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Informal Report

**EVALUATION OF POLYARYL ADHESIVES IN
ELASTOMER-STAINLESS STEEL JOINTS**

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ABSTRACT

Polyaryl thermoplastic adhesives (polyetheretherketone, PEEK, polyphenylene sulfide, PPS, polyphenylethersulfone, PES) have been evaluated for their ability to bond elastomer to metal for use in geothermal environments. The strength of the elastomer-to-metal joints made from various blends of adhesives were determined using peel tests. The various parameters involved in making the joints were temperature, time and atmosphere, in addition to the type of adhesive. Physical chemical analyses have aided endeavors to determine the cause of adhesion failure in the joint. These include differential thermal analyses, thermal gravimetric analyses, infrared spectroscopy and electron spectroscopy for chemical analyses.

Our tests showed that joints made of adhesive blends which contained greater than 50% PES survived simulated geothermal conditions (200°C and water vapor pressure of 200 psi) for weeks without significant decrease in peel strength. The chemical components of the adhesive appear to be highly stable under the conditions required to make the joints and in subsequent exposure to the simulated geothermal environment. These are remarkable results in comparison to previously tested adhesives.

INTRODUCTION

The primary objective of this program is to develop an adhesion system which can bond elastomer to metal, and which can be used as drill pipe or casing protectors suitable for use in geothermal wells that would remain intact for a minimum of 48 hours.

Previous reports have determined that an ethylene propylene diene termonomer (EPDM) (L'Garde formulation Y267) elastomer can survive simulated downhole conditions.¹ The diene used in this formulation (Nordel 1660 by Dupont) is 1,4-hexadiene, which is not as reactive as the other commonly used cyclopentadiene or ethylidene norbornene. Stainless steel was chosen in previous studies due to its resistance to corrosion in the harsh geothermal environments.² Although these two materials work satisfactorily, the adhesion between metal and elastomer have not survived the simulated geothermal conditions. An adhesive, Megum V12588 coated over primer Megum 3270, had demonstrated greater adhesion than other systems tested, however, was still not satisfactory when subjected to autoclave conditions in steam or brine at 200-300°C.²

End use requirements for drill pipe protectors (as specified by GDO) are that there be no loss of bond after 48 hours in brine at 290°C and 5000 psi, or in steam at 260°C and 660 psi while rotating at 100 rpm under a radial load of 3500 lb. Future tasks include rotating head seals, which require no loss of bond after 24 hr. in brine at 240°C and 425 psi, or in steam at 200°C and 130 psi; and blow-out prevention seals, which require no loss of bond after a 90 day exposure to brine at 250°C and 450 psi, or in steam at 200°C and 400 psi.

In this study, we have compared the Megum V12588/3270 system and an "improved" V555/3270 system with some recently developed thermoplastic adhesives. Polyaryl polymers such as polyphenyletherether ketone (PEEK), polyphenylene sulfide (PPS), and polyphenylether sulfone (PES), have been developed in recent years (Figure 1). PEEK is the most studied due to its excellent thermal stability, toughness, low flammability and chemical resistance. PPS and PES also maintain all of these attributes and furthermore, PEEK and PPS are semi-crystalline, which can add considerable strength.

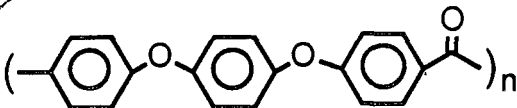
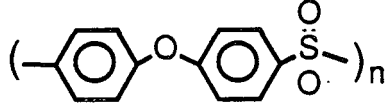
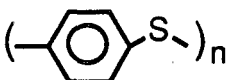
| POLYMER | STRUCTURE | T _g (°C) | T _m | T _c |
|---------|---|---------------------|----------------|----------------|
| PEEK |  | 183 | 345 | 290 |
| PES |  | 225 | 320* | |
| PPS |  | 150 | 295 | 195 |

Figure 1. Structure, glass transition temperature (T_g), melting temperature (T_m), and crystallization temperature (T_c) of various polyaryl thermoplastic adhesives.

Joints were prepared using an alcoholic slurry of various adhesives and peel strengths of the resulting joints were measured. Approximately 40 lbs/in² is the predicted requirement for a drillpipe casing protector.³ Physical chemical methods were used to determine the critical factors involved in the bonding process.

EXPERIMENTAL

Materials

The metal used in all cases was AISI 304 stainless steel (SS). PEEK and PES were bought from ICI, (Wilmington, DE) and PPS was bought from Phillips 66 Company (Bartlesville, OK). The Megum adhesive systems were gifts from The Ore and Chemical Corp., (New York, NY). The partially cured calendered roll of EPDM elastomer was provided by L'Garde, Newport Beach, CA.

Measurements

Differential thermal analyses (DTA) and thermogravimetric analyses (TGA) were carried out on a DuPont 990 Thermal Analyzer system. DTA samples of the pure adhesives (PEEK, PES and PPS) were made using 10 mg of the dry solid; the PE and PS series were prepared by melting the adhesive mixture (10 mg) in an open aluminum pan at 400°C for 30 min and the pans were covered after the mixture had cooled. TGA samples of the PE and PS series were prepared by melting the adhesive mixture onto a stainless steel strip.

After hardening upon cooling, they were peeled off and broken into smaller fragments. Infrared spectra were run on a Perkin Elmer 298 spectrometer. The IR samples were prepared by melting the adhesive mixture between two NaCl plates. The ASTM D-903 180° peel test was used to quantitate the strength of the elastomer-to-metal joint.

Electron spectroscopy for chemical analyses (ESCA) was carried out on a V.G. Scientific ESCA 3MK II. An Al Ka (1486.6 eV) x-ray source was used as the excitation radiation. The binding energies or chemical shifts were calibrated to the hydrocarbon C_{1s} binding energy of 285.0 eV. Each peak was designated to certain chemical states according to literature.⁴

RESULTS & DISCUSSION

Unlike previously investigated adhesives, which are liquid at room temperature, the polyaryl polymers have melting temperatures between ≈300-400°C. This feature complicates the joint-making process as the adhesive cannot be applied onto the metal surface as a liquid at room temperature. Although PES is soluble in certain organic solvents, PEEK and PPS are insoluble in all solvents at ambient temperature. Furthermore, the elastomer begins to degrade severely at the melting temperature of the adhesives ≈400°C. In order to circumvent this problem, the slurried adhesive (in isopropanol) is applied to the metal surface and allowed to melt at 400°C. The elastomer is then laid on top of the adhesive and the temperature is allowed to cool down to 300°C where it is kept for 3 hours. Using this method, some degradation of the rubber still existed, however, use of lower temperatures resulted in drastically reduced bond strength in the joints.

The method that worked most satisfactory for air-cured samples was as follows: The adhesive was mixed into a slurry (45% w/w in isopropanol) and applied onto clean 1 in. by 3 in. stainless steel strips in a 1 in.² area. These were placed in a cold oven along with weights (1 in.² by 6 in., 680 g) and all were heated to 400°C for ≈30 min. When the adhesive had completely melted, a strip of EPDM elastomer (1 in. by 5.25 in.) was placed over the now liquid adhesive and the hot metal weight was placed on top of the EPDM.

