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***Polytetrafluoroethylene-rich Polyphenylenesulfide Blend Top
Coatings for Mitigating Corrosion of Carbon Steel in 300°C
Brine***

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Abstract

We evaluated usefulness of a coating system consisting of an underlying polyphenylenesulfide (PPS) layer and top polytetrafluoroethylene (PTFE)-blended PPS layer as low friction, water repellent, anti-corrosion barrier film for carbon steel steam separators in geothermal power plants. The experiments were designed to obtain information on kinetic coefficient of friction, surface free energy, hydrothermal oxidation, alteration of molecular structure, thermal stability, and corrosion protection of the coating after immersing the coated carbon steel coupons for up to 35 days in CO₂-laden brine at 300°C. The superficial layer of the assembled coating was occupied by PTFE self-segregated from PPS during the melt-flowing process of this blend polymer; it conferred an outstanding slipperiness and water repellent properties because of its low friction and surface free energy. However, PTFE underwent hydrothermal oxidation in hot brine, transforming its molecular structure into an alkylated polyfluorocarboxylate salt complex linked to Na. Although such molecular transformation increased the friction and surface free energy, and also impaired the thermal stability of PTFE, the top PTFE-rich PPS layer significantly contributed to preventing the permeation of moisture and corrosive electrolytes through the coating film, so mitigating the corrosion of carbon steel.

Introduction

In geothermal power plants, a high temperature steam mixed with brine containing minerals such as silicate and silica, is extracted under pressure as a resource of renewable energy from wells, 300 to 3,000 m deep. The extracted steam then flows into the steam separator for purification. The steam separator plays a pivotal role in minimizing the extent of erosion of the turbine blades brought about by the brine-laden steam containing hard mineral particles impinging on the blade's surfaces. Thus, the metal components of separators must possess excellent resistance to corrosion and fouling at hydrothermal temperatures up to 210°C because once the topographical features of the internal surfaces of separators are altered by a build up of scale, pitting corrosion, and enhanced asperity due to abrasive wear, their maximum efficacy in improving the quality of steam diminishes. Currently, despite it's being very expensive, Inconel 625 Ni-Cr alloy is extensively used to deal with such an alteration.

If Inconel 625 can be replaced by an inexpensive carbon steel coated with cost-effective, high temperature-stable, anti-corrosion and anti-fouling materials, there is no doubt that the cost of separators would be considerably reduced. Hence, emphasis in this study was directed towards developing and evaluating candidate materials as the internal coatings for carbon steel separators. Like Inconel 625, the coating to be developed must not only offer good corrosion- and scale-preventing performance at brine temperatures up to 210°C, but also its surfaces must offer the following three important properties; 1) slipperiness, 2) water repellency, and 3) resistance to abrasive wear.

In our previous study [1], we evaluated the usefulness of polytetrafluoroethylene (PTFE) as the anti-oxidant polymeric additive to polyphenylenesulfide (PPS) coating at a brine temperature of 200°C. The results revealed that the PTFE not only abated the hydrothermal oxidation of PPS, but also made the surface of the coating less susceptible to moisture. The principal reason for such contribution was due to the phase segregation of PTFE from PPS in the melt-flowing process of these mixed polymers at 320°C; the segregated PTFE favorably migrated toward the outermost surface site of coating. Hence, the PTFE occupying the superficial layer of the coating played a very important role in creating two advanced properties; one was the improved hydrophobic surfaces offering

an outstanding water repellency, and the other was a minimum uptake of oxygen by the coating's surfaces, reflected in its inertness to reactions with scales [2]. However, one drawback of PTFE was that its chemical inertness caused poor adherence to the organic polymer and metal substrates. This fact meant that blending PTFE impaired the outstanding adherence of PPS to these substrates. Thus, the PPS/PTFE blend polymer was only used in the top layer of coating deposited on the underlying bulk PPS layer adhering to the primed metals. Nevertheless, as the top coating layer, it was successfully applied to the anti-corrosion and anti-fouling internal liner for the 20-ft.-long carbon steel heat exchanger tubes. In fact, during our 27- mo.-long field validation test of this lined tube at a geothermal power plant operating at brine temperature of $\sim 160^{\circ}\text{C}$, the liner remained intact [3]. Although some scales were deposited on the liner's surfaces, there were no signs of any chemical and physical bonding between the scales and liner, allowing it to scour off easily from liner's surfaces using hydroblasting cleaning device at low-pressure. Thus, we convinced that this blend polymer coating withstood brine at 160°C , and adequately protected the heat exchanger tubes against corruptions, erosions, and scale deposits. Additionally, as is well known, the hydrophobic surfaces of PTFE had the lowest coefficient of friction corresponding to the lowest surface free energy among the conventional polymers [4]. Since the slippery surface of polymer contributes to lowering of its frictional resistance, PTFE's surfaces appear to possess good slipperiness, suggesting the potential use of this blend polymer as a coating for steam separators. Thus far, all the laboratory and field tests for this coating were conducted at brine temperatures up to 200°C . Since the continuous operating temperature of the steam separator is $\sim 210^{\circ}\text{C}$, this coating would be required to possess hydrothermal stability at least of 250°C . So, if this coating withstands 300°C brine, it would guarantee that it would satisfactorily extend the useful lifetime of the carbon steel steam separators at 210°C .

