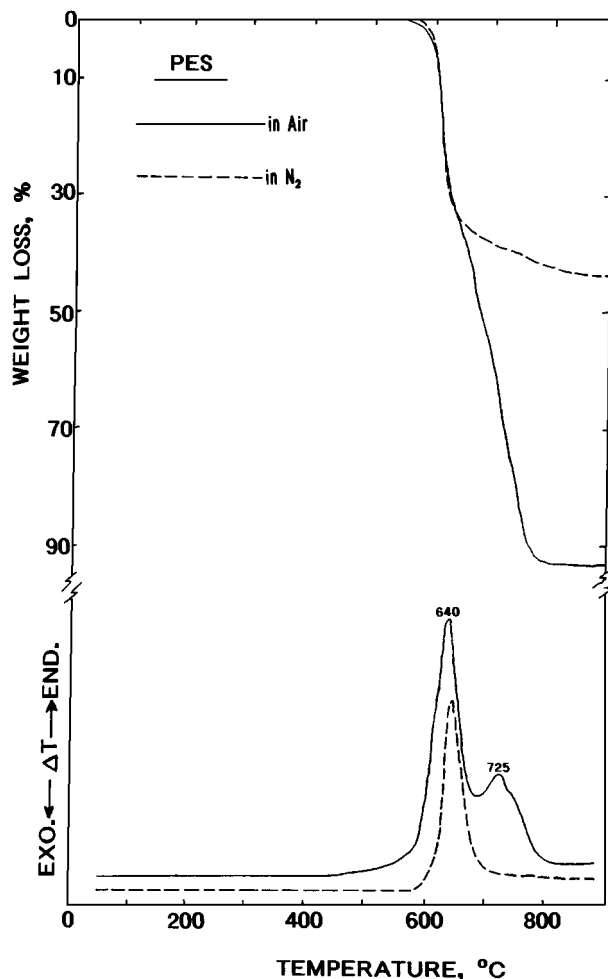

Figure 1 TGA and DTA curves of PES at temperature from 50 to 900 °C under N_2 and air.

double that of the sample pyrolysed in N_2 at the same temperature. Nevertheless, PES appears to have excellent thermal stability at temperatures up to 500 °C.

Assuming that PES polymer has repeated melting-crystallization characteristics at temperatures ranging from 50 to 400 °C in air or N_2, its cyclic DSC curve was investigated at a heating-cooling rate of ± 10 °C min^{-1}. Samples were prepared as follows. Uncovered aluminum DSC pans were filled with approximately 5 mg of PES, and then placed in an oven at 400 °C in air or N_2 for 2 h. The melted samples were subsequently cooled to room temperature at the rate of -10 °C min^{-1}. The pans were then sealed with aluminum covers. The sealed samples were heated again to 400 °C at the rate of $+10$ °C min^{-1} and immediately cooled to 100 °C at the rate of -10 °C min^{-1}. Cooling from 400 °C to low temperatures was accomplished using a DuPont mechanical cooling accessory equipped with a DSC. Fig. 2 shows the resulting cyclic DSC curves for the PES samples prepared in N_2 or air at 400 °C. There was no evidence of an exothermic peak in either case, suggesting that PES does not have the melt-crystallization behavior [4]. The curves showed a weak and a broad endothermic peak around 220 and 370 °C, respectively. The former peak reveals the glass transition temperature (T_g), and the latter corresponds to the melting point (T_m) [5].
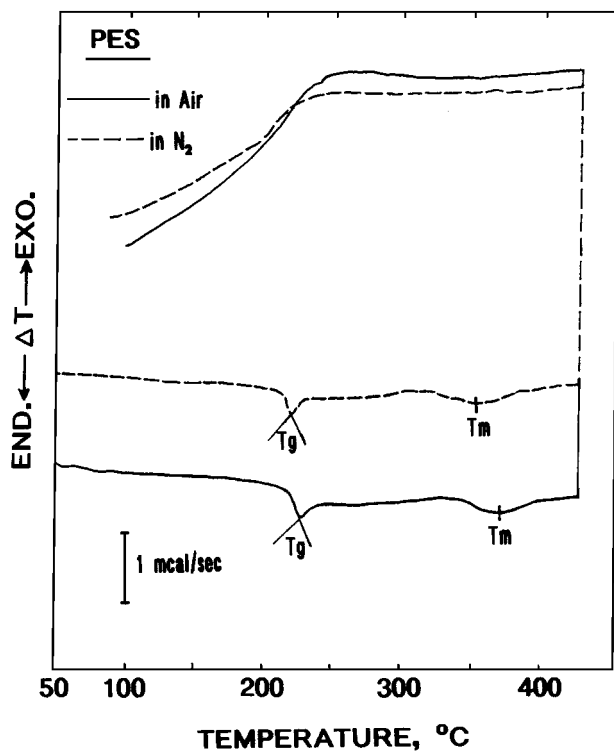
Figure 2 Cyclic DSC scans, ranging from 50 to 450 °C, for PES prepared in N_2 or air at 400 °C.