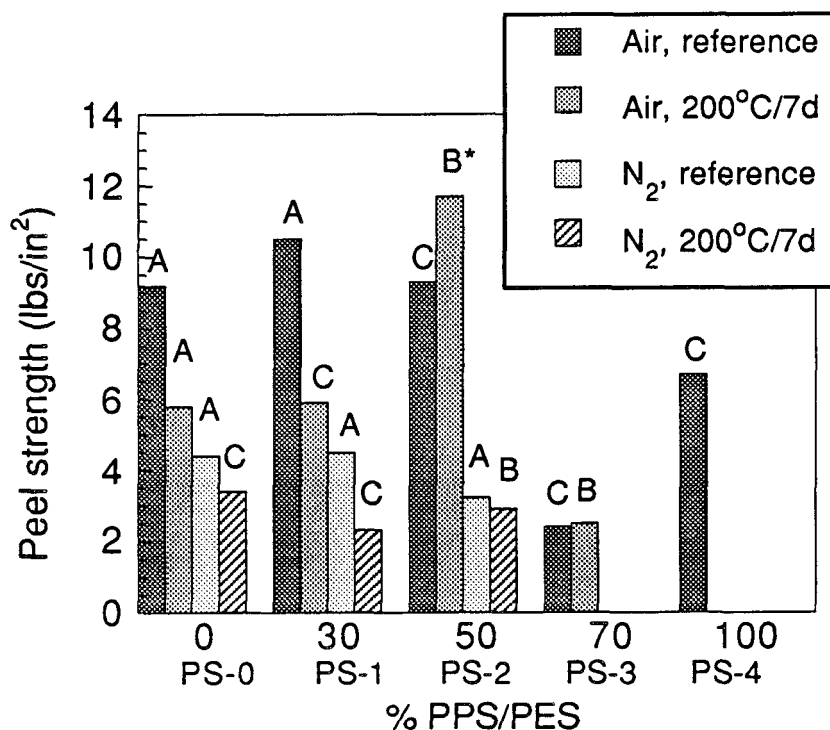


Figure 2. Comparison of peel strengths of elastomer-to-metal joints made with various proportions of PPS and PES under air and nitrogen atmospheres, with and without exposure to autoclave conditions of 200°C for 7 days. A, failure existed between elastomer and adhesive; B, failure existed within the adhesive itself; and C, the failure existed between metal and adhesive; *, the rubber tore before the joint had failed.

The oven door was left slightly ajar for ≈ 10 min. until the temperature had dropped to $\approx 300^\circ\text{C}$. It was maintained at this temperature for 3 hours, at which time, the joint system was allowed to cool slowly to $\approx 100^\circ\text{C}$ over 1 hour. The peel strengths of these joints are shown as the first two bars in Figures 2 and 3.

Joints were cured in nitrogen using a procedure similar to that cured in air except that the oven door remained closed after the EPDM was introduced in order to maintain the nitrogen atmosphere. This, however, resulted in prolonged heating of the EPDM at temperatures exceeding 300°C . The initial melting temperature was therefore reduced to 350°C for the PS series and 375°C for the PE series. The peel strengths of these joints are shown as the third and fourth bars in Figures 2 and 3.

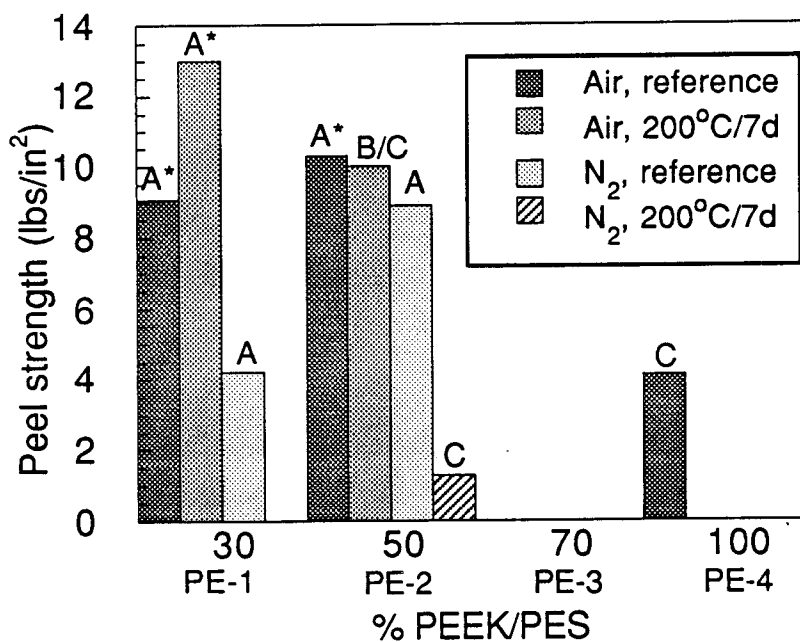


Figure 3. Comparison of peel strengths of elastomer-to-metal joints made with various proportions of PEEK and PES under air and nitrogen atmospheres, with and without exposure to autoclave conditions of 200°C for 7 days. A, failure existed between elastomer and adhesive; B, failure existed within the adhesive itself; and C, the failure existed between metal and adhesive; *, the rubber tore before the joint had failed.

As a point of reference, Megum 3270 primer was applied onto the stainless steel strip in a 1 in.² area at room temperature. After drying for 30 min., the adhesive was applied over the primer and the EPDM was placed on top with the metal weight used for the thermoplastics. This was allowed to cure at 200°C for 2 hours. Both samples were peeled apart quite easily and after autoclave exposure, the elastomer was not bonded at all to the metal.

The bond strength of joints made with PES (PS-0) was the greatest of the three pure adhesives (Figures 2 and 3). After exposure to autoclave conditions (200°C for 7 days) there was no adhesion in the joints made with pure PEEK (PE-4) or pure PPS (PS-4). These latter two joints had failures between SS and adhesive, while those made with pure PES had failures between EPDM and adhesive. We then reasoned that a blend of PES with either PPS or PEEK should improve the bond strength between both interfaces and hence entries in both series displayed higher peel strengths than pure PPS or PEEK. Blends of PEEK with PPS were also tried but the temperature required for melting these blends was

≈430°C, which resulted in severe degradation of the elastomer. Blends of PEEK and PES have been reported previously and compared to the corresponding block copolymers.^{5,6}

In general, our data showed that:

- 1) Blends containing greater than 50% PES had the greatest peel strengths: PS-0, -1, -2, PE-1 and -2.
- 2) Air-cured samples had greater peel strengths than those cured in nitrogen both for reference and autoclaved samples.
- 3) The region of failure in the adhesion system for the outstanding reference samples shown in Figures 2 and 3 were usually between elastomer and adhesive (break region A).
- 4) After exposure to autoclave conditions for 1 week, only PE-1 still retained adhesion failures between elastomer and adhesive.

The adhesives had extruded to some extent and possessed a lighter opaque color after autoclave exposure, which was probably due to hydrolysis. For example PS-0 was clear with a slight biege tint and after autoclave exposure, it had a white enamel appearance. Nevertheless, the PS-2, PE-1 and PE-2 joints still remained strong, if not stronger than the control samples.