Based upon the above information, emphasis in the current study was directed towards assessing the ability of this blend polymer system prepared by varying the ratio of PTFE to PPS to protect the carbon steel against corrosion in a CO_2 -laden brine at 300°C . Also, we investigated the alterations in the chemical state of unblended PTFE due to hydrothermal oxidation after exposure to hot brine. To obtain this information, this study had the following two major objectives: One was assessing the changes in the

surface energy, the degree of oxidation, and the coefficient of friction of the coatings as a function of exposure time to estimate the extent of slickness and water repellency; the other was measuring thermal decomposition and the alterations of molecular structure to investigate the coating's hydrothermal stability. All the information then was integrated and correlated directly with the corrosion-related data obtained from AC electrochemical impedance spectroscopy (EIS).

Experimental

Materials

The polytetrafluoroethylene (PTFE) powder under the commercial trade name "SST-3H" supplied by Shammrock Technologies was used as a slip-enhancing and anti-oxidant polymeric additive to polyphenylenesulfide (PPS); it has a particle size of ~ 40 μm . The PPS powder with a particle size of < 20 μm was supplied by Ticone. PTFE-blended PPS powder, with a PPS/PTFE ratio of 90/10, 80/20, 70/30, and 60/40 by weight, were prepared in a rotary blender. The AISI 1008 carbon steel panels (62.5 mm x 62.5 mm) were used as the substrate. Before depositing these coatings, the alkali-cleaned panels were immersed for 20 min in a 70°C zinc phosphating solution consisting of 5 wt% zinc orthophosphate, 10 wt% phosphoric acid, 1 wt% manganese (II) nitrate hexahydrate, and 84 wt% water to cover the steel's surface with a layer of crystalline zinc phosphate (Zn.Ph) primer. Then, the Zn.Ph-primed steel panels were rinsed with water at 25°C, and dried in an oven at 100°C for 30 min to remove any moisture. The Zn.Ph primer not only provides cathodic protection of the underlying steel against corrosion, but also acts as an intermediate coupling layer that directly links the steel and the coating.

Coating Technology

As mentioned in the introduction, the PPS/PTFE blend polymer was only used as a top coating layer because of a poor adherence of PTFE to organic, inorganic, and metallic substrates. Accordingly, the coating systems deposited on the primed carbon steel's surface consisted of multi layers, which were prepared in the following step: First, the primed steel was immersed in a slurry consisting of 45wt% PPS and 55wt% isopropyl alcohol, and then it was withdrawn. Second, the slurry-covered panel was left for at least

twelve hours to allow the alcohol to volatilize at room temperature. Finally, the panel was baked for 2 hours at 320°C to ensure the melt-flow of PPS, and then was cooled off at room temperature. This entire process, called “dipping-withdrawing-baking-cooling”, was repeated to superimpose the second coating layer of PPS slurry over the first one. Further, this process was repeated one more time to assemble a total of three layers of PPS before depositing the top coating systems containing PTFE. Afterward, a top coating layer of 100/0, 90/10, 80/20, 70/30, and 60/40 PPS/PTFE ratios was overlaid on this PPS underlying layer, using the same coating process. The composition of slurries for these PPS/PTFE blends was same as that of the single PPS, corresponding to 45wt% blend power and 55wt% alcohol. The thickness of these coatings without Zn.Ph primer ranged from 340 to 380 μm .

Measurements

The coated test panels were exposed for up to 35 days to a CO₂-laden brine solution (0.5wt% sodium hydrogen carbonate, 13 wt% sodium chloride, and 86.5 wt% water) at 300°C under a hydrothermal pressure of 8.3 MPa. X-ray photoelectron spectroscopy (XPS) was used to identify the chemical compositions and states of the coating's surface before and after exposure in brine at 300°C. Fourier transform infrared (FT-IR) was used to support XPS data, particularly for information on the alteration of chemical structure after exposure. The contact angle analyzer was used to determine the changes in surface free energy of the coatings as a function of exposure time. To obtain this information, two liquids, water and glycerol, were dropped on the coating's surface, and then their contact angles were measured within the first 20 seconds after dropping these liquids. Using the kinetic coefficient of friction (KCOF) tester conforming to ASTM D1894 Standard Test Method for Static and Kinetic Coefficients of Friction of Plastic Film and Sheeting, the value of KCOF was measured for 0-, 3-, 7-, and 14-day exposed coatings' surfaces (100 mm x 250 mm). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to investigate the thermal behaviors including the melting and crystalline energies, and the onset of decomposition temperature for unexposed and exposed coatings. AC electrochemical impedance spectroscopy (EIS) was used to evaluate the ability of the exposed coating layers to

protect the steel from corrosion. The specimens were mounted in a holder, and then inserted into an electrochemical cell. Computer programs were prepared to calculate theoretical impedance spectra and to analyze the experimental data. Specimens with a surface area of 13 cm^2 were exposed to an aerated 1.0 M sodium chloride electrolyte at 25°C , and single-sine technology with an input AC voltage of 10 mV (rms) was employed over a frequency range of 10 KHz to 10^{-2} Hz.

