

Effect of Plasma Treatments on the Steam-Sour Gas Resistance and Lubricity of Elastomers*

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Synopsis

Elastomers are widely used in drilling and logging applications as static seals such as casing packers and dynamic seals such as *o*-rings for drill bits. Static seals often fail in service because of thermochemical degradation due to the combined effects of steam and sour gas at elevated temperatures that are characteristic of deep wells. Dynamic seals frequently fail because of abrasive wear that occurs even at the low temperatures that prevail in shallow wells. We have shown that improved steam-sour gas resistance of a fully formulated ethylene-propylene rubber at elevated temperatures can be achieved by coating the rubber with a thin film of plasma polymerized tetrafluoroethylene. Thus, no change in the mechanical properties of the coated rubber was observed after exposure to steam and sour gas at 275°C for 48 h. In contrast, the shear modulus of the uncoated rubber increased by 96% after the same exposure. While the effectiveness of the fluorocarbon coating decreased at longer exposure times, short-term protection of elastomers could be beneficial in certain logging operations. It was also found that the coefficient of friction of a nitrile rubber (Buna N) was reduced by 20% after treatment with a carbon tetrafluoride plasma. This enhanced lubricity could lead to better wear characteristics in conventional drill bits where the seal is in contact with a moving metal surface. The surfaces of the plasma treated elastomers were characterized by water contact angle, scanning electron microscopy, and electron spectroscopy for chemical analysis.

INTRODUCTION

Elastomers are widely used as seals in various oil well drilling and logging operations. Typical applications are casing packers, *o*-rings for cable heads, and drill bit seals. Static (stationary) seals such as cable-head *o*-rings often fail as a result of the thermochemical degradation that takes place in deep wells where the temperatures can range as high as 275°C and the atmosphere contains both steam and sour gas. In contrast, drill bit seals are internal seals and are partially protected from the effects of steam and sour gas, but, because they are in contact with moving metal surfaces and borehole detritus, failure frequently occurs because of abrasive wear even at the relatively mild temperatures (<100°C) that prevail in shallow wells.

Most of the studies on the degradation of elastomers were carried out under conditions which can be classified as thermooxidative. In contrast, down-hole conditions are reducing and hydrolytic in nature and very few studies have been done in which elastomers were exposed to this kind of environment. In one paper, Ender reported on the qualitative effect of steam and sour gas on a variety of polymeric materials, including several elastomers.¹ Because of the current interest in the exploitation geothermal resources, the brine resistance of various

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commercial, and developmental elastomers at elevated temperatures has been investigated by Hirasuna et al.,² Muellar et al.,³ and Arnold et al.⁴ Since brine is also a hydrolytic-reducing type of medium, these studies are pertinent.

Hendrickson et al.⁵ showed that the chief failure mode of elastomeric seals in drilling bits was abrasive wear. In an effort to overcome this problem elastomers were encapsulated in either poly(*p*-chloroxylylene) or copoly(tetrafluoroethylene-perfluoropropylene), materials with low coefficients of friction. Unfortunately, these encapsulated seals had a tendency to delaminate in service and, because they were not very flexible, were hard to install.

The primary purpose of this study was to determine the feasibility of improving the steam-sour gas resistance of elastomers at elevated temperatures or the lubricity of elastomers at ambient temperatures by use of plasma treatments and coatings. While plasma treatments have been used to protectively coat metals and ceramics,⁶ the application of this technique to coat elastomers has apparently not been investigated. It will be shown that these goals can be achieved without significantly reducing the flexibility of the elastomers. A secondary objective of this study was to correlate the results obtained with the physical and chemical changes that occurred on the surface of the elastomers.

EXPERIMENTAL

Plasma Reactors

The plasma reactors used in this study are shown in Figures 1 and 2. The reactor shown in Figure 1 is a capacitively coupled system where the discharge is generated between two aluminum electrodes using an rf power source operating at 13.56 MHz (International Plasma Model PM 101). The monomer was introduced beneath the electrodes and then pumped over the elastomeric sub-

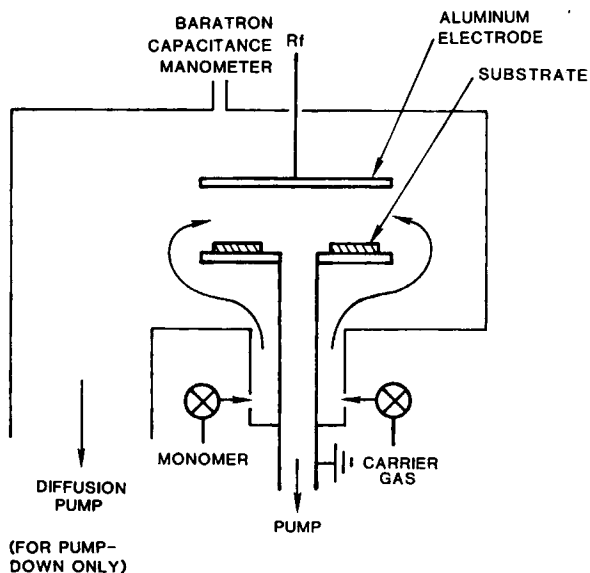


Fig. 1. Schematic diagram of the capacitively coupled plasma reactor.