Pretreatment of the EPDM surface

The failure of the strongest joints (control) existed between the adhesive and the elastomer. In no case was the failure between adhesive and metal. The strength of the metal-to-PEEK bond was demonstrated by Sugama and Carciello⁷ where metal-to-metal joint strengths were 10^3 times greater than those reported here using metal-to-elastomer joints (modified ASTM method D-1002).

It was therefore our desire to increase the strength of the bond between the EPDM and adhesive by modifying the surface of the EPDM. Different chemical modifications were employed and the results are shown in Table I. For each treatment, a contact angle was measured using an equilibrium sessile drop method with three different liquids. The contact angle was significantly reduced in entry 6. The treatment involved cleaning with acetone, followed by oxidation with dichromate for 30 min. at 60°C. Treatment for 15 min. did not appear to be adequate and a 1 hour treatment did not improve the contact angle.

Table I. Contact angle (in degrees) of three liquids on the surface of EPDM elastomer which had undergone various surface pretreatments.

| Entry | Treatment | Time (min.) | H ₂ O | DMSO | glycerol |
|-------|--|-------------|------------------|------|----------|
| 1 | None | | 86 | 53 | 79 |
| 2 | Acetone wash | | 79 | 63 | 89 |
| 3 | 30% H ₂ SO ₄ /7.5% K ₂ Cr ₂ O ₇ at 60°C, acetone prewashed | 1 | 85 | 65 | 88 |
| 4 | " | 5 | 90 | 69 | 81 |
| 5 | " | 15 | 90 | 64 | 81 |
| 6 | " | 30 | 40 | 32 | 76 |
| 7 | " | 60 | 94 | 58 | 83 |
| 8 | " but not acetone prewashed | 30 | 87 | 72 | 81 |
| 9 | 10% aqueous NaOH 60°C | 1 | 87 | 79 | 86 |
| 10 | " | 5 | 106 | 70 | 82 |
| 11 | " | 30 | 77 | 80 | 90 |
| 12 | 5% NaOH in 50% EtOH 60°C | 1 | 107 | 66 | 84 |
| 13 | " | 5 | 98 | 63 | 80 |
| 14 | " | 30 | 85 | 51 | 85 |
| 15 | 10% KOH in EtOH 60°C | 15 | 98 | 74 | 85 |
| 16 | " | 30 | 100 | 64 | 86 |

The contact angle is a measurement of surface tension, which is a measurement of intermolecular forces. Ideally when there is great attraction between the liquid and the surface, the liquid completely wets the surface and the contact angle is 0°. The greatest physical attractive forces are ionic and polar forces, which arise from permanent electric dipoles and their induction effects on polarizable molecules, as compared to dispersion (London) forces which arise from internal electron motions.

Elastomers, such as rubber are low energy surfaces and consist mostly of non-polar hydrocarbons. The adhesives, on the other hand, consist of polar functional groups, i.e. ether, sulfone, ketone or sulfide. If the non-polar rubber surface could be derivatized into more polar groups, then stronger attractions could occur. The chromate treatment of EPDM is one method of oxidation which can increase the number of carbonyl groups. These could be in the form of ketones, aldehydes or carboxylic acids, all of which are considerably more polar than the starting hydrocarbon, thus enhancing the attractive forces.

These forces, at least for the substrate, can be determined by use of the equation:

$$1 + \cos \theta = \frac{2\sqrt{\gamma_s^D} \sqrt{\gamma_{lv}^D}}{\gamma_{lv}} + \frac{2\sqrt{\gamma_s^P} \sqrt{\gamma_{lv}^P}}{\gamma_{lv}}$$

where g = surface tension or the surface free energy, the D designates the dispersion component and P designates the polar component, the lv subscripts refer to known values for the liquid and the s subscripts refer to the substrate values which can be determined using two liquids. Values of g_s^P and g_s^D are shown in Table II. As the equation shows, the surface tension is directly related to the cosine of the contact angle.

Table II. Surface free energies (polar and dispersion forces) of pretreated EPDM elastomers determined using various combinations of liquids.

| Liquid | CONTROL | | Cr ₂ O ₇ /H ₂ SO ₄ , 60°C/0.5 hr. | | Cr ₂ O ₇ /H ₂ SO ₄ , 60°C/0.5 hr., not acetone washed | | KOH/EtOH, 60°C, 0.5 hr. | |
|------------------|---------|---------|--|---------|---|---------|----------------------------|---------|
| | g_s^P | g_s^D | g_s^P | g_s^D | g_s^P | g_s^D | g_s^P | g_s^D |
| H ₂ O | 5.0 | 23.0 | 44.7 | 12.3 | 10.8 | 9.6 | 0.4 | 2.8 |
| DMSO | | | | | | | | |
| glycerol | 8.2 | 14.8 | 142.0 | 19.4 | 12.7 | 8.9 | 0.6 | 0.9 |
| H ₂ O | | | | | | | | |
| glycerol | 26.7 | 2.2 | | | 11.5 | 9.8 | | |
| DMSO | | | | | | | | |

These values show that the surface free energies increased with the chromate treatment. As would be predicted, the polar component increased tremendously, but the dispersion component remained the same. In contrast, the surface free energies have decreased with the alcoholic base treatment and both components had decreased. This treatment is often used as a powerful solublizing agent that can remove most contaminants off of surfaces. In the treatment of elastomer, it could have created a smoother low energy surface.

Table III. Comparison of peel strengths and regions of failure using PS-1 in EPDM-SS joints with pretreated EPDM and control samples. A, failure existed between elastomer and adhesive; and C, the failure existed between metal and adhesive.

| PS-1 CONTROL | | KOH/EtOH, 60°C, 0.5 hr. | | Cr ₂ O ₇ /H ₂ SO ₄ , 60°C, 0.5 hr. | |
|---------------|----------------|-------------------------|----------------|--|----------------|
| Peel strength | Failure region | Peel strength | Failure region | Peel strength | Failure region |
| 9.3 | A | 3.0 | C/A | 2.3 | C |
| 9.1 | A | 4.2 | C | 0 | C |
| 13.2 | A | | | | |

The pretreated elastomer had overall decreased strengths in the peel tests shown in Table III. In each case, the failure that occurred between elastomer and adhesive before pretreatment, occurred between metal and adhesive after pretreatment. Implications are that

oxidation of the EPDM surface had enhanced the attraction between EPDM and adhesive, but why the attraction between metal and adhesive had decreased is not clear.

Longterm adhesion

There does not appear to be a substantial reduction in peel strength in a comparison of the 12-week with the 1-week autoclave-exposed samples shown in Figure 4. PS-0, however, appeared to soften after it was autoclaved for 1 week, because the metal was still bonded to the elastomer, but not in the original position. PS-0 was therefore not included in the 3-week peel test. PS-2 peel strengths had decreased slightly at 3 weeks, but the others had strengths that were similar to the previous 1-week sample. The break regions of PS-1 and PE-2 have changed from having failures between the metal and adhesive to failures between the EPDM and adhesive in the 3-week exposure. By 12 weeks, all the failures had occurred within the adhesive, probably via hydrolysis, except PE-1 where the elastomer had failed before the joint.