Results and Discussion

Surface Chemistry

Figure 1 gives the XPS chemical composition of the coating surfaces with the 100/0, 90/10, 80/20, 70/30, and 60/40 PPS/PTFE ratios. The atomic fraction of bulk PPS coating's surface without any PTFE was composed of 12.8 % S, 81.6 % C, and 5.6 % O. When a 10 % of the total PPS mass was replaced by PTFE, as much as 42.8 % of the F atom was detected from the coating's surfaces, while the fraction of the S atom attributed to the PPS markedly fell to 3.4 %. Since the F arose from the PTFE, this finding strongly verified that the PTFE phase had segregated from the PPS phase during the melt-flowing process of this blend polymer powder at 320°C , and that the segregated molten PTFE phase then occupied most of the coating's superficial layer. Correspondingly, the fraction of C atom for the 90/10 ratio coating also decreased ~ 38 %, compared with that of the 100/0 ratio coating because of the lack of PPS containing C-rich phenyl rings in the superficial layer. With a 20 % replacement of PPS by PTFE, the S atom was not detected, whereas a respective amount of F atom was found. All XPS measurements were made at an electron take-off angle of 40° , which corresponds to an electron-penetration depth of ~ 5.0 nm. Thus, the outermost surface site of ~ 5 nm depth for the 80/20 ratio coating appears to be occupied by only PTFE. Further replacement of PPS by PTFE to 30 and 40 % resulted in some increase in the fraction of the F atom and some reduction of the C atom. The fraction of the oxygen atom tends to decline with a decreasing PPS/PTFE ratio. For instance, a value of 0.7 % O for the 60/40 PPS/PTFE ratio coating was tantamount to $\sim 88\%$ lower than that of the 100/0 ratio, underscoring that the PTFE acted as anti-oxidant of the coating. In the other words, the PTFE occupying the top surface

layer of the coating restrained the incorporation of oxygen into it during melt-flowing fabrication process in an air oven at 320°C.

Based upon the above information, the focus now turned to assessing the susceptibility of PTFE to the reactions with hot brine at 300°C. The factors to be assessed included the changes in chemical compositions and states of PTFE's surfaces after exposure for 14 days to hot brine. Figure 2 depicts the changes in XPS O/C, F/C, and O/F atomic ratios for the coating's surfaces before and after exposure as a function of PPS/PTFE ratio. As seen, the feature of atomic ratio-PPS/PTFE ratio curves for the exposed coatings differed from that of the unexposed one. Among the differences were 1) the incorporation of additional oxygen into the coating's surfaces, reflecting the increase in O/C and O/F ratios, and 2) the decrease in amount of F atom accompanying the decrease in F/C atomic ratio. Regarding the difference 1), the O/C atomic ratio for the exposed 100/0 PPS/PTFE ratio coating raised 6.7-fold to 0.47, compared with that of the unexposed coating with same ratio, suggesting that 300°C hot brine initiated hydrothermal oxidation of the PPS's surfaces. When some portions of the PPS were replaced by PTFE, the O/C atomic ratio declined with a decreasing proportion of PPS to PTFE. This finding strongly demonstrated that the PTFE occupying the outermost surface site of the coating acted as an anti-oxidant, retarding the rate of hydrothermal oxidation of the coating. A 0.08 O/C ratio for the 60/40 ratio coating was 5.9 times lower than that of the 100/0 ratio. Correspondingly, the O/F atomic ratio decreased with more incorporation of PTFE into the PPS, from 0.35 for 90/10 ratio to 0.09 for 60/40 ratio. However, the tangible evidence was that the PTFE underwent some degree of hydrothermal oxidation. Of particular interest was the difference 2), namely, the decrease in F/C ratio means that some F atoms were eliminated from the PTFE during the 14 days exposure. Consequently, the values of 0.6, 0.96, 1.06, and 1.07 F/C ratio for the exposed 90/10, 80/20, 70/30, and 60/40 PPS/PTFE ratio coatings were equivalent to ~ 29, ~ 21, ~ 17, and ~ 20 % reduction, respectively, compared with those for the unexposed coatings with these ratios. Such elimination of F atom might be related directly to its hydrothermal oxidation.