Etching time (min)	Atomic fraction (%)					
	C	O	Cr	Mn	Fe	Ni
0	71.4	27.4	0.5	0.0	0.7	0.0
10	53.6	41.2	1.8	1.0	2.1	0.3
30	50.5	43.0	2.1	1.2	2.5	0.7
40	45.4	46.2	2.5	1.3	3.8	0.8
60	41.6	49.1	2.8	1.6	3.9	1.0

3.2. Surface treatments of SS and EPDM

One important aspect for improving the extent of adherence of the SS substrate to the adhesive is the preparation and modification of its surfaces prior to depositing the adhesive. In this study, the conventional acid-etching method [6] was employed as a way to improve adherence of the SS surfaces. Simply, the SS panels were immersed for up to 60 min in a nitrichydrochloric acid (3 wt % HNO_3-7 wt % HCl-90 wt % water) at 60 °C. Then, the surfaces were washed with a deionized water at room temperature for 1 min, and then dried for 15 min at 50 °C. The changes in atomic composition of the etched surfaces as a function of immersion time were monitored using XPS (Table I). For the "as-received" SS, the dominant elements occupying at the outermost surface sites were carbon and oxygen, while few chrome and iron atoms were present. Assuming that C and some O are associated with organic surface contaminants, the remaining Cr, Fe, and O atoms seem to originate from their oxide compounds formed on the SS surfaces. After the immersion for 10 min, two additional atoms, Mn and Ni, were incorporated into the top surfaces; meanwhile, the amount of C dropped ∼ 25%, whereas the O, Cr, and Fe atoms increased. Extending the immersion time to 30 min resulted in an increasing amount of all the atomic species, excepting the carbon. The amount of carbon markedly reduced as the immersion time was further prolonged to 60 min, reflecting the removal of carbon-related contaminants from the SS's surfaces.

To assess the adherent property of treated SS surfaces to the PES adhesive, the treated and untreated SS surfaces were coated with the PES slurry, and heated for 2 hours at 300 °C to accomplish PES's melt flowing. After heating, the PES-coated SS specimens were left for 5 hours at room temperature to complete the melt-solid phase transition of PES. Subsequently, the interfacial SS side was physically removed from the PES adhesive, and then examined by XPS to survey the content of sulfur atom originating from the PES. If a large amount of S atom was detected on the dislodged SS interfaces, it is possible to rationalize that the adherent behavior of SS surfaces to the PES is good. Fig. 3 shows the plots of the amount of S versus the etching times. The amount of S increases with an extending time during the first 40 minutes of treatment; beyond this time, it seem to level off. Accordingly, there is no doubt that the adherence of SS to the PES depended mainly on the atomic composition of its etched surfaces; namely, two chemical factors play an important role in improving the interfacial bonds between the SS and PES. One is the elimination of carbon-related contaminants from the SS surfaces by chemical etching, and the other reflects the incorporation of more Cr and Fe atoms into the topsurface layer. Therefore, an etching time of at least 40 min is required to attain a desirable chemical composition of the SS's surfaces.