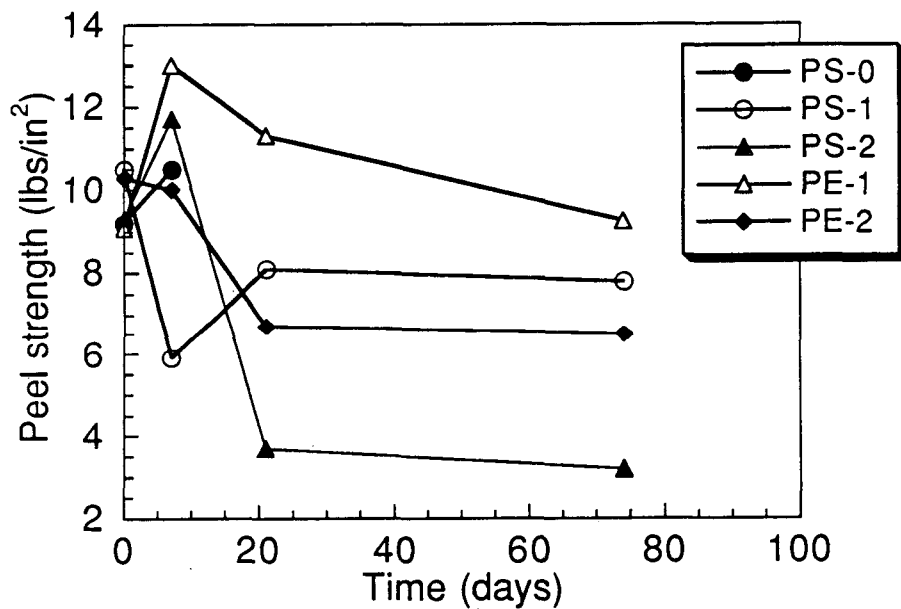


Figure 4. Peel strengths of EPDM-steel joints using various adhesives as a function of exposure time under autoclave conditions (200°C and 200 psi).

Physical chemical analyses

ELASTICITY

Although it was suggested by L'Garde that the EPDM elastomer should be cured in a nitrogen environment, visual observation of the elastomer cured in air did not appear to be significantly different from that cured in nitrogen. However, the elasticity of the EPDM was quantitated after it had been heated to a temperature of 300°C in both air and nitrogen for the time periods shown in Figure 5 and some differences were noted.

The results indicate that the elasticity is maintained at $\approx 50\%$ of the initial value after 3 - 6 hours of heating at 300°C in a nitrogen atmosphere as compared to only $\approx 10\%$ of the initial value after heating at 300°C in an air atmosphere. This is most likely due to excessive oxidative degradation of the EPDM.

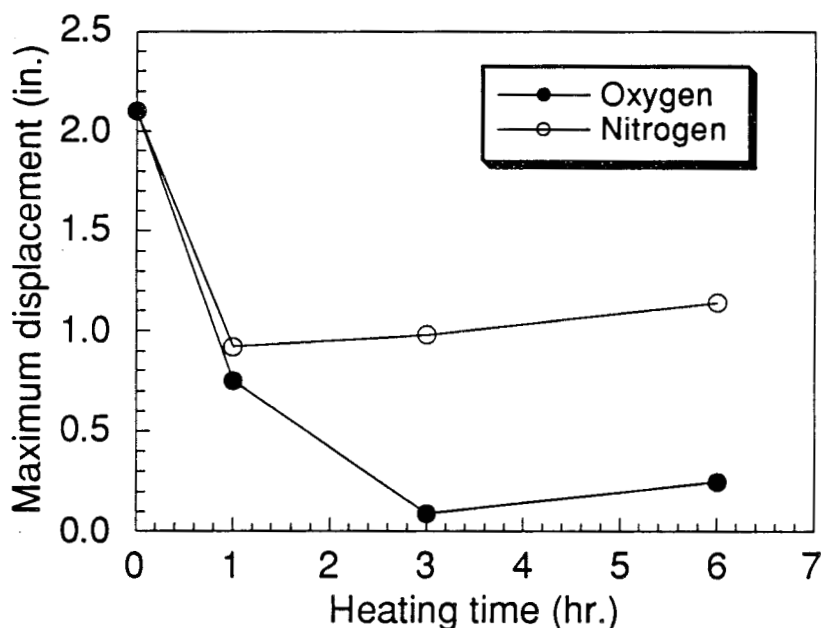


Figure 5. Elasticity of EPDM elastomer after heating at 300°C at various time periods under nitrogen and oxygen environments.

Ideally the elastomer-to-metal joints should be cured under nitrogen since our procedures required exposure to greater (approximately) than 300°C temperatures for a

period greater than 3 hours. However, even this significant loss of elasticity displayed after 3 hours in an air environment could not compensate for the greater loss in peel strength of the nitrogen-cured specimens.

THERMAL GRAVIMETRIC ANALYSES

TGA data show that the onset temperature of thermal degradation (T_d) of EPDM analyses run in air is only $\approx 20^\circ\text{C}$ less than that in nitrogen (Table V) However, the percent weight loss reached $\approx 100\%$ in air at $\approx 530^\circ\text{C}$, compared to 62% in nitrogen at 800°C . As far as the TGA data are concerned, there appears to be no advantage in using a nitrogen-cured elastomer because temperatures of $>500^\circ\text{C}$ are not utilized. Although the elasticity data show that at temperatures of 300°C , some physical and chemical changes have occurred, it was not manifested in weight loss.

Table IV. Thermogravimetric analyses data. Thermal decomposition temperature (T_d), differential thermal gravimetry maximum temperature (DTG_{max}), and percent weight loss are shown as a function of the atmosphere of analyses (flow of 90 ml/min.), adhesive composition and state and the atmosphere used in curing.

| Adhesive | T_d ($^\circ\text{C}$) | DTG_{max} ($^\circ\text{C}$) | % Wt. loss by 800°C | Atmosphere of curing | Atmosphere of analyses |
|----------|----------------------------|---|-----------------------------------|----------------------|------------------------|
| PEEK | 560 | 605 | 50 | | nitrogen |
| PEEK | 520 | 590,640 | 100 | | air |
| PES | 470 | 580 | 57 | | nitrogen |
| PES | 480 | 570,660 | 100 | | air |
| PPS | 450 | 530 | 57 | | nitrogen |
| PPS | 450 | 525,590-640 | | | air |
| EPDM | 380 | 480 | 62 | | nitrogen |
| EPDM | 360 | 480,560,570 | 100 | | air |
| PS-1 | 440 | 540 | 48 | air | nitrogen |
| PS-2 | 440 | 535 | 52 | nitrogen | nitrogen |
| PS-2 | 450 | 540 | 57 | air | nitrogen |
| PS-3 | 440 | 540 | 51 | nitrogen | nitrogen |
| PS-3 | 440 | 540 | 53 | air | nitrogen |
| PS-3 | 460 | 530,570,610 | 100 | nitrogen | air |
| PS-4 | 450 | 540 | 49 | nitrogen | nitrogen |
| PE-1 | 470 | 570 | 48 | nitrogen | nitrogen |
| PE-2 | 490 | 580 | 52 | nitrogen | nitrogen |
| PE-3 | 560 | 595 | 49 | nitrogen | nitrogen |
| PE-4 | 540 | 590 | 47 | nitrogen | nitrogen |

The T_d 's for pure solid adhesives are proportional to their melting temperatures; PEEK > PES > PPS. The T_d 's are remarkably similar for samples run in nitrogen and in air. Although the TGA profiles of samples cured in air versus nitrogen were not different, the percent weight loss by 800°C was inevitably ≈100% for analyses run in air and ≈50-60% in nitrogen, as was also shown with EPDM. However, as these differences are not apparent until temperatures of ≈500°C or greater are reached, the nitrogen environment holds no advantage over air for our purposes.