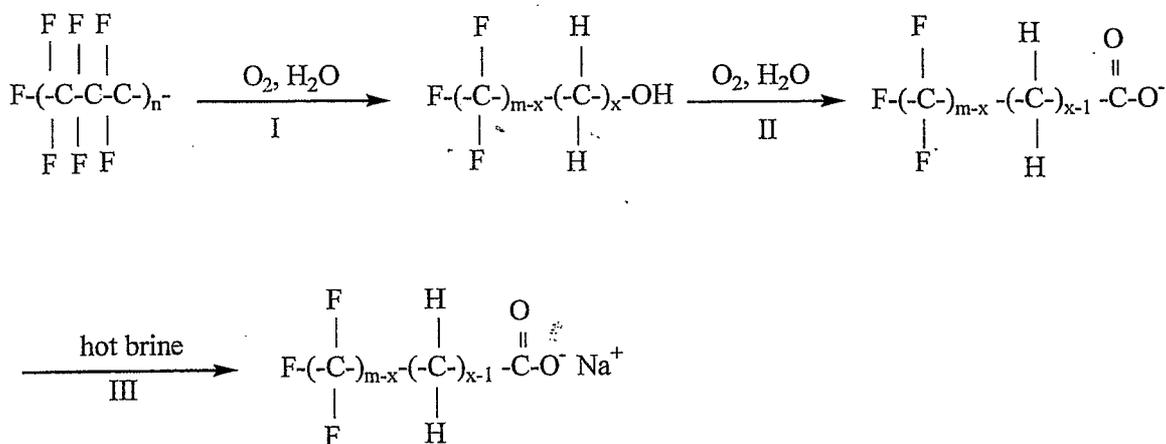
To better understand the molecular alterations of PTFE brought about by hydrothermal oxidation at 300°C, we inspected the XPS C_{1s} core-level spectra excited

from the following three sample surfaces; 1) the “as-received” PTFE powder, 2) the PTFE film fabricated by melt-flowing of this powder at 320°C, and 3) the 14-day exposed PTFE film (Figure 3). To set a scale in the XPS spectra, the binding energy (BE) was calibrated with the C_{1s} of the principal CF_2 -backbone carbon peak fixed at 292.0 eV as an internal reference [5]. The spectral feature of the “as-received” PTFE powders (a) indicated the presence of two resolvable Gaussian components at the BE positions of 286.0 and 292.0 eV. According to the literature [6,7], the former peak originates from the C in the backbone $-C-C-$ linkage of the PTFE, and the latter reflects the C in the C-F bond of $-CF_2$ group. In contrast, the spectral feature (b) of the PTFE film made at 320°C was characterized by an extensively wider peak in BE range of 290 to 283 eV, and by a decay in the magnitude of excitation at 292.0 eV attributed to the $-CF_2$. Curve fitting revealed that at least three additional Gaussian components at 286.6, 288.0, and 289.5 eV were incorporated into the original peak. The signal at 286.6 eV is assignable to the C in the alcohol ($-C-OH$) group. The contributor to the peak at 288.0 eV is the C in the ketone ($C=O$) or aldehyde (CHO) groups, while the peak at 289.5 eV is attributed to the C in the carboxylic acid ($-COOH$), ester ($-COOR$) or carboxylate ($-COO^-$) groups [8]. Since these new components are likely to be associated with the oxidation derivatives formed by the thermal oxidation of PTFE, it is possible to rationalize that some $-CF_2$ groups in the PTFE were replaced by these oxidation derivatives. The curve (c) representing a further expansion of overall peak, and a considerable attenuation of the peak at 292.0 eV, was obtained from the sample after 14 days exposure, strongly demonstrating that during this exposure time, more $-CF_2$ groups were replaced by the oxidation derivatives.

Our study next focused on identifying the chemical compounds of these oxidation derivatives. The four samples, the “as-received” PTFE powder, the PTFE film made at 320°C, and the 7-day- and 14-day-exposed films, were analyzed using FT-IR (Figure 4). As expected, the spectrum (a) of the “as-received” PTFE powder included several prominent bands in two separate regions, 1240-1150 cm^{-1} and 640-500 cm^{-1} that were related to the stretching vibration of C-F bond in the $-CF_2$ groups [9]. Compared with this spectrum, a quite different feature (b) was obtained from the film sample made by melt-flowing of powder; in particular, four additional peaks appeared at 3436, 2931, 2872, and 1596 cm^{-1} . The peaks at 3436 and 1596 cm^{-1} were due to the O-H stretching mode in the