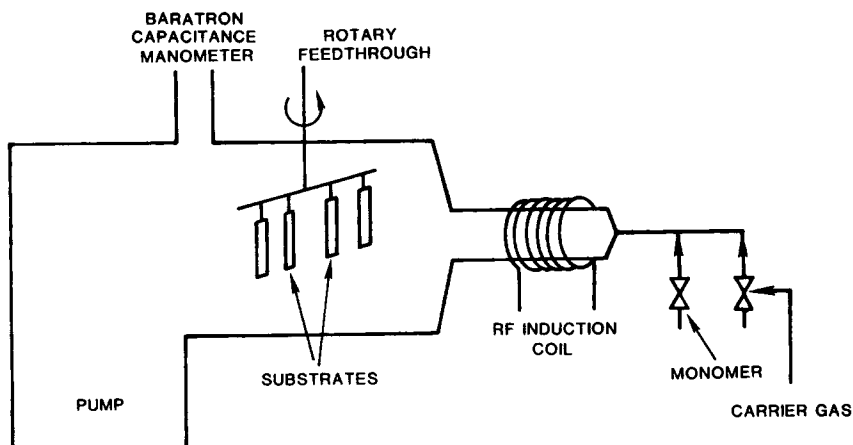


Fig. 2. Schematic diagram of the inductively coupled plasma reactor.

strates which were located on the lower electrode. The exposure time was 140 min on each side of the elastomers. In all these runs the power level was maintained at 30 W and the flow rate of the gases was adjusted to maintain a total gas pressure of 0.3 Torr.

In the inductively coupled reactor (Fig. 2), the monomers were introduced upstream from the externally located rf coil. The elastomeric substrates were placed on a motorized swivel located about 8 in. downstream from the coil and rotated to ensure uniformity of deposition or surface treatment.

Materials

The elastomers used in this study were copoly(ethene-propene) (E540-80), copoly(1,1-difluoroethane-hexafluoropropene) (V747-75), and copoly(2-propenitrile-1,3-butadiene) (N552-90). These rubbers, which contained fillers and other proprietary ingredients, were obtained from Parker Seal Co. The abbreviations in the parentheses are the Parker Seal designations for the formulations. In this paper, E540-80 will be referred to as EPR, V747-75 as FER, and N552-90 as BNR. EPR, FER, and BNR stand for ethylene-propylene rubber, fluoroelastomer rubber, and butadiene-nitrile rubber, respectively. The gases used to generate the discharges were tetrafluoroethylene (TFE), carbon tetrafluoride (CF_4), and argon. With the exception of tetrafluoroethylene, these gases were used without further treatment or purification. In the case of TFE, the inhibitor was removed by condensation prior to introducing the gas into the reactor. Sour gas, a mixture of 34% H_2S , 56% methane, and 10% carbon dioxide, was used to simulate a down-hole environment. All these gases were obtained from Matheson Corp.

Exposure Tests

The elastomers, both unmodified and modified by plasma treatments, were exposed to sour gas (46%) and steam (54%) at 275°C/ambient in a temperature-controlled tube furnace. Exposure times were 48 and 96 h.

Characterization Procedures

The surfaces of the plasma-modified elastomers were characterized by water-contact-angle measurements, scanning electron microscopy (SEM), and electron spectroscopy for chemical analysis (ESCA). The instruments used to carry out these analyses were as follows: Rame-hart Model A-100 goniometers (contact angle measurements); Hitachi S-500, (scanning electron microscope); and PHI Model 548 ESCA/Auger Electron Spectrometer (ESCA). In addition, thin films of the coatings made from TFE were characterized by infrared using a Perkin-Elmer Model 21 Double Beam Spectrophotometer and by thermogravimetric analysis using a DuPont Model 951 Thermogravimetric Analyzer. The shear modulus of the elastomers (both treated and untreated) was determined with a direct recording torsional pendulum (Plas-tech Equipment Corp.).

The coefficient of friction was determined using a pin-plate device. With this device, a spherically tipped steel pin was placed in contact with a rotating specimen of the elastomer which was mounted on a metal plate. In these tests, the pin was loaded vertically with a 252 g weight and the plate was rotated at 40 rpm. The tangential force generated between the metal pin and the elastomer was monitored using a load cell. The coefficient of friction was calculated as the ratio of the tangential force to the vertical force (252 g).

RESULTS AND DISCUSSION

Effect of Plasma Treatments on Dynamic Mechanical Properties

The change of shear modulus of EPR and FER that was observed as a result of plasma treatments is summarized in Table I. The main effect of plasma treatments is that they cause the shear modulus to increase. The magnitude of the effect varies over a wide range and appears to be dependent on both the monomer used to create the plasma and the substrate material. While in some cases, the increase in modulus was appreciable (~39%), these increases were relatively small compared to those observed when the elastomers were encapsulated in poly(*p*-chloroxylylene) or copoly(1,1-difluoroethene-hexafluoropropene). In these cases, the moduli increased by about 2000–3000%.⁴ The increase in moduli caused by plasma treatments can be ascribed to crosslinking processes and, in the case of TFE plasmas, film deposition. In spite of the in-

TABLE I
Effect of Plasma Treatments on the Shear Modulus^a of EPR and FER

Treatment	Shear modulus, G' (MPa)	
	EPR σ	FER σ
None	7.33 ± 0.71	3.10 ± 0.29
C ₂ F ₄ /cap	8.34 ± 0.79	3.50 ± 0.31
C ₂ F ₄ /ind	7.46 ± 0.73	3.47 ± 0.33
CF ₄ /cap	8.32 ± 0.81	3.57 ± 0.36
CF ₄ /ind	8.26 ± 0.78	3.47 ± 0.32
Argon/cap	7.43 ± 0.72	4.32 ± 0.41
Argon/ind	7.72 ± 0.76	4.20 ± 0.40

^a Average of five specimens.

creases in moduli that were observed after plasma treatment, the elastomers were still quite flexible and elastic. This was not the case for the encapsulated elastomers.