The pure adhesives, PE-4 and PS-4 had identical TGA profiles to the powder samples. PS-0 could not be run due to technical difficulties as the analyses were not reproducible, probably due to the relatively large pieces of hardened adhesive which could not be broken any further. The TGA of the blends were identical to that of the faster degrading component. For example, the analyses of the PS series are essentially that of PPS. The analyses of the PE series are similar to that of PES, except PE-3 that shows the TGA is similar to that of PEEK.

DIFFERENTIAL THERMAL ANALYSES

Table V. DTA parameters of the various adhesives that were heated at 400°C for 0.5 hr.: Glass temperature, T_g ; melting temperature, T_m ; crystallization temperature, T_c .

| Adhesive | T_g (°C) | T_m (°C) | T_c (°C) |
|----------|------------|------------|------------|
| PS-0 | 228 | — | 223 |
| PS-1 | 230 | 255, 273 | 192 |
| PS-2 | 95, 225 | 255, 273 | 192 |
| PS-3 | 100, 225 | 258, 275 | 185 |
| PS-4 | 105 | 275 | 195 |
| PE-1 | 200 | 255, 340 | 282, 217 |
| PE-2 | 135 | 337 | 285 |
| PE-3 | 140 | 335 | 287 |
| PE-4 | 145 | 340 | 290 |

DTA showed that both PEEK and PPS are semi-crystalline solids while PES is completely amorphous (Table V). Heating the PS and PE samples for 30 min. at 400°C showed no difference in enthalpy than the pure adhesive powder samples. Prolonged exposure to heat, however, did result in the appearance of new peaks for PEEK. After 1 hour of heating PEEK in air at 400°C, a second crystallization peak at 270°C and of equal intensity was observed, after 1.5 hours, only the lower temperature peak was observed and after 2 hours, a very broad peak appeared tailing toward even lower temperatures was

observed. This new presumably oxidized product had appeared previously when heated in air but not in nitrogen.⁷

Because of the lack of weight loss determined by TGA analyses and because of the difference in DTA between nitrogen- and air-cured samples, we presume that new oxidized products are probably formed. 1:1 PES: PEEK or PE-2 (400°C/0.5 hr + 300°C/3 hr) showed a T_c and T_m identical to pure powder PEEK but as slightly broader peaks. However, after 1 hr. of heating at 400°C, PE-2 showed a sharp peak at 265°C (instead of 290°C) and after 2 hr. of heating, the broad peaks that were observed with PEEK after 2 hr. became apparent.

Blends of the adhesives showed no new peaks arising from new compounds that were not already observed in the pure adhesives. The intensity in ΔT of melting and crystallization processes from the blends were proportional to the amount of PPS or PEEK, since PES is amorphous.

The most crystalline samples did not constitute the most successful joints. In fact, in each series, the 70% and 50% PES blends performed best after exposure to autoclave conditions. Crystallinity, therefore does not appear to play a critical role in adhesion strength.

DTA's were run on each adhesive where the joint had survived autoclave exposure after 1, 3 and 7 days exposure (not shown). The glass temperatures were carefully noted, but there were no significant deviations from the reference samples, indicating the absence of any new product formation.

INFRARED SPECTROSCOPY

The IR spectra support the DTA data in that there does not appear to be any new frequencies that emerged as a result of the heating process used for making the joints. The blends of polymers show IR spectra with the additive peaks of the constituent pure polymers. The spectra of the pure polymer adhesives, PS-0 and PE-4 can be readily distinguished from PS-4. Unfortunately, the characteristic C-S stretching modes for PPS in PS-4 are predominantly found in Raman rather than in IR spectroscopy.

ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSES

CONTROL SAMPLES OF EPDM-ADHESIVE INTERFACE

Peel strength data show that the blends containing >50% PES have the strongest joints. Of the pure adhesives, PES had the greatest bond strength and was the only one to survive 1-week autoclave exposure. It had joint failure between adhesive and elastomer, contrary to PEEK and PPS, which had failure between SS and adhesive. An ESCA analyses of the three adhesives are shown in Table VI for the powder and heated samples in comparison to the theoretical value (calculated according to the molecular formula).

Table VI. ESCA parameters including: 1) The theoretical values, 2) the experimental values of the powder form and 3) the experimental values after heating in air at 400°C/0.5 h (Δ) of pure and blended adhesives.

| ADHES. | | %S | S B.E. (eV) | %C | C B.E. (eV) | %O | O B.E. (eV) |
|--------|---------------|------|----------------|------|----------------------------------|------|--------------------------------------|
| PES | theoretical | 6.2 | | 75.0 | | 18.8 | |
| | powder | 5.8 | 168.2 | 78.2 | 285.0 291.2 | 16.0 | 532.0 533.5 |
| | Δ | 8.5 | 167.9 163.3 | 74.1 | 285.0 292.0 | 17.5 | 529.2 532.2 533.6 |
| | | | | | | | |
| PEEK | theoretical | | | 86.4 | | 13.6 | |
| | powder | | | 86.9 | | 13.1 | |
| | Δ | | | 83.9 | 285.0 286.4 286.8 291.7 | 16.2 | 529.2 531.0 531.5 533.8 |
| PPS | theoretical | 14.3 | | 85.7 | | | |
| | powder | 1.1 | 161.2 | 64.9 | | 3.2 | 529.8 |
| | | 2.2 | 168.1 | | | 28.5 | 531.8 |
| | Δ | 20.2 | 163.9 | 76.4 | 285.0 291.1 | 3.4 | 531.8 532.2 |
| PS-2 | theoretical | 10.2 | | 80.4 | | 9.4 | |
| | Δ | 14.3 | 163.5 168.4 | 80.3 | 285.0 291.8 | 5.4 | 529.0 532.4 |
| PE-2 | theoretical | 3.1 | | 80.7 | | 16.2 | |
| | Δ | — | | 74.4 | 285.0 292.0 | 22.9 | 528.9 531.6 533.9 |
| EPDM | 300°C 3 hr | | | 88.9 | 285.0 | 0.9 | 530.7 |
| | | | | | | 3.8 | 531.3 |
| SS | | %Fe | | %C | | 6.4 | 533.2 |
| | | 2.9 | | 63.4 | 285.0 | 33.7 | 529.8 (16.4%) 531.8 (83.6%) |

The blended samples which contained $\geq 50\%$ PES (PS-0, PS-1, PS-2, PE-1, PE-2) all had joint failures between elastomer and adhesive except PS-2, where it occurred between metal and adhesive. An ESCA analyses of the interfacial area between EPDM and adhesive showed that sulfur is present on the EPDM surface as SO_4 or SO_2 only in PS-1 and PE-1 (Table VIII). Sulfur is absent on all the other EPDM surfaces. PS-1 and PE-1 also happen to have the greatest peel strengths after autoclave exposure.