The focus next centered on investigating the effectiveness of oxidized EPDM surfaces in improving its adherence to the PES. EPDM was oxidized by heating it for up to 45 min in an air oven at 300 °C. Fig. 4 shows the changes in the XPS O/C ratio of EPDM surfaces as a function of heating time. The O/C ratio gradually increases as the heating time prologs before leveling off at about 30 min. The O/C ratio of 0.16 for the 30-min-heated EPDM surfaces was twofold higher than that of the untreated surfaces, suggesting that a substantial amount of oxygen had been incorporated. The investigation was further extended to identify the oxidation products formed on the EPDM surfaces. Fig. 5 shows the XPS C_{1s} and O_{1s} core-level spectra of the EPDM surfaces before and after heating for 30 min at 300 °C. In the C_{1s} region, the spectrum of (a) a specimen from untreated EPDM indicated the presence of two resolvable Gaussian components at 285.0 eV as the principal peak and at 288.1 eV as the shoulder one. The former peak can be ascribed to the hydrocarbon-type carbon, CH_n, and the latter one is due to the carbon in C=O group (e.g. alcohol, ketone, hydroperoxide, or aldehyde) [7]. Hence, a possible interpretation of this information is that a certain amount of oxygen functional groups such as C=O was already present in the topsurface layer. When this surface was heated, its spectrum (b) was characterized by the emergence of two additional peaks
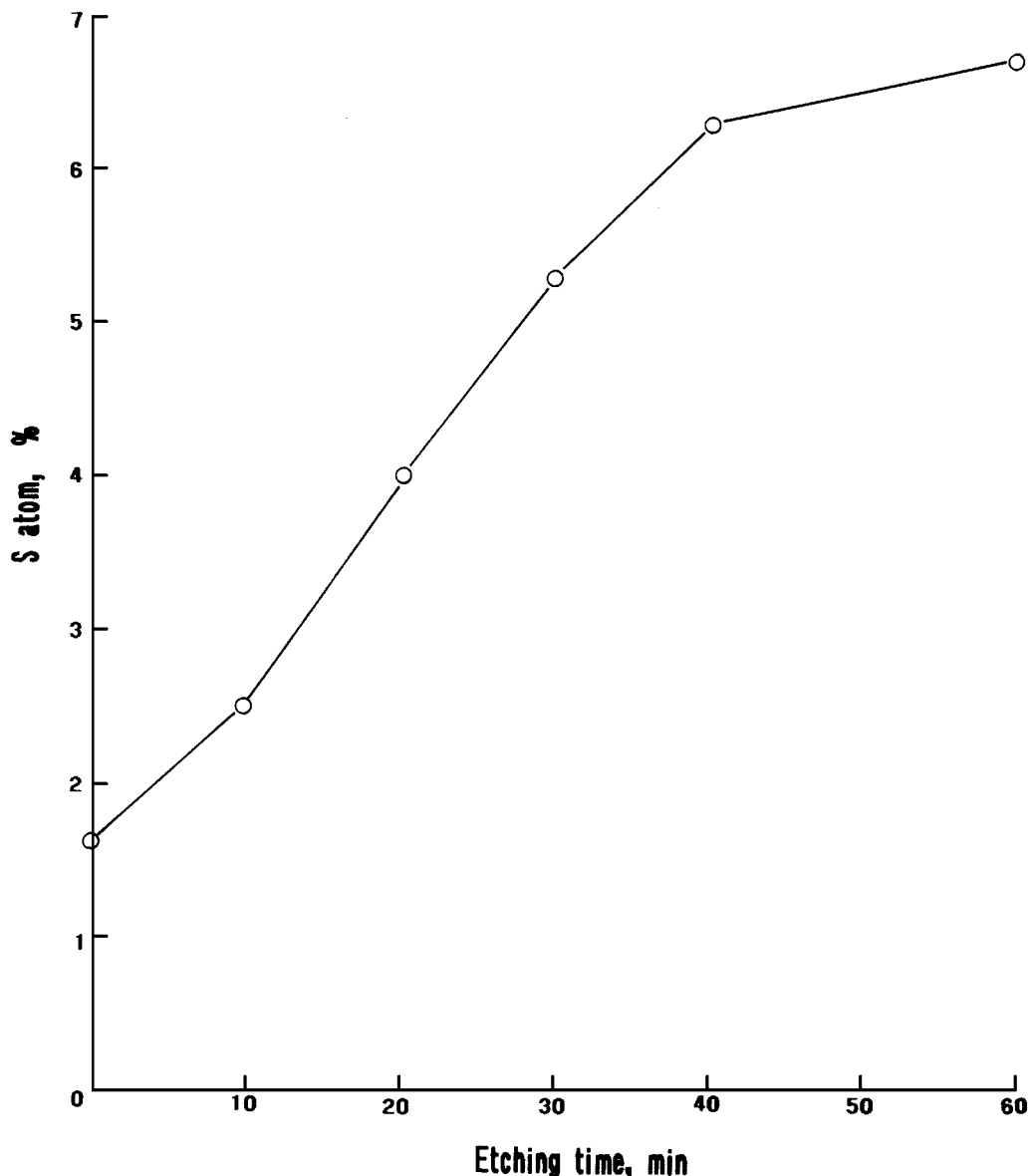
Figure 3 Changes in the amount of S atom on the interfacial SS side removed from PES as a function of etching time of SS surfaces.

at 286.4 and 289.5 eV. According to the literature [8], these signals are assignable to the carbon in the $-CH_2O-$ (e.g. ether or alcohol) and in the $-COO-$ (e.g. carboxylic acid or ester), respectively. The inspection of O_{1s} region for this sample strongly supported this assessment. The spectrum (c) of the untreated samples represented the excitation of a symmetrical signals peak at 532.1 eV, revealing O in the ketone or aldehyde. Oxidizing this sample (see spectrum (d)) led to the introduction of a new signal at 533.6 eV, corresponding to the ester oxygen in carboxyl groups [9]. Since the contributors to the main signal at 532.1 eV include most oxygen functional groups, except for the ester oxygen [9], this signal may belong to the O in the combined oxygen groups of alcohol, ketone, aldehyde, and hydroperoxide. Hence, it is apparent that the 300 °C-oxidized EPDM surfaces have an abundance of functional oxygen groups.