Stability Studies

The changes that occur in the shear modulus of a fully cured elastomer after environmental exposure can provide information concerning general types of degradation processes that took place as a result of exposure. Thus, an increase in the shear modulus of a fully cured elastomer indicates that the degradation process involved either crosslinking or chain stiffening. Conversely, a decrease in the shear modulus is indicative of either chain scission processes or plasticization. Frequently, all of these processes occur and the shear modulus simply reflects the most predominant process.

The environmental stability of both plasma treated and untreated specimens of EPR is shown in Figure 3. These curves indicate that TFE and argon plasma treatments had a beneficial effect on environmental stability for the first 48 h, but no effect when the exposure period was extended to 96 h. Thus, whereas the shear modulus of untreated EPR doubled after a 48-h exposure, the modulus of TFE treated specimen was unchanged; in the case of the argon plasma treatment the modulus increased by only 36%. Treatment with CF_4 plasma had no discernible effect on stability. After exposure for 96 h, the moduli of untreated and all plasma treated EPR specimens decreased by $\sim 20\%$. The plasma treatments discussed here were carried out using capacitive coupling. Similar stability trends were found when the plasma treatments were carried out by inductive coupling.

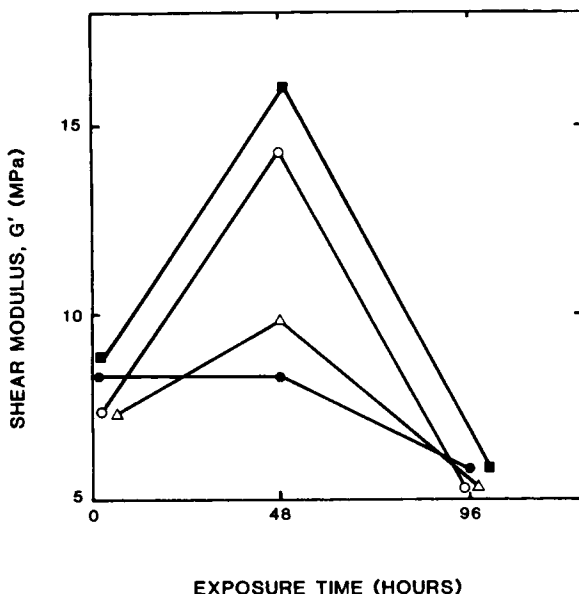


Fig. 3. Environmental stability of untreated and plasma treated EPR. Conditions: temp, 275°C; pressure, ambient; atmosphere, 46% sour gas, 54% steam. (○) Untreated, (●) C_2F_4 capacitive, (■) CF_4 , capacitive, (△) argon capacitive.

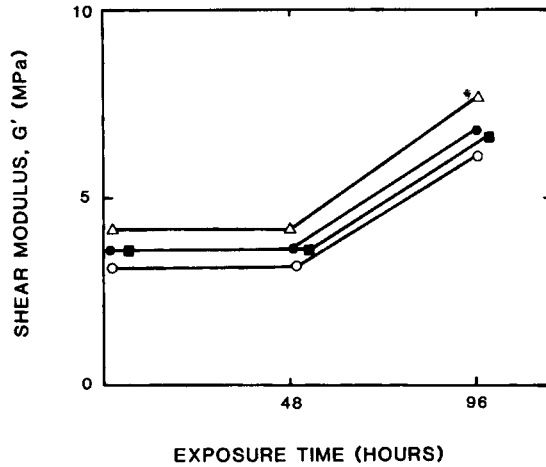


Fig. 4. Environmental stability of untreated and plasma treated FER. Conditions: temp, 275°C; pressure, ambient; atmosphere, 46% sour gas, 54% steam. (O) Untreated, (●) C₂F₄ capacitive, (■) CF₄ capacitive, (Δ) argon capacitive.

The stability of the treated and untreated FER in a steam-sour gas environment at elevated temperatures is shown in Figure 4. In this stability test, no change in the moduli of either treated or untreated FER specimens was observed after a 48-h exposure. After 96 h, the moduli of all FER specimens, both treated and untreated, increased by almost 100%. It is apparent from this data that there was no discernible effect that could be attributable to the capacitively coupled plasma treatments. Similar stability trends were observed when the plasma treatments were carried out in the inductive mode.

The effect of "dry" vs. "wet" sour gas on TFE plasma modified and unmodified specimens of EPR and FER are shown in Figures 5 and 6. For EPR, it appears that dry sour gas is less deleterious than wet sour gas and that treatment with TFE plasma was beneficial in the wet sour gas environment. In contrast, for

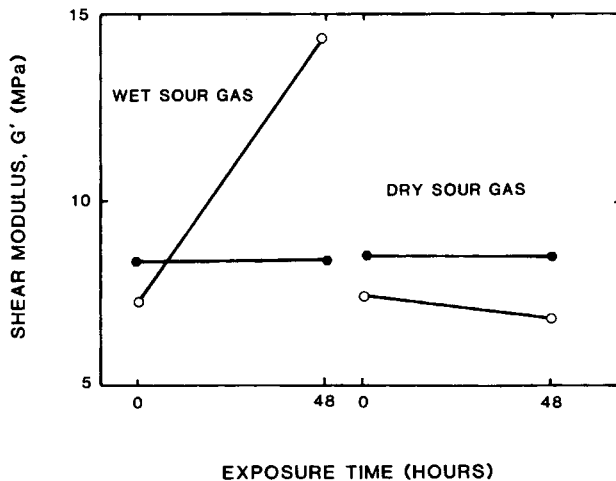


Fig. 5. Effect of dry vs. wet sour gas on the shear modulus of untreated and plasma polymerized tetrafluoroethylene (PPTFE)-coated EPR. (O) Untreated, (●) C₂F₄ capacitive.