In the PE series, the experimentally determined percentages of carbon and oxygen on the adhesive surface are fairly similar to the theoretical value (Table VII). However, in the PS series, the experimental differs from the theoretical values markedly. The sulfur content in all the samples are too low if present at all. The sulfur spectrum of PS-2 shows a sulfonyl and sulfide peak, but PS-1 only shows the sulfide peak. In PS-0 and PS-2, the oxygen content is too high and in PS-1, the carbon content is too high, relative to the theoretical values. Sulfur, is not detected in PE-2 where 3% is expected and 1% is detected in PE-4, where none is expected.

Table VII. ESCA parameters of the *adhesive* surface of the EPDM-adhesive interface in EPDM-stainless steel lap-joints. A, failure existed between elastomer and adhesive; B, failure existed within the adhesive itself; and C, the failure existed between metal and adhesive; *, the rubber tore before the joint had failed.

| ADHES. | FAILURE | %S | B.E. (eV) | %C | B.E. (eV) | %O | B.E. (eV) |
|--------|---------|-----|----------------|------|-------------------------|------|----------------|
| PS-0 | A | — | — | 69.3 | 285.0 388.0 | 30.7 | 533.1 |
| PS-1 | A | 1.5 | 163.8 | 93.1 | 285.0 | 5.4 | 532.4 |
| PS-2 | C | <1 | 164.7 169.0 | 69.8 | 285.0 289.2 291.1 | 30.2 | 531.5 |
| PE-1 | A* | 1.5 | 168.5 | 81.6 | 285.0 291.9 | 16.9 | 532.7 |
| PE-2 | A* | — | — | 80.6 | 285.0 | 19.4 | 529.2 531.0 |
| PE-4 | C | 1.1 | 169.5 | 88.6 | 285.0 | 10.3 | 532.5 |

By visual inspection, some EPDM is left on the PS-1 surface as a black powdery material. This would account for the high carbon and low oxygen content. In addition,

PS-1 is deposited on the EPDM surface, which would account for the lower carbon and higher oxygen and sulfur detected. The EPDM surface of the interfacial section to PS-2, PE-1 and PE-2 also have the lower carbon and higher oxygen content that was detected with PS-1 (Table VIII), which could indicate the presence of adhesive on the EPDM surface, except that sulfur should also be present, particularly with PS-2 (10%). This cohesive failure within the EPDM appears to correlate with superior strength in joints.

Table VIII. ESCA parameters of the *EPDM* surface of the EPDM-adhesive interface in EPDM-stainless steel lap-joints. A, failure existed between elastomer and adhesive; B, failure existed within the adhesive itself; and C, the failure existed between metal and adhesive; *, the rubber tore before the joint had failed.

| ADHESIVE | FAILURE | %S | B.E. (eV) | %C | B.E. (eV) | %O | B.E. (eV) |
|----------|---------|-----|-----------|------|-----------|------|-----------|
| PS-0 | A | — | — | 95.2 | 289.2 | 4.8 | 533.1 |
| PS-1 | A | <1 | 169.4 | 84.5 | 285.0 | 15.5 | 532.2 |
| | | | | | 288.0 | | 533.3 |
| | | | | | | | 534.8 |
| PS-2 | C | — | — | 86.8 | 285.0 | 13.2 | 532.6 |
| | | | | | 286.3 | | 534.0 |
| | | | | | | | 534.3 |
| PE-1 | A* | 1.0 | 168.7 | 81.8 | 285.0 | 17.2 | 532.8 |
| | | | | | 283.8 | | |
| | | | | | 291.9 | | |
| PE-2 | A* | — | — | 93.1 | 285.0 | 6.9 | 529.2 |
| | | | | | | | 531.0 |
| PE-4 | C | — | — | 90.1 | 285.0 | 9.9 | 532.5 |
| | | | | | | | 534.0 |

CONTROL STAINLESS STEEL-ADHESIVE INTERFACE

Four samples were analyzed, of which PS-0 and PE-2 had joint failures between the EPDM and adhesive, and PS-2 and PS-4 had joint failures between the SS and adhesive. The %S was substantial on all 4 adhesive surfaces ($\approx 10\%$ in 3 and 1% in PE-2) interfacial to SS and was greater than that for the adhesive surfaces interfacial to EPDM (Tables IX and X). The experimental values correlate approximately to the theoretical values, although the %S in PS-0 is slightly high and that in PS-4 is slightly low compared to the predicted 6,

10 and 14% for PS-0, PS-2 and PS-4, respectively. There were also substantial amounts of sulfur observed on the SS surface, particularly with PS-4. Here, the chemical composition was very similar for each surface (within 4%) indicating that PPS was present on both surfaces and therefore a cohesive failure of PPS.

Table IX. ESCA parameters of the *adhesive* surface of the stainless steel-adhesive interface in EPDM-stainless steel lap-joints. A, failure existed between elastomer and adhesive; B, failure existed within the adhesive itself; and C, the failure existed between metal and adhesive; *, the rubber tore before the joint had failed.

| ADHESIVE | FAILURE | %S | B.E. (eV) | %C | B.E. (eV) | %O | B.E. (eV) |
|----------|---------|-----|-----------|------|-----------|------|-----------|
| PS-0 | A | 8.3 | 164.0 | 68.5 | 285.0 | 23.2 | 532.8 |
| | | | | | 286.3 | | |
| PS-2 | C | 9.9 | 164.0 | 79.2 | 285.0 | 10.9 | 532.1 |
| | | | 169.3 | | 291.1 | | |
| PS-4 | C | 9.4 | 163.8 | 83.4 | 285.0 | 7.2 | 532.2 |
| PE-2 | A* | 1.4 | 168.7 | 80.2 | 285.0 | 18.4 | 531.7 |
| | | | | | 291.9 | | 532.8 |

Table X. ESCA parameters of the stainless steel surface of the stainless steel-adhesive interface in EPDM-steel lap-joints. () indicates very small peak intensity.

| ADHES. | %S | B.E. (eV) | %C | B.E. (eV) | %O | B.E. (eV) | %Cr | B.E. (eV) |
|--------|------|-----------|------|-----------|------|-----------|-----|-----------|
| PS-0 | 2.4 | (163.8) | 44.3 | 285.0 | 48.5 | 530.8 | 4.7 | 577 |
| | | 168.8 | | (291) | | | | 588 |
| PS-2 | 2.7 | 164.0 | 52.5 | 285.0 | 38.4 | 530.8 | 6.3 | 577.2 |
| | | (168.0) | | (291.1) | | | | 587.0 |
| | | (169.0) | | | | | | |
| PS-4 | 10.2 | 163.9 | 79.3 | 285.0 | 10.5 | 530.2 | - | - |
| PE-2 | 2.0 | 167.7 | 48.4 | 285.0 | 44.3 | 530.8 | 5.3 | 577.0 |
| | | | | 291.4 | | | | 586.6 |

Iron, Fe has never been detected in any appreciable quantity on any analyzed surface except the 3% on the SS control (Table IV). Cr, on the other hand, has been detected in

5-6% on 3 out of 4 SS surfaces (those bonded with PS-0, PS-2, and PE-2 but not PS-4) although none was detected on the SS control.