To substantiate the efficacy of these functional oxygen groups in enhancing the interfacial bonds at the interfaces between PES and EPDM, both the oxidized and non-oxidized EPDM surfaces were coated with PES slurry, and then heated for 2 hours. After cooling them,

the interfacial PES side was physically removed from the EPDM and inspected by XPS to identify the locus of bond failure. Table II shows the atomic fractions of interfacially failed PES sides in the PES/non-oxidized or/oxidized EPDM joints. No S was detected on the interfacial PES side separated from the oxidized EPDM. Since the source of S atom comes from the PES, this result can be taken as an evidence that the loss of interfacial bond occurs in the EPDM layer. In other words, the functional oxygen groups yielded at the surfaces of oxidized EPDM contribute significantly to improving its adherence to the PES adhesive. In contrast, the PES side from the non-oxidized EPDM had a 4.9% S, manifesting that the magnitude of adherence of the non-oxidized EPDM to the PES is very little, if any. Hence, the interfacial bond failure in this joint system can be defined as an adhesive failure mode that the disbondment takes place at the interfaces between the EPDM and PES. Inspecting the chemical composition of the interfacial EPDM side opposite to the PES strongly supported this fact; namely, there was no excitation of an S signal (data not shown).
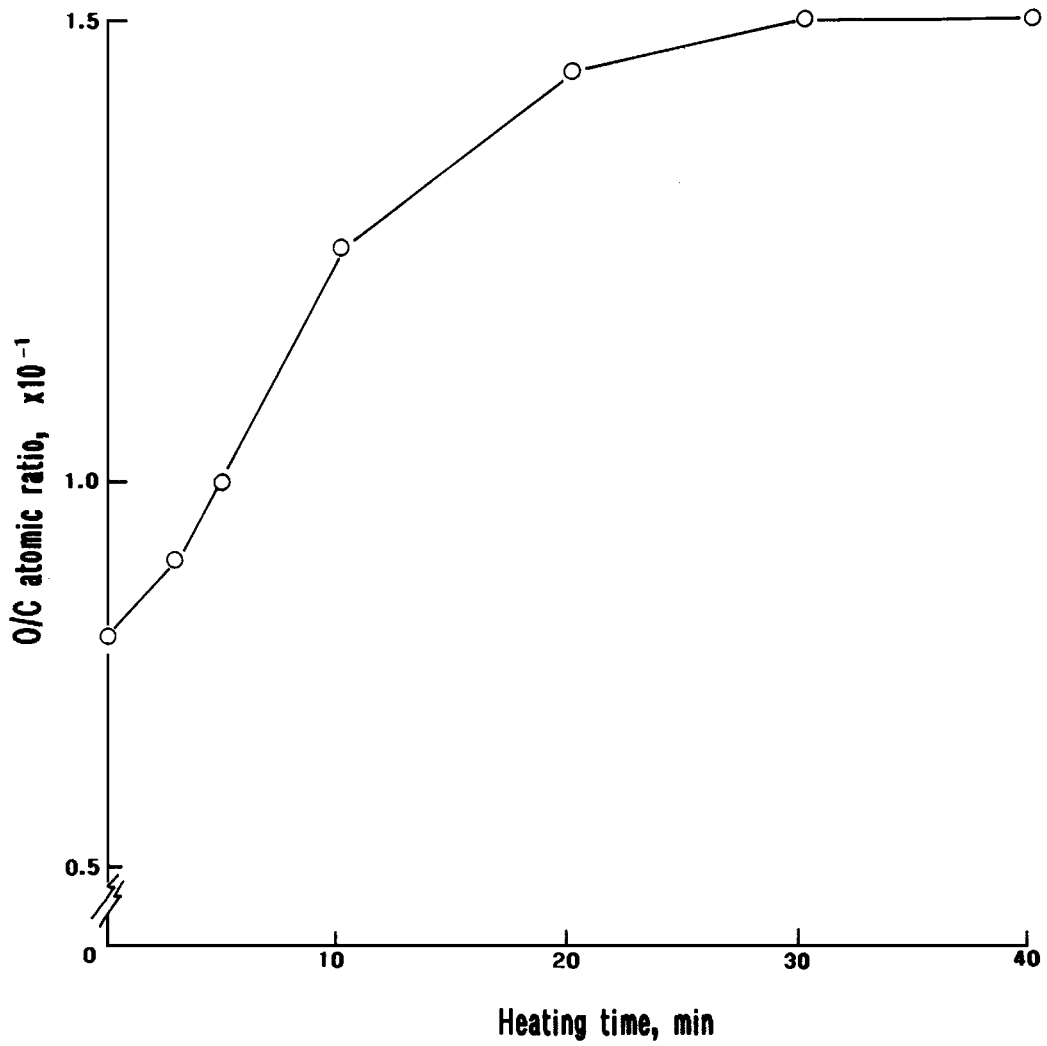
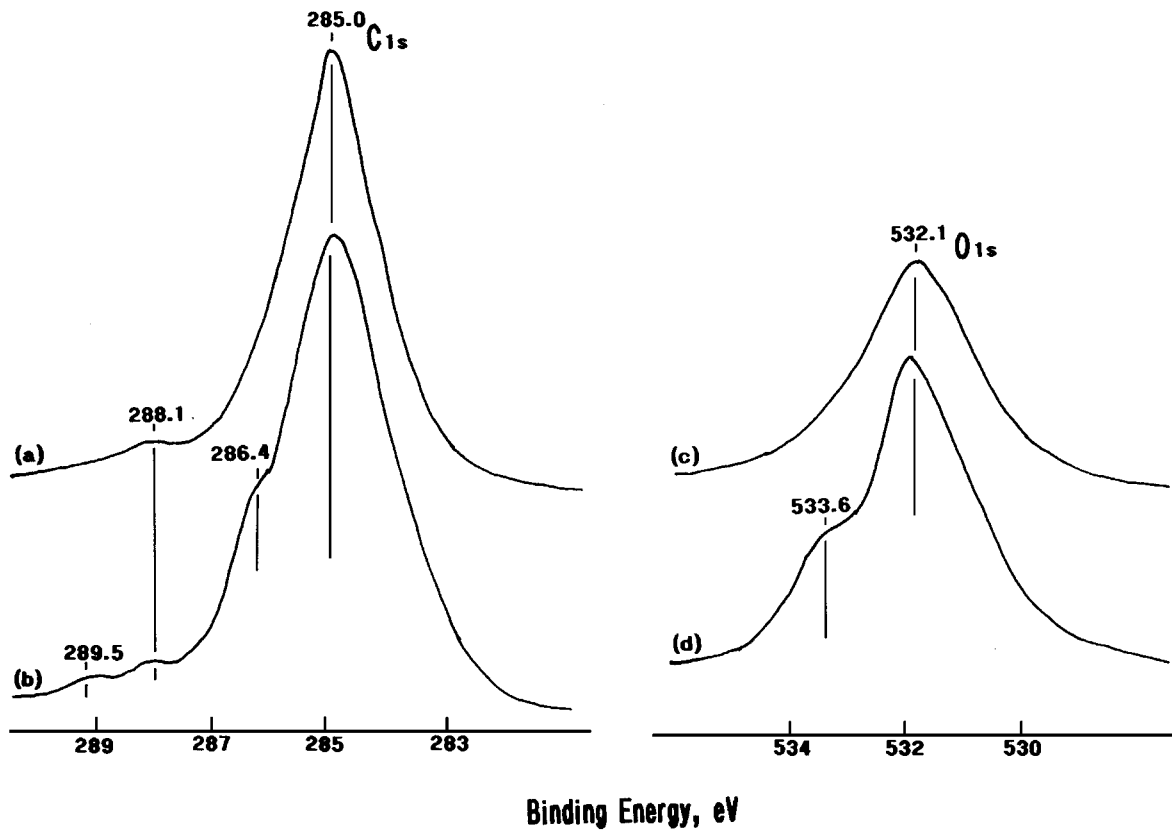*Figure 4* O/C atomic ratio versus heating time for EPDM surfaces.