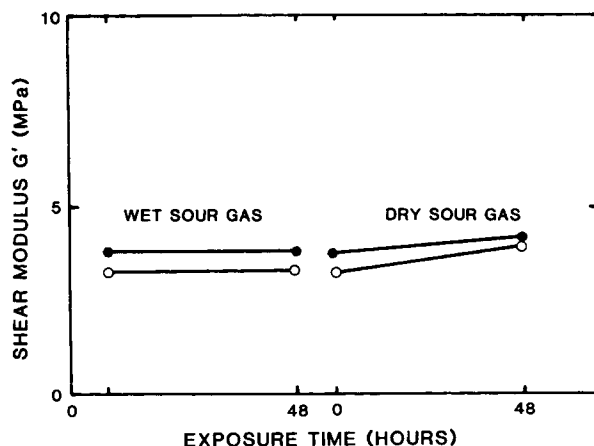


Fig. 6. Effect of dry vs. wet sour gas on the shear modulus of untreated and plasma polymerized tetrafluoroethylene (PPTFE)-coated FER. (○) Untreated, (●) C₂F₄ capacitive.

FER, neither wet nor dry sour gas appeared to affect the shear modulus significantly. In this series of experiments the exposure times were limited to 48 h.

Stability comparisons between untreated specimens of EPR and FER are easily made when the exposure time to the steam-sour gas environment was only 48 h. It is clear, for example, that during the 48-h exposure period untreated FER was more stable than untreated EPR; the modulus of EPR doubled while no change in the modulus of FER was observed. The increase in the modulus of EPR suggests that the chief mode of degradation was crosslinking. Dynamic modulus measurements were not so enlightening, however, for the 96-h exposure test. In this test, the modulus of FER doubled while the modulus of EPR decreased to 21% of its original value after having increased by 100% during the first 48 h. If this decrease in modulus was caused by plasticization by steam and/or sour gas, one would expect the modulus of the exposed elastomer to increase with time either upon standing or upon evacuation. Since neither of these two possibilities was observed, it is likely that the decrease in modulus was caused by a change in the predominant mode of degradation from crosslinking to chain scission.

The improvements in environmental stability that were realized by treatment of EPR with TFE and argon plasmas can be attributed to the formation of a protective surface coating in the case of TFE and surface crosslinking in the case of argon. It is believed that both these treatments functioned as barriers to the diffusion of the chemically active components of the environment, namely, steam, hydrogen sulfide, and carbon dioxide.

It is clear that the effect that these plasma treatments had on environmental stability were relatively short-lived; i.e., the effect was practically nil after 48 h. The primary cause for the demise of the beneficial effect of the TFE derived coating was that it completely volatilized after 48 h. Evidence for the volatilization of the TFE-derived coating will be presented later. The transience of the effect of argon treatments is probably attributable to the fact that crosslinking is limited to a depth of 3–10 μm of the surface⁷ and is therefore susceptible to chemical attack by reactive components in the environment. The environmental conditions to which these materials were subjected were, in fact, so severe that it is unlikely that any modification or treatment would be very long lasting.

Friction Measurements

The effect of plasma treatments on the coefficient of friction of BNR and EPR is shown in Figures 7 and 8, respectively. The variation of coefficient of friction vs. cycle time is attributable to surface contamination and the establishment of a wear track. It is evident from the data shown in Figure 7 that the coefficient of friction of BNR was significantly reduced by treatment with all three plasmas,

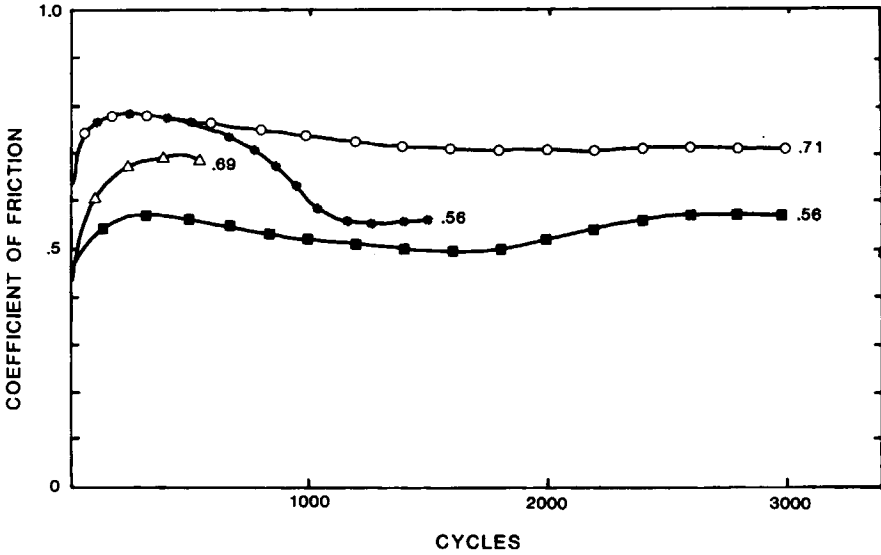


Fig. 7. Coefficient of friction vs. cycle number for untreated and plasma-treated specimens of BNR. (O) Untreated, (●) C₂F₄ capacitive, (■) CF₄ capacitive, (Δ) argon capacitive.