The carbon and oxygen compositions of PS-0, PS-2 and PE-2 are very typical for metal surfaces where C:O \approx 1 (Table IX). Sulfur exists on the SS surfaces of PS-0, PS-2 and PE-2 as SO₄ or SO₂. PS-4, as predicted contains only a sulfide peak. PS-0 and PS-2 also contain sulfide peaks but for PS-0, this is unusual because sulfide would more likely be oxidized to a sulfonyl than vice versa. The aromatic carbon satellite peak was observed on all the SS surfaces. A single O_{1s} peak at 530.2-530.8 eV was seen on every SS surface, indicative of ArSO₃H or a metal oxide such as Cr₂O₃. The M-O-C peak at 531.6 eV for O_{1s} may be observed in several instances: PS-2 (to SS), EPDM (to PE-2) and PE-2 (to SS).

On the adhesive side, a single O_{1s} peak was observed at 532.1-532.8 which roughly corresponds to sulfonyl (531.8) or ether (533.2) peaks. In general, the % oxygen on the adhesive that was in contact with SS was lower than that in contact with EPDM. The % carbons were roughly the same and the sulfur had made up the difference in greater concentration in the former case. There were higher concentrations of sulfur on the adhesive side in contact with the SS probably because of the greater cohesion existing at this interface, which is demonstrated by the region of failure, i.e. the weaker EPDM-adhesive boundary.

AUTOCLAVED SAMPLES

Samples were exposed to hot steam and water at 200°C and 200 psi for 3 weeks. The sulfur concentration is higher on both surfaces in the PS series but is not detected at all in the PE series although theoretically, the % sulfur is lowest for PE-1 and PE-2 (Tables XI and XII). The form of the sulfur is consistent with the original structure of the polyaryl compound on both surfaces.

The failure locus had changed in some instances from that observed after 1 week of autoclave exposure. After 3 weeks, the region of failure was exclusively between the adhesive and elastomer. In addition, PS-1 and PS-2 had failures within the adhesive. In contrast, at 1 week exposure, PS-1 and PE-2 had failures between the SS and adhesive. It appears that with time and extensive hydrolysis, this particular region has increased in strength. The adhesive was deposited on both sides of the surface for the PS series and therefore failure occurred through a cohesive mode within the adhesive.

Table XI. ESCA parameters of the *adhesive* surface of the steel-adhesive interface in EPDM-steel lap-joints that were exposed to autoclave conditions for 3 weeks. A, failure existed between elastomer and adhesive; B, failure existed within the adhesive itself; and C, the failure existed between metal and adhesive; *, the rubber tore before the joint had failed.

| ADHESIVE | %S | B.E. (eV) | %C | B.E. (eV) | %O | B.E. (eV) | FAILURE |
|----------|-------|------------------|------|-----------|------|-----------|---------|
| PS-0 | 7.9 | 168.0 | 73.1 | 285.0 | 18.9 | 532.0 | — |
| PS-1 | 6.4 | 168.0 | 72.1 | 285.0 | 21.5 | 531.9 | A/B |
| PS-2 | (5.4) | 163.8 (69.3%) | 81.1 | 291.0 | 11.1 | 532.5 | A/B |
| | (2.4) | 168.6 (30.7%) | | 285.0 | | | |
| PE-1 | — | — | 97.9 | 285.0 | 2.1 | 532.2 | A* |
| PE-2 | — | — | 96.7 | 285.0 | 3.3 | 533.0 | A |

Table XII. ESCA parameters of the EPDM surface of the steel-adhesive interface in EPDM-steel lap-joints that were exposed to autoclave conditions for 3 weeks.

| ADHESIVE | %S | B.E. (eV) | %C | B.E. (eV) | %O | B.E. (eV) |
|----------|-------|------------------|------|----------------|------|-----------|
| PS-0 | 5.4 | 168.3 | 80.1 | 285.0 (291) | 14.5 | 532.3 |
| PS-1 | (2.3) | 163.7 (42.1%) | 84.5 | 285.0 | 10.1 | 531.2 |
| | (3.1) | 168.6 (57.9%) | | | | |
| PS-2 | (3.1) | 164.1 (73.1%) | 91.1 | 285.0 | 4.7 | 532.5 |
| | (1.1) | 168.8 (26.9%) | | | | |
| PE-1 | — | — | 97.9 | 285.0 | 2.1 | 532.7 |
| PE-2 | — | — | 97.3 | 285.0 | 2.7 | 532.6 |

The sulfur content in the PS series was consistently between 6.5 - 8% on the adhesive surface and 4 - 5.5% on the EPDM surface. All the samples showed sulfonyl peaks and in addition, PS-1 and PS-2, showed sulfide peaks. The carbon content on the surface of the adhesive was different from that of the EPDM, indicating an adhesive failure. The aromatic carbon satellite peak was seen in only 1 out of 5 instances including the PE series. The

oxygen content was slightly higher for each surface containing the PS series, than was expected for the pure adhesive, indicating perhaps some oxidation or hydrolysis. However, in comparison with the non-autoclaved control samples, the oxygen content was substantially less, except in the case of PS-1 and the EPDM bonded to PS-0. The O_{1s} peaks in the 3 week samples seem to correlate with a sulfonyl and/or an ether peak.

The autoclaved samples appear to be cleaner, in that their elemental composition resembles that of the adhesive more so than the control samples. We had, however predicted that the autoclaved samples would contain substantially more oxygen due to hydrolysis. Interestingly, the opposite was found in the majority of the samples; the oxygen content was greater for the control samples. This could, perhaps be due to extensive oxidation on the surface due to the high heat used in the air environment (which could mask the sulfur) and was subsequently washed away in the aqueous environment. The % oxygen was greater for the adhesive surface than the EPDM surface by 5 - 10%, which was a smaller difference than that for the control samples.

Both surfaces of the PE series in Tables XI and XII have notably high carbon and low oxygen percentages, which is similar to the chemical composition of EPDM. It therefore appears that EPDM is deposited on both sides, indicating cohesive failure within the surface layer of EPDM. This could also explain the absence of sulfur found on the surface. Whether the samples were autoclaved or not, the chemical composition of both surfaces were similar to each other, much more so than in the PS series. Of the control samples, sulfur was only found in PE-1 on both the EPDM and adhesive surface, as a sulfonyl peak, which indicates cohesive failure within the adhesive.

COMPARISON WITH PREVIOUS STUDIES

Lap-shear strengths using PEEK or PPS between two metal strips (SS and cold-rolled steel, CRS) have been studied previously.^{7,8} With PEEK, the strongest joints were created using SS in a nitrogen environment. Conversely, with PPS, the strongest joints were created again using SS, but in an air environment. In the case of PEEK, the following factors appeared to be the most important for high strength in lap-shear joints:

- 1) Interaction between PEEK and the iron (III) oxide, Fe_2O_3 layer on the surface of CRS must exist, as failure occurred in PEEK cured in nitrogen which did not have enough oxide.