hydroxyl, $-\text{OH}$, group and the C-O antisymmetric stretching in carboxylate, $-\text{COO}^-$, groups, respectively. The remaining two peaks are attributable to the stretching of $-\text{C}-\text{H}$ bond in $-\text{CH}_2-$ linkages. The spectrum (c) of the 7-day exposed film sample showed another two new bands at 1384 and 791 cm^{-1} originating from the C-O symmetric stretching and scissoring, respectively, in the $-\text{COO}^-$ groups, while the bands at 3436 and 1596 cm^{-1} had become more intense. Further growth of these bands was observed from the spectrum (d) from the 14-day exposed film. These findings strongly verified that some OH and COO^- groups were incorporated into the molecular structure as it was baked at 320°C , meaning that the PTFE underwent thermal oxidation, yielding these oxidation derivatives. However, there was no clear evidence on what the species of counter cation to the $-\text{COO}^-$ anion is. The Na^+ as the counter ion was detected by XPS for all the samples after exposure to hot brine, reflecting the formation of the $-\text{COO}^- \text{Na}^+$ salt complex.

The literature on atmospheric degradation routes of fluoropolymers, primarily PTFE and polyvinylidene fluoride, states that polyfluorinated carboxylate compounds are derived through the oxidation of polyfluorotelomer alcohols, $\text{CF}_3(\text{CF}_2)_n\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$, where $n=2,4$, or 6 , [10]. Thus, integrating the data obtained from the XPS and FT-IR studies, the oxidation pathways of the PTFE coating can be represented in the three reaction schemes as shown below:



First, the melt-flowing process of PTFE at 320°C in air led to the rupture of C-F bonds and C-C backbone linkages to yield an intermediate polyfluorocarbon derivative as molecular fragments. Then, this derivative reacted with atmospheric moisture during the cooling process to substitute hydrogen in place of the F atom eliminated by C-F bond breakage, and also to incorporate the hydroxyl group, as reflected in the formation of the alkylated polyfluoroalcohol (scheme I). In this melt-flowing-cooling process, some of the alkylated polyfluoroalcohols underwent a further oxidation to become converted into alkylated polyfluorocarboxylate (scheme II) that is susceptible to the reactions with the Na cation in hot brine. Finally, an alkylated polyfluorocarboxylate salt complex linked to Na was generated during exposure (scheme III).

Surface Energy

The magnitude of water repellency and slipperiness of polymer's surface depended preliminary on the surface free energy; namely, a low surface free energy improves both characteristics [11]. In this study, the surface free energy, γ_s , which is the sum of two contributors, the dispersion, γ_s^d , and polar, γ_s^p , force components, was computed using the empirical equation (1) based upon the general equilibrium at the interfaces between a solid and a liquid [12].

$$\gamma_{LV} (1 + \cos \theta) / 2 (\gamma_L^d)^{1/2} = (\gamma_s^d)^{1/2} + (\gamma_s^d \gamma_L^p / \gamma_L^d)^{1/2} \text{ ----- (1),}$$

where γ_{LV} is the surface tension of liquid, θ is contract angle of liquid droplets placed on the polymer's surface, and γ_L^d and γ_L^p refer to the dispersion- and polar-force components, respectively, of the liquid. Two liquids, water and glycerol, were used and their parameters, γ_{LV} , γ_L^d , and γ_L^p , were 72.8 mJm⁻¹, 21.8 mJm⁻¹, and 51.0 mJm⁻¹ for water, and 63.4 mJm⁻¹, 37.0 mJm⁻¹, and 26.4 mJm⁻¹ for glycerol [13].

Table 1 gives the changes in four parameters, the contact angle, γ_s^d , γ_s^p , and γ_s , for the coatings' surfaces made with the 100/0, 90/10, 80/20, 70/30, and 60/40 PPS/PTFE ratios as a function of exposure time. Figure 5 plots the γ_s value versus the exposure time for these coatings. For the coatings' surfaces before exposure to CO₂-laden brine at 300°C, the γ_s of bulk PPS coating without any PTFE was 24.3 mJm⁻¹. This value fell considerably to 5.2 mJm⁻¹ when a 10wt% of the total PPS mass was replaced by PTFE.

Since the PTFE that is segregated from the PPS phase in the melt-flowing process occupies the superficial layer of coating, this finding strongly demonstrated that PTFE plays very important role in markedly reducing the surface free energy of the blended coating. Literally, further replacement to 20wt% led to a further drop in surface free energy to a 3.6 mJm^{-1} . With a 60/40 PPS/PTFE ratio, the surface free energy was only 1.7 mJm^{-1} , corresponding to ~ 14 fold magnitude lower than that of the bulk PPS. Hence, the surface free energy of blend coating appears to be governed by the amount of PTFE. In the other words, incorporating more PTFE strikingly enhanced the extent of hydrophobicity of the coating's surface accompanying a very high contact angle of both water- and glycerol-droplets over its surfaces. Correspondingly, the surfaces of the PTFE-rich PPS coating displayed outstanding water repellency and slipperiness.