Figure 5 XPS C_{1s} and O_{1s} core-level spectra for (a) and (c) non-oxidized EPDM surfaces, and (b) and (d) a 300 °C-30-min-oxidized ones.

3.3. Bond durability of PES coupling adhesive

Based upon the information described above, two adherends, the 45-min-acid etched SS and 300 °C-30-min-oxidized EPDM, were used to conduct the bond durability testing of EPDM-to-SS PES adhesive joints after exposure for up to 70 days in steam at 200 °C. The joint specimens were prepared in the manner described in the Experimental section, and their bond durability was evaluated by determining their 180°-peel strength. Fig. 6 shows the changes in peel strength of the joint specimens as a function of exposure time. No peeling

was determined from the specimens after exposure for up to 5 days, representing a strong coupling efficacy of the PES adhesive in linking the EPDM to SS. However, when the exposure time was extended to 15 days, the specimens had a peel strength of 5.3 KN/m. With further exposure time, peel strength had declined to 2.4 KN/m after 70 days. This information verifies that the coupling formation by PES adhesive undergoes the damage during a long-term exposure period in a steam at 200 °C. However, there was no clear evidence whether the damage is due to the hydrothermal degradation of PES itself or to the susceptibility of the interfacial bond structure at the interfaces between PES and EPDM or SS to hot steam hydrolysis.