- 2) Excessive amounts of Fe_2O_3 can result in cohesive failure in this layer, as in the case of PEEK cured in air on CRS.
- 3) Formation of an Fe-O-C or Cr-O-C complex results in a stable bond, as in PEEK cured in nitrogen on SS.
- 4) Formation of highly crystalline PEEK, which occurred when cured in nitrogen on SS.

In the case of PPS:

- 1) Presence of FeS weakened the bond between CRS and PPS and is apparent on both surfaces in nitrogen but not in air.
- 2) FeSO_4 or $\text{Fe}_2(\text{SO}_4)_3$ is apparent on the PPS side (which was in contact with SS) in air. This data together with the lap-shear strengths indicate that these species are probably responsible for the stronger bond.
- 3) The PPS surface showed no iron or chromium but the SS surface showed sulfur, more carbon and less oxygen and iron than the control.

The chemical composition of the SS bonded to PS-4 (PPS) in this study differs markedly from the SS bonded to PPS in the SS-joints previously reported. The control SS samples in the two studies were similar, except Cr was not detected in this study. The adhesive was heated slightly longer for the EPDM joints (400°C, 30 min.) than the SS lap-joints and yet the oxygen content was 5 times greater in the latter. The low 24% carbon on the SS surface off PPS in the SS joints was not observed on any surface under any circumstance in this study. In the EPDM-SS joints, the 79% C for the SS (off PS-4) was notably greater than the SS surfaces of the other 3 adhesives (44 - 52%). The PPS side was similar in both joints which in turn were similar to bulk PPS. It appears that in the SS lap-joints using PPS, the reaction products between PPS and the Fe on the SS remain on the surface of the SS while the PPS surface is unchanged. Joint failure then, must have occurred between the PPS and reaction product layer. In contrast, the joint failure of EPDM-SS joints (control) in this study for PS-4 occurred between metal and adhesive and more specifically within the PPS layer close to the metal. The chemical composition on the SS surface is very similar to the PPS surface and PPS itself. The reaction products noted previously were not observed here.⁸

Visual observation indicated that the SS in EPDM-SS joints contained areas of PPS on the surface. Since the area of detection for ESCA is only a few square millimeters, it is

possible the bare metal surface (which comprised $\approx 50\%$ of the total area), was not detected, otherwise the chemical composition would have been identical to that for the SS-SS joint system. The other 3 SS surfaces appeared to have less adhesive as the % sulfur was \approx one fifth the amount found in PS-4 and the % carbon was lower with the % oxygen higher. These were more indicative of the metal surface itself except that the concentration of chromium is higher.

The sulfur on the SS surfaces that was bonded to PS-0 and PE-2 was in the form of SO_2 or SO_4^{2-} . SS bonded to PS-2 and PS-4 predominantly showed the sulfide peaks and the SO_2 in PS-2 showed up only in small quantity. PES that was heated for 30 min. at 400°C , showed a S peak from the adhesive side at 163.3 eV (Table VI), which could perhaps be the same product that showed up at 164.0 eV in PS-0 that was bonded to SS (Table IX). These results would indicate that the SO_2 is reduced to sulfide or disulfide with time and/or heat, as PES powder shows only the SO_2 peak. However, this is highly unlikely in an oxidizing environment. The metal in the SS could perhaps act as an oxidizing agent, however the sample heated to $400^\circ\text{C}/.5$ hour was not an interfacial specimen. PES was simply melted on top of the SS and the surface was analyzed. Other data include: PES $350^\circ\text{C}/.5$ h + $300^\circ\text{C}/3$ h in air shows a B.E. of 168.0 eV; PES $400^\circ\text{C}/.5$ h in nitrogen shows a B.E. of 168.1 eV; PES on EPDM in air shows a B.E. of 164.6 eV, PES on EPDM in nitrogen shows a B.E. of 168.8 eV. All data show the expected presence of the sulfonyl peak, except the PES on EPDM in air.

The presence of Cr on the SS (bonded to PS-0, PS-2 and PE-2) could not be compared to the previous studies as only PPS and PEEK were analyzed and these showed no Cr. Other work has demonstrated that gamma-irradiation induced the migration of alkali metals to the surface of supported silver catalysts.⁶ Perhaps an analogous mode is in operation here which causes the Cr to appear in such high concentration.

In our endeavors, PEEK joints cured in oxygen had greater strength than those cured in nitrogen. In the metal-metal lap joints, crystallinity and the amount of Fe_2O_3 at the interface played a significant role, however with EPDM joints, the actual preparation of the joint differed depending on whether it was air or nitrogen cured.

CONCLUSION

We have determined some of the critical factors involved in promoting the strength in elastomer-to-metal joint systems which can be used for geothermal applications. The thermoplastic adhesives are quite thermally stable, but have high melting temperatures at

which the elastomer, unfortunately begins to degrade. Although this is not apparent by TGA, elasticity measurements confirm that even at temperatures 50-100°C below the melting temperatures of the adhesives, there exists greater physical change of EPDM heated in air than in nitrogen atmospheres. However, peel strength data show that joints cured in nitrogen do not have comparable strengths to those cured in air, most notably when subjected to autoclave exposure.

TGA determined T_d 's refer to the temperature at which immediate decomposition occurs. However, if the time at each temperature were lengthened to 30 min. or 2 hr., lower T_d 's should be observed. Therefore, thermal decomposition could very well occur after 2 hr. at 400°C even though the $T_d = 560^\circ\text{C}$. This could explain the presence of new peaks arising in the DTA of PEEK and its blends at temperatures below the T_d .

DTA showed that the blends retained their crystallinity under the conditions used for the joint-making process and have not oxidized to other products. For example, the degradation demonstrated by PEEK at 400°C/1 hr. in air was not observed. Crystallinity per se does not appear to be a critical factor here, as the two most outstanding blends are less than 30% crystalline (PE-1 and PS-1).

ESCA analyses showed that when the chemical compositions of each surface of an interface were very similar, that there generally existed a strong cohesive bond. This does not mean, however, that sulfur (indicative of the adhesive blends) need be present on both surfaces, which meant breakup within the adhesive. In the case of the autoclaved samples of PE-1 and PE-2, EPDM was found on both surfaces indicating cohesive failure within the EPDM. When the chemical compositions of each surface were dissimilar, failure in adhesion was indicated and hence, a weak bond.

Tremendous improvement over previously investigated adhesive systems have been shown here using certain thermoplastic systems (PS-0, PS-1, PS-2, PE-1 and PE-2) that were cured in air. When previous systems showed only spotty bonding at best after exposure to autoclave conditions for a few hours, these air-cured joint systems are still completely bonded after >5 weeks of exposure to autoclave conditions at 200°C and 200 psi. Although the pretreatment of the EPDM seemed encouraging from determination of contact angles, peel strength data showed that none had improved the strength of the control samples.

Currently the peel strengths have not yet reached the desired goal of 40 lbs, although in several cases, the actual peel strengths are not known because the elastomer had torn before

an accurate measurement was determined. Use of higher pressures in the joint-making process should improve the peel strength.

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