Upon exposure for up to 14 days, the surface free energy of all the PTFE-blended PPS coatings increasingly raised in the first 7 days exposure, compared with a gradual increase in the bulk PPS coating. Although the ranking, by lower value of surface free energy for the 7-day exposed coatings was in the same order as that of the unexposed ones; namely, $60/40 > 70/30 > 80/20 > 90/10 > 100/0$ PPS/PTFE ratios, such a markedly increasing rate of surface free energy for the blend coatings demonstrated that PTFE is susceptible to reactions with the 300°C brine, reflecting an increase in the values of both the dispersion- and polar-force components. For the latter component, its increment represents the incorporation of some hydrophilic polar groups, such as OH, COOH, $\text{COO}^- \text{M}^+$, C=O, CHO, and the like, yielded by the interactions between the hot brine and the PTFE into the superficial layer of the coating, thereby resulting in a decrease in the contact angles of water- and glycerol-droplets in terms of the enhanced susceptibility to moisture. Subsequently, an increasing rate of surface free energy depended on the content of PTFE; adding more PTFE to PPS raised its rate, corresponding to the increase of a 7.1-, 9.2-, 10.9-, and 17.1-fold for 90/10, 80/20, 70/30, and 60/40 ratios, respectively. In contrast, for the bulk PPS, its increase after 7 days exposure was only 1.6 fold, implying that the susceptibility of PPS's surface to the reactions with hot brine is much less than that of the PTFE's surface. Beyond 7 days, the surface free energy for 70/30 and 60/40 ratio coatings gradually increased with an extending exposure time, while for 90/10 and 80/20 ratio coatings, it leveled off. In contrast, bulk PPS still showed a remarkable

increase. Nevertheless, the values of surface free energy for 90/10, 80/20, 70/30, and 60/40 PPS/PTFE blend coatings after 14 days exposure were 15, 20, 26, and 28% lower, respectively, than that of the bulk PPS after the same exposure time, verifying that highly concentrated PTFE in the superficial layer of the exposed coatings was essentially responsible for maintaining a good water repellency of the coating's surface.

Relating this finding to the previous XPS and FT-IR results, there is no doubt that the increase in surface free energy of the exposed PTFE was due primarily to the alteration of its molecular structure caused by 300°C brine-induced oxidation; the oxidation led to the incorporation of two polar groups, OH and COONa⁺, into the top surfaces of PTFE to form the alkylated polyfluorocarboxylate salt complex linked to Na.

Kinetic Coefficient of Friction

Figure 6 depicts the changes in the kinetic coefficient of friction (KCOF) value for the coatings' surfaces as a function of exposure time. Before exposure, the bulk PPS coating without PTFE had a KCOF of 0.36. This KCOF value fell by 33% to 0.24, when 10wt% of the total of PPS was replaced with PTFE. Further replacement to 20wt% led to the shift in the KCOF to a lower site. The lowest KCOF of 0.19 was obtained from the coatings made with 70/40 and 60/40 PPS/PTFE ratios, representing that the coatings' surfaces with these ratios displayed great slipperiness. This information clearly demonstrated that the PTFE reduced the friction of the coatings' surfaces. When they were exposed in 300°C brine, the KCOF for all coatings noticeably increased in the first 7 days of exposure; beyond that time, two coating systems, 100/0 and 90/10 ratios, revealed that their KCOF somewhat increased with a further extended exposure to 14 days. In contrast, the KCOF for the other remaining coatings with 80/20, 70/30, and 60/40 ratios leveled off after exposure for 7 days.

Relating this information to the results from the surface free energy of coatings, it appeared that the KCOF has a strong relationship to the surface free energy; namely, the increase in surface free energy of the coatings corresponds to the increment of the KCOF value.

Thermal Behaviors

This molecular transformation, PTFE \rightarrow alkylated polyfluorocarboxylate salt complex raised serious concern about whether the transformed PTFE still retains the great thermal stability that the non-transformed PTFE had. In response to this intriguing question, our first approach was to investigate the changes in endothermic melting and exothermic crystallization energies of PTFE as a function of exposure time using DSC. Figure 7 shows the typical cyclic DSC curve of unexposed PTFE at the temperature range of 50 to 400°C. This thermodynamic DSC scan had two peaks; one was the endothermic phase transition, T_m , at 323.5°C, attributed to the melting point of PTFE, and the other was the exothermic transition peak, T_c , at 308.5°C, which was due to the crystallizing temperature of melted PTFE on cooling. Correspondingly, two closed areas; ΔH_m and ΔH_c , of the endothermic and exothermic curves with the baseline, respectively, represent the fusion energy at melting point and the heat energy evolved during crystallization. The ΔH was computed using the following formula [14,15]: $\Delta H = TRA/hm$, where T , R , A , h , and m refer to the temperature scale ($^{\circ}\text{C in.}^{-1}$), the range of sensitivity ($\text{mcal s}^{-1} \text{ in.}^{-1}$), the peak area (in.^2), the heating rate ($^{\circ}\text{C s}^{-1}$), and the sample's weight (mg), respectively. As shown in the figure, the computed ΔH_m and ΔH_c values were 63.2 and 66.2 J/g, respectively.