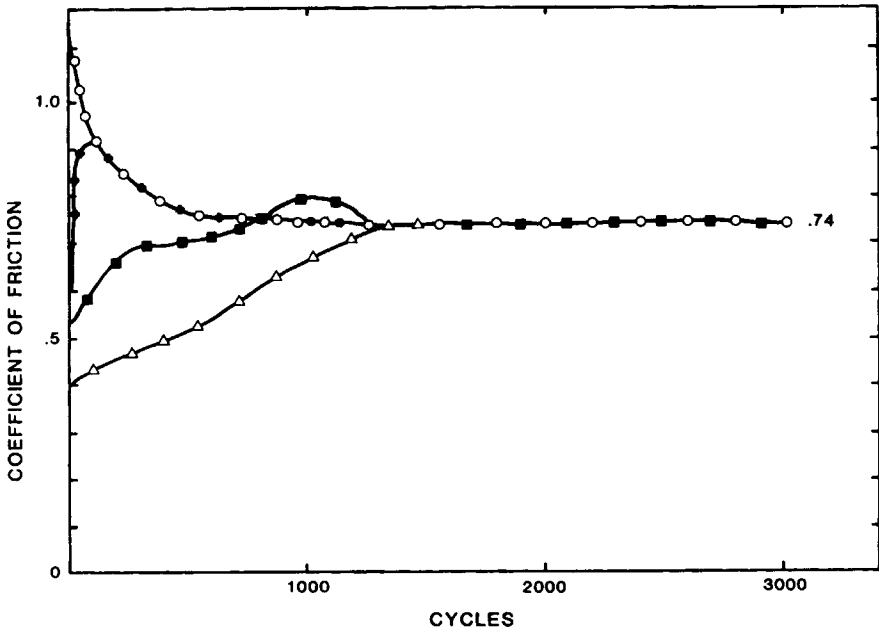


Fig. 8. Coefficient of friction vs. cycle number for untreated and plasma-treated specimens of EPR. (O) Untreated, (●) C₂F₄ capacitive, (■) CF₄ capacitive, (Δ) argon capacitive.

but differences were noted in the way the coefficient of friction changed with respect to the number of cycles. Thus, after 500 cycles, the coefficient of friction of the argon treated specimen increased from 0.46 to 0.69, the latter value being not much different than that of the untreated BNR (0.71). In contrast, the coefficient of friction of the CF_4 -treated specimens appeared to level off at 0.56, a value about 20% less than the untreated rubber. A coefficient of 0.56 is still significantly higher than that of commercial polytetrafluoroethylene (PTFE), which is reported to be ~ 0.1 .^{8,9}

The observation that the coefficient of friction of plasma-polymerized tetrafluoroethylene (PPTFE)-treated BNR went through a maximum with cycle number deserves some comment. The coefficient of friction was low in the early cycles because of the high lubricity of the PPTFE coating. The increase in the coefficient of friction reflects the contribution of the underlying rubber as the coating gets ploughed aside; the subsequent decrease in coefficient of friction is attributable to small particles of the coating which were seen falling back into the wear track. Apparently, these small particles became embedded in the wear track and were not readily dislodged.

This ploughing and gouging of the steel pin on the surface of the elastomer may not occur in actual dynamic seal applications where the rubber abuts a flat steel surface. It is conceivable, therefore, that, in some seal applications, PPTFE coatings may be more effective than might have been predicted on the basis of the above described pin-plate tests.

The effect of these plasma treatments on the lubricity of EPR was not very long lasting, as shown in Figure 8. It is evident from this figure that reduced coefficients of friction were realized in the early cycles; after 1000 cycles the coefficient of friction of both treated and untreated EPR specimens leveled out to 0.74.

The apparent permanence in the reduction of the coefficient of friction that was achieved by treating BNR, but not EPR with CF_4 plasma, can be rationalized on the basis of structural differences between these two elastomers. The structural difference is that the backbone of BNR contains carbon-carbon double bonds which could react with the fluorocarbon radicals produced in the CF_4 plasmas. Conceivably, such chemically bound fluorocarbon grafts could give rise to a more or less permanent reduction of the coefficient of friction.

Surface Characterization Studies

Measurement of the contact angle of water on a solid surface is a useful way of monitoring changes in the hydrophobicity or hydrophilicity of a given surface. Contact angle has been defined as the angle between the solid surface and the tangent of the liquid-vapor interface of a sessile drop.¹⁰ For water, then, an increase in the contact angle signifies a decrease in wettability, i.e., the surface becomes more hydrophobic. Conversely, a decrease of contact angle indicates an increase in the polarity or hydrophilicity of the surface. Water contact angle data on untreated and plasma-modified specimens of EPR and FER are summarized in Table II. It can be seen from this data that the wettability of these elastomers did change as a result of exposure to the plasmas. Treatments with fluorocarbon plasmas increased the contact angle while treatment with argon plasmas had the opposite effect. These results are consistent with what one

TABLE II
Water-Contact Angle of Plasma-Treated Elastomers

Ethylene/propylene rubber		Viton (a fluoroelastomer)
Untreated	92	90
C ₂ F ₄ /cap	105	105
C ₂ /F ₄ /ind	104	104
CF ₄ /cap	155	108
CF ₄ /ind	135	99
Argon/cap	57	56
Argon/ind	45	34

would expect if fluorocarbon or hydroxylic groups were introduced onto the surface, respectively. Thus, the contact angle of poly(tetrafluoroethylene), a very hydrophobic material in which the surface consists primarily of CF₂ groups, has a contact angle with water of 126°. ¹¹ In contrast, polymers which have oxygen and nitrogen in the repeating units of the chain are very hydrophilic, and the water contact angle is 0°. ¹² It is well known that oxygen is introduced into the surfaces exposed to argon plasmas. This is due to formation of free radicals followed subsequently by reaction of the free radicals with oxygen. ⁷

The increase in contact angle that was observed as a result of treatment with TFE plasmas can be attributed to the deposition of a polymeric fluorocarbon film. Film deposition by TFE discharges on nonelastomeric substrates has been reported in the literature. ¹³ Evidence that film deposition occurred on the elastomers used in this study will be presented later.