To gain this information, XPS examinations were carried out on both the interfacial failure SS and EPDM sides after the peeling tests of 70-day-exposed specimens. Table III shows the chemical compositions for these sides. There was no signal from the S atom for the interfacial SS side, reflecting a no transfer of PES to the SS side during the bond failure. The data also revealed that its chemical composition closely resembles that of 40-min-etched SS surfaces, except for a lower amount
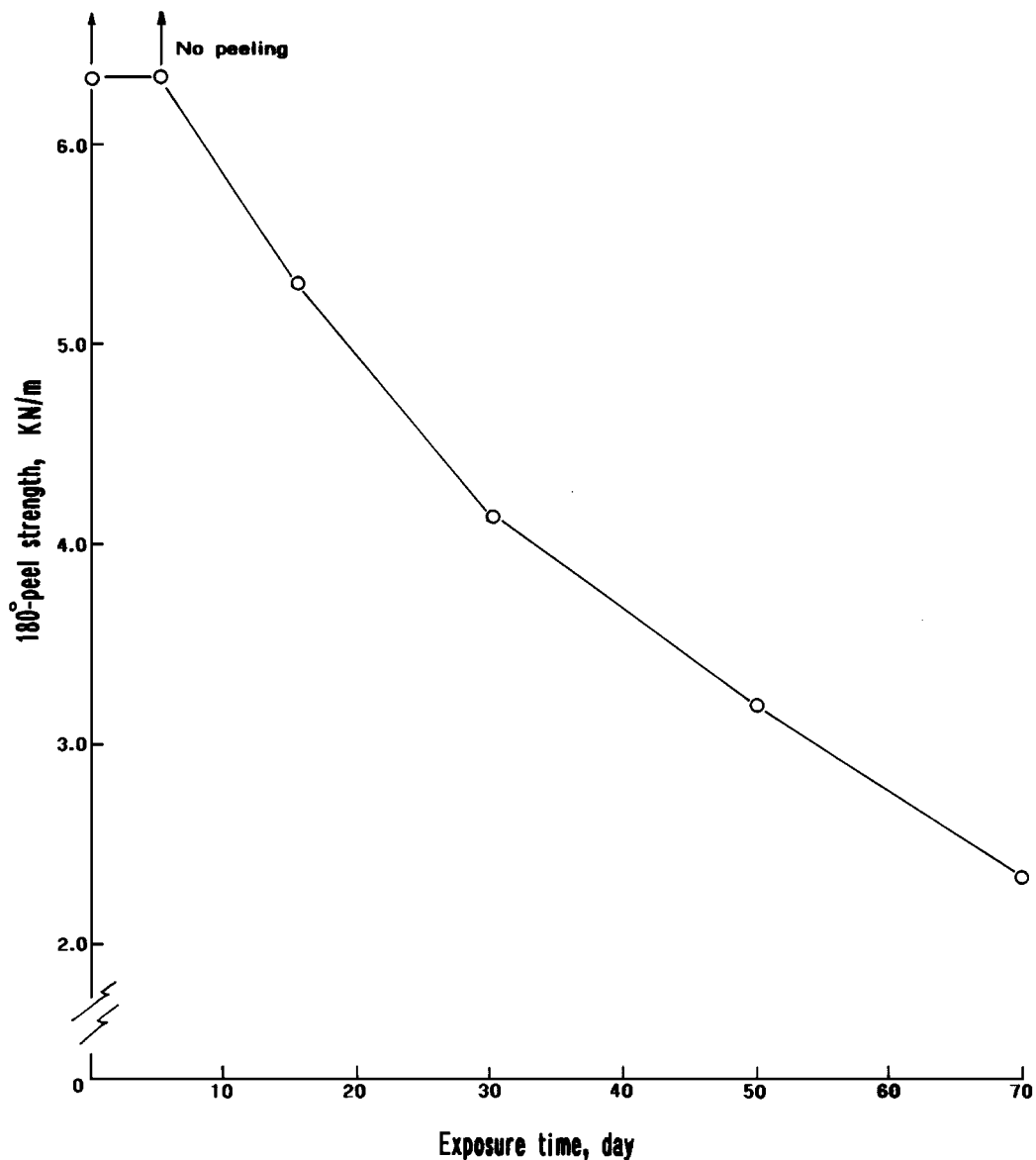
TABLE II XPS atomic composition of interfacial PES sides removed from oxidized and non-oxidized EPDM in the PES/EPDM joint systems

Joint system	Failed side	Atomic fraction (%)		
		C	O	S
PES/oxidized EPDM	PES	78.7	21.3	0.0
PES/non-oxidized EPDM	PES	75.9	19.2	4.9

Figure 6 Changes in 180°-peel strength of EPDM-to-SS adhesive joint specimens as a function of exposure time.

TABLE III Atomic fraction of both interfacial failure sides for EPDM-to-SS PES adhesive joint specimens after exposure for 70 days in steam at 200 °C