Table 2 lists the changes in four parameters, the T_m and T_c peaks, and the ΔH_m and ΔH_c energies, of the PTFE as a function of exposure time. Although there were no significant differences in T_m and T_c peak temperatures between 0 and 35 days exposure, the values of ΔH_m and ΔH_c energies depended on the exposure time; namely, they declined as exposure time was prolonged. In fact, the ΔH_m and ΔH_c values for the unexposed PTFE fell 6.3 and 8.6 % to 59.2 and 60.5 J/g, respectively, as it was exposed for 35 days. Thus, this finding can be taken as evidence that the total amount of PTFE decreased with an extending exposure time because of the increase in the extent of its transformation into the alkylated polyfluorocarboxylate salt complex.

To support this information, the onset temperature of thermal decomposition of three samples, the unexposed, and 14- and 35-day exposed PTFE, was measured by TGA (Figure 8). The thermal decomposition for the unexposed PTFE began at 481°C. When it was exposed for 14 days, the onset temperature of its decomposition shifted to a lower

site at 450°C, which was 31°C lower than that of the unexposed one. A further shift in temperature to lower site was observed from the 35-day exposed PTFE. A possible interpretation for such a shift is that an inherent thermal stability of PTFE was diminished by the increase in the extent of PTFE → salt complex transformation with prolonged exposure time.

Corrosion Protection

Good performance by the PTFE-blended PPS polymer in protecting the carbon steel separators against corrosion is one of the vital material criteria required in a coating made of this polymer. To obtain information on this, the zinc phosphated steel panels were covered with the coating systems consisting of the three bulk PPS layers as underlying coating, and a top layer with each of the PPS/PTFE ratios: 100/0, 90/20, 80/20, 70/30, and 60/40. The coatings were prepared in the sequences described earlier in the section of coating technology. The coated panels then were immersed for up to 35 days in the brine at 300°C. The unexposed, and 14- and 35-day exposed panels were used for observing the changes in appearance of the coatings and for the EIS test. All the test panels showed no changes in appearance after 14 days exposure as evidenced by the fact that all coatings remained intact. However, extending the exposure time to 35 days caused the generation of copious blisters on the bulk PPS coating without PTFE. A few blisters also were observed from the 90/10 ratio coating. Since the blistered coating panels were no longer suitable for the EIS test, these panels were eliminated from this test. In contrast, no blisters were noted on any other coatings. The blisters were due to the local delamination of coating from the underlying steel caused by the penetration of moisture through the coating layer. Thus, this finding strongly demonstrated that although the thickness of all coating films was almost the same, the top coating layer including PTFE played a pivotal role in restraining the permeation of moisture at 300°C and at the hydrothermal pressure of 8.3 MPa. Correspondingly, incorporating more PTFE into the top coating layer further reduced the rate of transportation of moisture through it. Figure 9 compares the Bode-plot features [the absolute value of impedance $|Z|$ (ohm-cm²) vs. frequency (Hz)] of three non-blistered panels made with 80/20, 70/30, and 60/40 ratios after 35 days exposure. Particular attention in the overall EIS curve was given to

the impedance value in terms of the pore resistance, R_p , which can be determined from the plateau in the Bode-plot occurring at sufficiently low frequencies. For the 80/20 ratio coating, the R_p value at a frequency of 10^{-2} Hz was 1.2×10^8 ohm-cm². This value raised more than one order of magnitude to 5.7×10^9 ohm-cm², as 30wt% of the PPS was replaced by PTFE. The feature of the curve for the 60/40 ratio coating closely resembled that of the 70/30 ratio coating. Since the R_p value reflects the magnitude of ionic conductivity generated by corrosive electrolytes passing through the coating layers, such a high R_p value for the 70/30 and 60/40 ratio coatings represents a very low uptake of electrolytes by these coatings. In other words, despite suffering from some hydrothermal oxidation, the PTFE-rich top coating layer served as an outstanding barrier in resisting the permeation of corrosive electrolytes. Figure 7 depicts the changes in R_p value at 10^{-2} Hz for the 100/0, 90/10, 80/20, 70/30, and 60/40 ratio coatings as a function of exposure time. Before exposure, the R_p value for all the coatings ranged from 5.1×10^9 to 7.4×10^9 ohm-cm². After the first 14 days exposure, no significant changes in R_p were noted for all coatings, demonstrating that over a short-term exposure, these coatings do offer as effective corrosion-preventing barrier as do the unexposed ones. However, as described early, prolonging exposure time to 35 days caused a failure of two coating systems, 100/0 and 90/10 ratios, because of the development of blisters. In contrast, there were no significant changes in R_p value for the 35-day exposed 70/30 and 60/40 ratio coatings, compared with that of the unexposed same coatings. Hence, although these coatings were exposed for 35 days, their ability to protect the underlying steel against corrosion still remained in effect.