The increase in contact angle that was observed when EPR and FER elastomers were exposed to CF₄ plasmas strongly suggests that fluorocarbon groups were incorporated onto the surface. ESCA data, which will be discussed later, indicated that incorporation of fluorocarbon groups did, in fact, occur. This finding was somewhat surprising inasmuch as CF₄ plasmas, at least in the absence of hydrogen as a comonomer, do not deposit films on glass. Instead, glass is etched by CF₄ plasmas. ¹⁴ It is conceivable that incorporation of fluorocarbon groups onto the surface of elastomers could occur by grafting. Another possibility is that the elastomer provided a source of hydrogen which allowed films to form. Hydrogen is purported to react with F₂ in the plasma to form HF which is then pumped away. ^{15,16} Fluorine, formed in CF₄ discharge, is believed to be the primary etchant the removal of which allows polymeric films to form.

The rather high water-contact angle that was observed when EPR, but not FER, was exposed to the CF₄ plasmas deserves some comment. The lower contact angle observed for FER may be attributable to a higher reactivity of the surface free radicals toward oxygen; subsequent reaction with oxygen could then lead to the formation of hydrophilic groups.

The morphologies of the surfaces of untreated EPR and EPR that had been exposed to CF₄, argon, and TFE plasmas are shown in Figures 9, 10, 11, and 12, respectively. The surface morphologies of EPR treated with CF₄ and argon plasmas were very similar. The surface of TFE-plasma-treated EPR became relatively smooth and slightly globular in nature. This morphology is consistent with film formation.

The infrared spectrum of PPTFE is shown in Figure 13. The major peak at 1220 cm⁻¹ is ascribed to the CF stretching mode. The peak at 1720 cm⁻¹ indi-



Fig. 9. SEM of untreated EPR (5000 \times).

cates the presence of carbonyl groups. Carbonyl groups were probably generated from reaction of residual free radicals with oxygen after removal from the plasma reactor. This spectrum is similar to those which have been previously reported for PPTFE.¹⁷

The carbon 1s ESCA spectrum of PPTFE deposited on EPR is shown in Figure 14. A broad doublet was observed over the binding energy range of 285–297 eV. Clark^{18,19} made the following structural assignments to fluorocarbon components

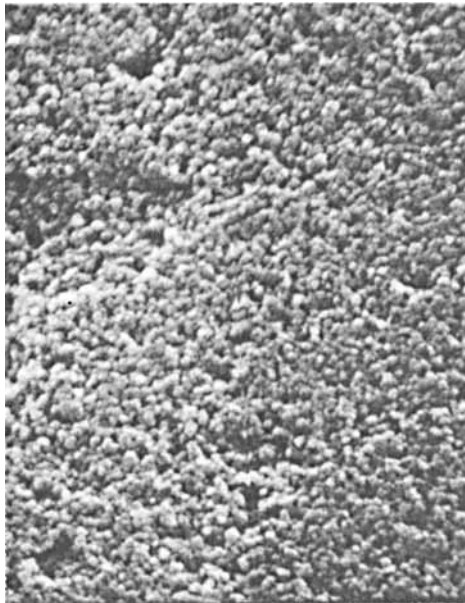


Fig. 10. SEM of EPR exposed to a capacitively coupled CF₄ plasma (5000 \times).

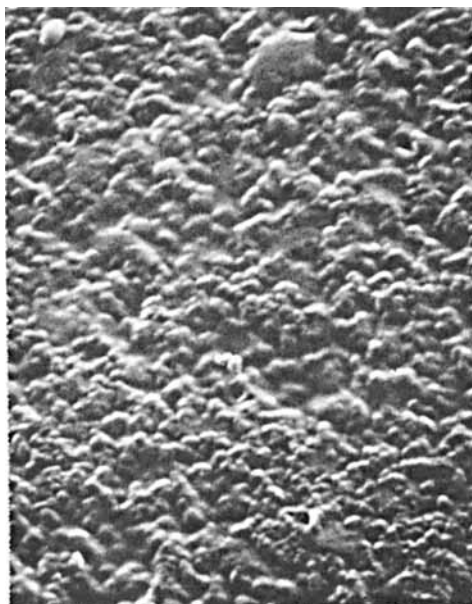


Fig. 11. SEM of EPR exposed to capacitively coupled argon plasma (5000 \times).

in this range: CF_3 (293.5 eV); CF_2 (291 eV); CF (288.5 eV) $\text{C}-\text{CF}_2$ (286.5 eV); and $\text{C}-\text{CF}$ (285.8 eV). In addition, carbon bonded to oxygen gives rise to binding energies in the range of 285–290 eV.²⁰ All of these species have been reported to be present in PPTFE.²¹ Because of the ambiguities arising from overlapping of all these lines, especially in the region of 290–285 eV, we opted to deconvolute this spectrum into three lines. This was done as follows. The

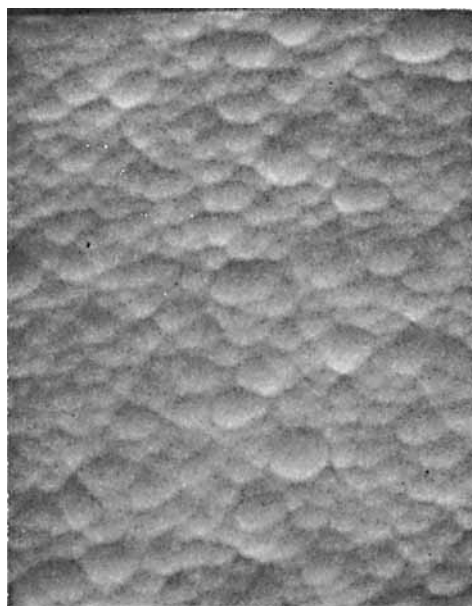


Fig. 12. SEM of EPR exposed to TFE plasma (4000 \times).