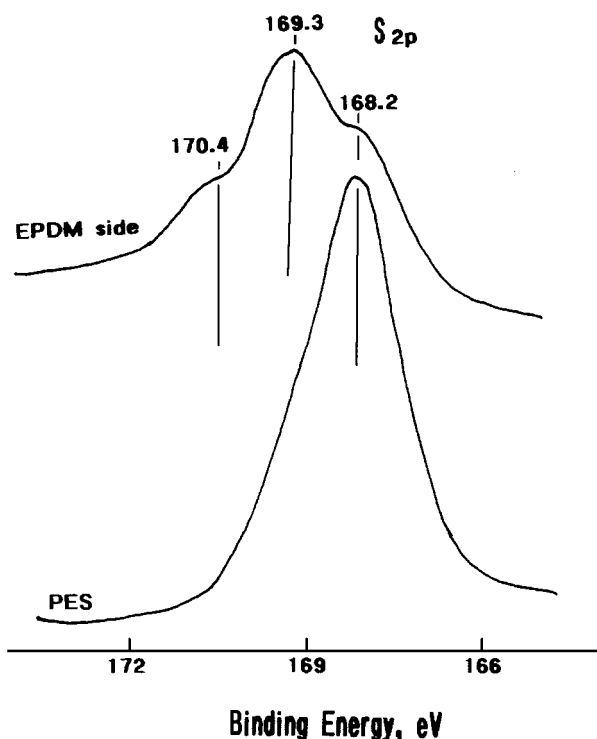| Failure side	Atomic fraction (%)						
	S	C	O	Cr	Mn	Fe	Ni
SS	—	45.7	49.2	2.0	1.0	1.4	0.7
EPDM	3.5	72.8	22.1	—	—	1.6	—

Figure 7 S_{2p} region for the bulk PES adhesive as reference spectrum and the interfacial EPDM side separated from SS in EPDM-to-SS adhesive joint specimens after exposure for 70 days in steam at 200 °C.

of Fe. Interestingly, the interfacial EPDM side involved 3.5% S and 1.6% Fe, which was related directly to the PES and SS, respectively. Because no other SS elements, such as Cr and Mn, were found, it is manifest that the PES containing some Fe was transferred to the EPDM side during failure. In other words, the PES adhesive seems to react preferentially with the Fe in the SS, rather than with other elements. Nevertheless, the bond failure for the 70-day-exposed joint specimens conceivably is generated in the SS adjacent to the PES.

Investigating the S_{2p} core-level spectrum (Fig. 7) of the interfacial EPDM side imparted more detailed information on why the failure occurs in the SS, but not in the EPDM. For comparison, the spectrum of the bulk PES surfaces served as the control. The bulk PES as the reference spectrum indicated the excitation of a symmetrical single peak at 168.2 eV, revealing S in the sulfone groups, $O=S=O$ [10]. The S_{2p} region on the interfacial EPDM side exhibited a quite different spectral feature from that of the reference one; namely, there were (1) the emergence of two new signals at the position of binding energy of 169.3 and 170.4 eV, and (2) a marked attenuation of the peak intensity at 168.2 eV originating from S in the sulfone. An XPS study on sulphur-oxygen bonds [11], suggested that the increase in the rate of oxidation of S results in a shift in peak position to a high BE site; for instance, sulfoxide ($> S=O$) around 165.9 eV, sulfone ($-SO_2-$) at $\sim$ 168.0 eV, sulfonic acid ($-SO_3H$) at $\sim$ 169.0 eV, and sulfate ($-SO_4$) at $\sim$ 169.8 eV. From this information, it is presumed that the contributor at 169.3 eV as the major peak is due to the formation of sulfonic acid produced by the oxidation of sulfone groups in the PES during the exposure in a hot steam. Such sulfone ($-SO_2-$) $\rightarrow$ sulfonic acid ($-SO_3H$) conformational transformation might cause the hydrothermal degradation of PES, seemingly suggesting that the PES is susceptible to oxidation reaction with a steam. Since Fe was the only metallic element detected on the failed EPDM side, a weak signal at the highest BE site of 170.4 eV might be attributable to S in the iron-sulfate compound. However, there is no evidence whether this Fe belongs to the ferric- or ferrous-sulfate. In trying to identify the contributor at 170.4 eV, two reference Fe compounds, iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and iron(III) sulfate pentahydrate [($Fe_2(SO_4)_3 \cdot 5H_2O$)], were inspected; the peak position from their S_{2p} spectra were 169.8 and 170.2 eV, respectively. Accordingly, the core line at 170.4 eV is more likely to be associated with S in the ferric sulfate [$Fe_2(SO_4)_3$], rather than in the ferrous sulfate ($FeSO_4$). If this interpretation is valid, it can be assumed that the amount of $Fe_2(SO_4)_3$ reaction product yielded at the interfaces between the SS and PES increases with an lengthening exposure time. Since this reaction product is soluble in water, this can be taken as the reason why the peel strength of the joint specimens declined with prolonged exposure time. Although there is no experimental evidence about its derivation, the following hypothetical hydrothermal oxidation pathway of the PES may account for these observed changes:
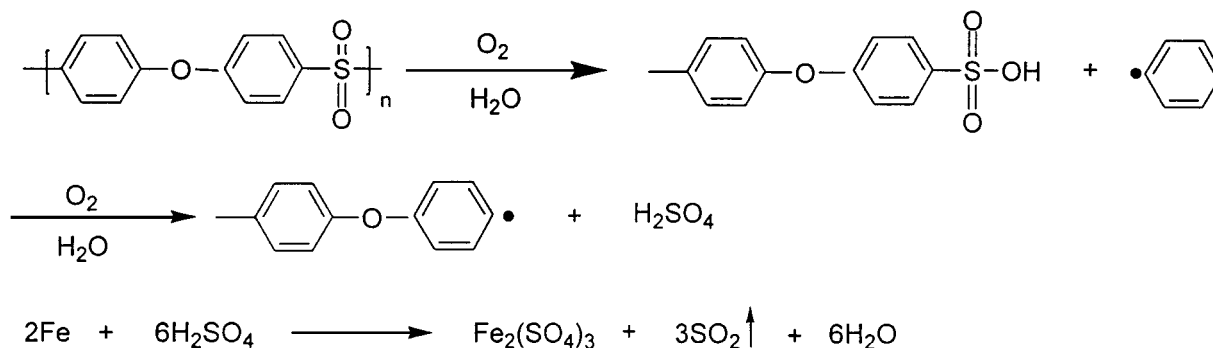
First, the sulfone $\rightarrow$ sulfonic acid conformational change may take place in the hydrothermally oxidized PES structure, leading to the breakage of S-C bond in the diary sulfones which yield a fragmental aryl radical derivative. A second hydrothermal oxidation process causes the decomposition of polyethesulfonic acid, forming other fragmental derivatives, the aryl radical and the H_2SO_4. Finally, hot concentrated H_2SO_4 reacts with Fe in the SS to form $Fe_2(SO_4)_3$.