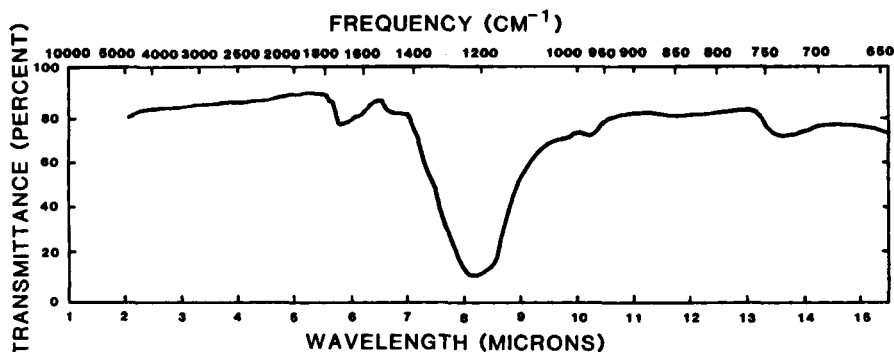


Fig. 13. Infrared spectrum of PPTFE (capacitive) film on NaCl.

experimental data were fit to the equation:

$$Y_i = A + Bx_i + \sum_{j=1}^n C_j e^{-\frac{4 \ln 2 (x_i - x_j)^2}{\sigma^2}}$$

where Y_i is the intensity at energy x_i , the x_j are the energy positions of the components in the spectra, the C_j are the intensities of the components, σ is the full width of half-maximum of the components, and n is the number of components. A and B represent the parameters used to make base-line corrections. From previous work on carbon, where there was only one component present, the σ value was determined for our instrument to be 3.4 eV and was fixed at this value for the present study. The first two lines at the higher binding energies are clearly assignable to CF_3 and CF_2 groups. The third line covers all the contributions of the lower binding energy groups.

The carbon 1s spectrum of the surface of EPR treated with a capacitively coupled CF_4 plasma is shown in Figure 15. Again a broad doublet was observed over the range which would include carbons bonded to fluorine. This spectrum was deconvoluted into four lines rather than three because of tailing in the lower bond energy region. The lower line was assigned to CH_x ; this line probably represents a contribution by the EPR substrate. The remaining three lines were

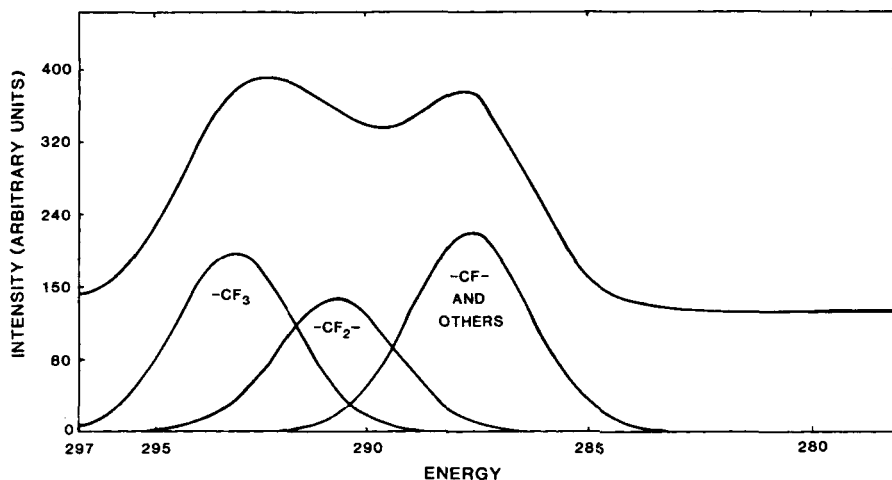


Fig. 14. Carbon 1s ESCA spectrum of PPTFE film (capacitive) on EPR.

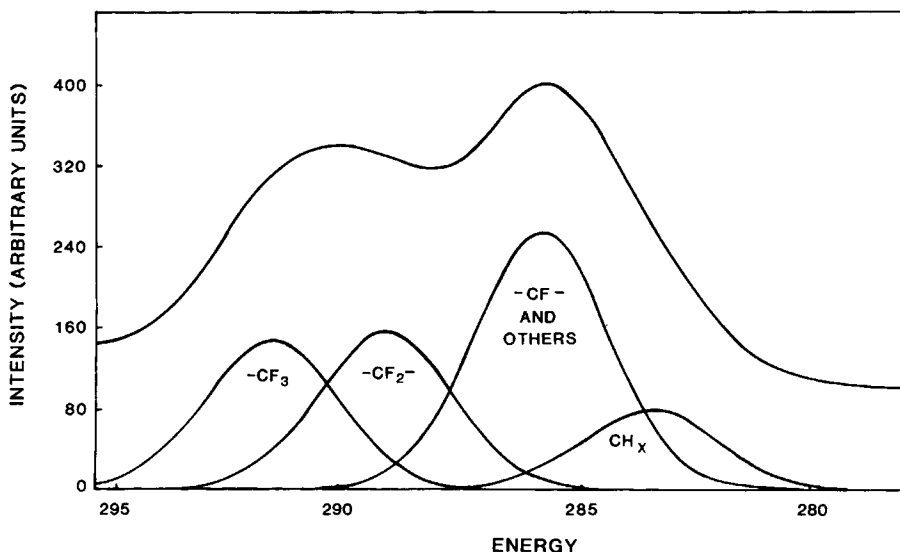


Fig. 15. Carbon 1s ESCA spectrum of surface of EPR treated with CF_4 plasma (capacitive).

assigned to CF (and others), CF_2 , and CF_3 in order of increasing binding energy. These data, taken in conjunction with SEM data which showed surface pitting, are consistent with the hypothesis that either grafting or surface fluorination occurred. Differentiation between these two processes would be difficult since CF_2 can arise via grafting of CF_2 radicals onto the surface or by fluorination of CH_2 with F atoms; both these species are present in the CF_4 plasma.