4. Conclusion

Polyphenylethersulfone (PES) thermoplastic was used as hot-melt adhesive to couple ethylene-propylene-diene terpolymer (EPDM) which can serve as a geothermal drill-pipe or casing protector, with stainless steel (SS) substrates. Its usefulness was assessed by investigating the changes in bond strength as a function of exposure time in steam at 200 °C. The modification and preparation of both the EPDM and SS surfaces played an important role in improving their adherence to the PES, incorporating oxygen functional groups into the EPDM surfaces by oxidizing them at 300 °C and removing carbon-related contaminants from SS surfaces by acid-etching treatment at 60 °C. In fact, no peeling was determined from the EPDM-to-SS PES adhesive joint specimens after steam-exposure for up to 5 days. However, although there was no delamination and buckling of the EPDM from the SS after long-term exposure for 70 days, peel strength declined to a 2.4 KN/m, corresponding to approximately two fold lower than that of the 15-day-exposed specimens. The reduction in peel strength was due to the hydrothermal oxidation of PES, leading to the conformational transformation of sulfone groups within the PES into a fragmental sulfonic acid derivative. Further oxidation of the polyphenylethersulphonic acid derivative generated two additional fragmental derivatives, the aryl radical and the H_2SO_4. The hot H_2SO_4 derivative favorably reacted with Fe in the SS to form the water-soluble $Fe_2(SO_4)_3$ reaction product at the critical interfacial boundary region between PES and SS. This was the reason why the loss of adhesion occurred in the SS adjacent to the PES. Furthermore, an abundance of $Fe_2(SO_4)_3$ yielded in a long-term exposure might cause the formation of a weak boundary layer, thereby resulting in a decrease in the peel strength of the specimens. Consequently, adding an antioxidant to PES may be required to alleviate and minimize the rate of its hydrothermal oxidation.

References

1. P. E. CASIDY, in "Polymer Science and Technology," Vol. 37, edited by L -H. Lee (Plenum Press, New York, 1988) p. 187.
2. M. MIURA, N. CARCIELLO, T. SUGAMA and L. E. KUKACKA, Evaluation of Polyaryl Adhesives in Elastomer-Stainless Steel Joints, Brookhaven National Laboratory Report, BNL-48089, October, 1992.
3. H. ULRICH, "Introduction to Industrial Polymers" (Hanser Publishers, New York, 1993) p. 153.
4. T. E. ATTWOOD, T. KING, V. J. LESLIE and J. B. ROSE, *Polymer* **18** (1977) 369.
5. P. C. DAWSON and D. J. BLUNDELL, *ibid.* **21** (1980) 577.
6. R. C. SNOGREN, "Handbook of Surface Preparation" (Palmerton Publishing Co., Inc., New York, 1974) p. 271.
7. D. S. EVERHART and C. N. REILLEY, *Anal. Chem.* **53** (1981) 665.
8. D. BRIGGS, D. M. BREWIS and M. B. KONIECZO, *J. Mate. Sci.* **14** (1979) 1344.
9. D. BRIGGS and M. P. SEAH, "Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy" (John Wiley & Sons, New York, 1984) p. 385.
10. C. E. MIXAN and J. B. LAMBERT, *J. Org. Chem.* **38** (1975) 1350.
11. B. J. LINDHERG, K. HAMRIN, G. JOHANSSON, U. GELIUS, A. FAHLMAN, C. NORDLING and K. SIEGBAHN, *Physica Scipta* **1** (1970) 286.