To answer the question what happens to the PPTFE coating after exposure to steam and sour gas at elevated temperatures, aged specimens of PPTFE-coated EPR were analyzed by SEM and ESCA over a wide range of bonding energies. In addition, a TGA analysis of the PPTFE film which had been deposited on aluminum and then removed was carried out. A SEM of the surface of PPTFE-coated EPR after aging is shown in Figure 16. The surface was found to be highly contoured; this may be due to a change in the morphology of PPTFE, or it may represent the underlying surface of the substrate after removal of the PPTFE. Since no fluorine was detected by ESCA, it is evident that the film had been stripped off as a result of the environmental exposure. The TGA analysis (Fig. 17) indicates that loss of the film was probably caused by the influence of temperature only. Crosslinking via activated species of inert gas (CASING) and heat post-treatments under vacuum²² should be tried to improve the thermal stability of these PPTFE films.

SUMMARY AND CONCLUSIONS

The feasibility of using plasma-polymerized tetrafluoro-ethylene coatings to environmentally protect ethylene-propylene rubber against such hostile down-hole components as sour gas and steam at 275°C was demonstrated. Because the coating volatilized under these conditions, the enhancement of stability was limited to about 48 h. Consequently, this protective plasma treatment would be beneficial only for certain logging operations which require

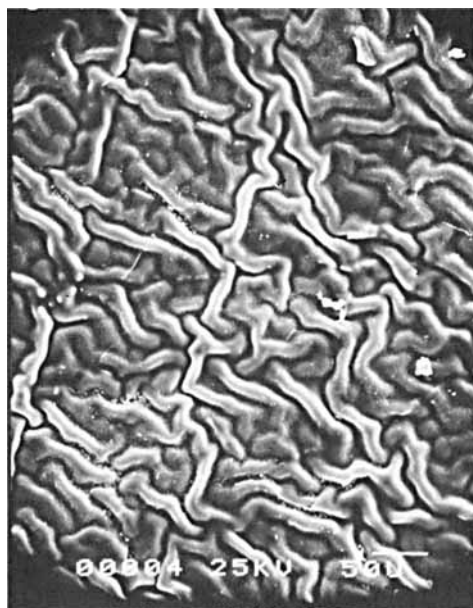


Fig. 16. SEM of PPTFE coated EPR after 48-h exposure to steam and sour gas at 275°C.

less than 48 h to complete. Electron spectroscopy for chemical analysis and infrared analysis revealed that the chemical structure of the plasma-polymerized tetrafluoroethylene on ethylene-propylene rubber was no different than that which was reported to be deposited on other substrates; i.e., the film contained a significant fraction of CF_3 groups and oxygen. Less dramatic but significant improvements in the chemical resistance of ethylene-propylene rubber toward

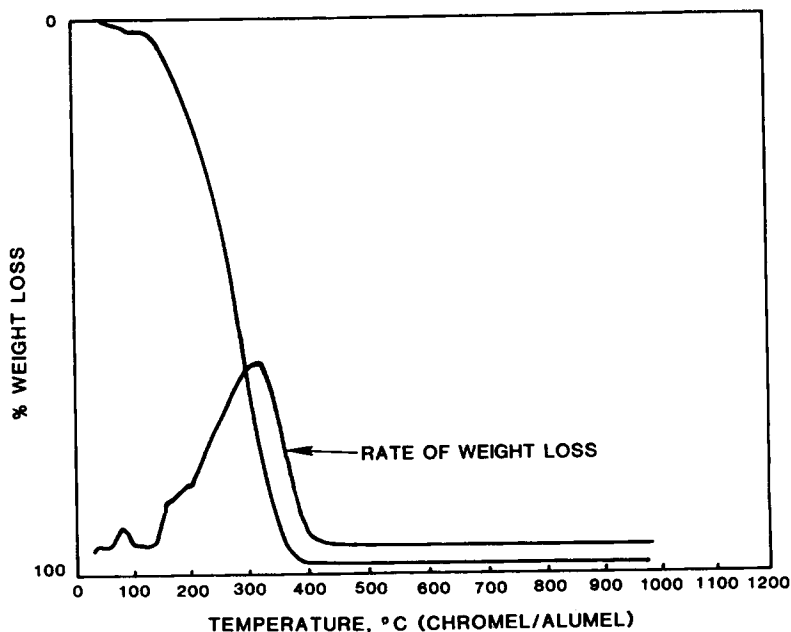


Fig. 17. Thermogravimetric analysis of PPTFE (inductive).

steam and sour gas was realized with argon plasma treatments. Because fluoroelastomers proved to be more stable than ethylene-propylene rubber in a steam-sour gas environment, no improvement in stability was realized when fluoroelastomers were treated with plasmas.

One effect of all the plasma treatments was to reduce the ambient coefficient of friction of both ethylene-propylene rubber and nitrile rubber. With the exception of nitrile rubber treated with a carbon tetrafluoride plasma, this effect proved to be temporary, i.e., the original coefficient of friction was restored after 500–1000 rotational cycles with a pin-plate device. In the case of nitrile rubber exposed to a carbon tetrafluoride plasma, a 20% reduction in the coefficient of friction was realized which was unchanged after 3000 rotational cycles. This finding is relevant to dynamic seal applications such as *o*-rings for drill bits where seal life is generally found to increase with increasing lubricity. Because of its inherent thermal instability, nitrile rubber, either treated or untreated, is not recommended for use in deep wells where the temperature might exceed 125°C.

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