Conclusions

The self-segregating character of polytetrafluoroethylene (PTFE) from the polyphenylenesulfide (PPS) in the melt-flowing process of PTFE/PPS blend powder gave it a high potential as a slip-and water repellent-enhancing, anti-corrosion coating for carbon steel steam separators operating at brine temperature of $\sim 210^\circ\text{C}$ in geothermal power plants. The segregated PTFE polymer occupied the outermost surface site of coating film. Correspondingly, the surface free energy of this blend polymer coating depended on the PPS/PTFE ratios; this energy significantly declined as more PPS was

replaced by PTFE, from 24.3 mJm^{-1} for 100/0 PPS/PTFE ratio to 1.7 mJm^{-1} for 60/40 ratio. In other words, the surfaces of PTFE-rich PPS coating offered enhanced water repellency. However, PTFE underwent hydrothermal oxidation when the blend polymer coating was immersed for up to 35 days in the CO_2 -laden brine at 300°C . This oxidation led to the rupture of backbone C-C linkages and C-F bonds within the PTFE, reflecting the transformation of PTFE's molecular structure into an alkylated polyfluorocarboxylate salt complex linked to Na. Such transformation not only caused the increase in kinetic coefficient of friction (KCOF) and surface free energy of the coatings, but also impaired PTFE's thermal stability, from a decomposition temperature of 481°C for unexposed PTFE to one of 438°C for 35 days of exposure. A marked increase in surface free energy occurred in the first 7 days exposure; beyond that time, it almost leveled off. After exposure for 14 days, the surface free energy of the PTFE-rich PPS coatings made with the 70/30 and 60/40 ratios was ~ 26 and ~ 28 % lower, respectively, than that of the bulk PPS without PTFE. Such changes in surface free energy were correlated directly with the changes in the KCOF value; the increased surface free energy corresponded to the increment of KCOF value. A very low KCOF value of 0.19 was obtained from the 70/30 and 60/40 PPS/PTFE ratios before exposure, reflecting a great slipperiness of coating's surface. Although the increased surface free energy and KCOF raised concerns over the diminution of maximum efficacy of PTFE in enhancing the water repellency and slipperiness of the coating, the top coating layer with 70/30 and 60/40 ratios offered great protection of carbon steel against corrosion in 300°C brine. In fact, even though a coating consisting of an underlying PPS layer and top PPS/PTFE blend layer was exposed for 35 days to hot brine, the PTFE-rich top layer considerably reduced the rate of transportation of moisture and corrosive electrolyte through the coating. In contrast, bulk PPS and PTFE-poor PPS blend top coating systems failed after 14 days exposure, as shown by the presence of blisters on the coated steel panels.

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Table 1. Surface free energy and its components for various PPS/PTFE ratio coatings after and before exposure.

PPS/PTFE	Exposure time days,	Contact angle, degrees		Disperse force component, γ_s^d , mJm ⁻¹	Polar force component, γ_s^p , mJm ⁻¹	Surface free energy, γ_s , mJm ⁻¹
		Water	Glycerol			
100/0	0	90.7	76.4	15.7	8.6	24.3
	3	71.1	72.5	5.8	26.8	32.6
	7	64.9	66.6	6.6	31.1	37.7
	14	59.9	64.7	4.7	38.9	43.6
90/10	0	118.1	115.6	2.3	2.9	5.2
	3	77.3	78.6	4.9	22.7	27.6
	7	70.0	76.5	2.1	34.7	36.8
	14	66.6	70.0	4.8	32.3	37.1
80/20	0	124.8	121.7	1.9	1.7	3.6
	3	80.6	80.6	5.5	19.3	24.8
	7	73.2	78.6	2.4	30.8	33.2
	14	73.1	80.0	1.6	33.1	34.7
70/30	0	129.5	125.9	1.6	1.1	2.7
	3	84.6	82.6	6.8	15.0	21.8
	7	77.3	81.8	2.5	27.0	29.5
	14	75.3	81.2	1.9	30.3	32.1
60/40	0	134.4	132.1	0.9	0.8	1.7
	3	88.2	84.6	8.0	11.6	19.6
	7	77.3	84.3	2.9	26.1	29.0
	14	77.3	84.4	1.1	30.5	31.6

Table 2. Changes in the thermal behaviors of PTFE as a function of exposure time in 300°C brine.

Exposure time, days	T_m , peak °C	T_c , peak °C	ΔH_m , J/g	ΔH_c , J/g
0	323.5	308.5	63.2	66.2
7	323.0	308.3	61.8	63.6
14	323.3	307.2	60.7	61.7
35	323.6	307.9	59.2	60.5

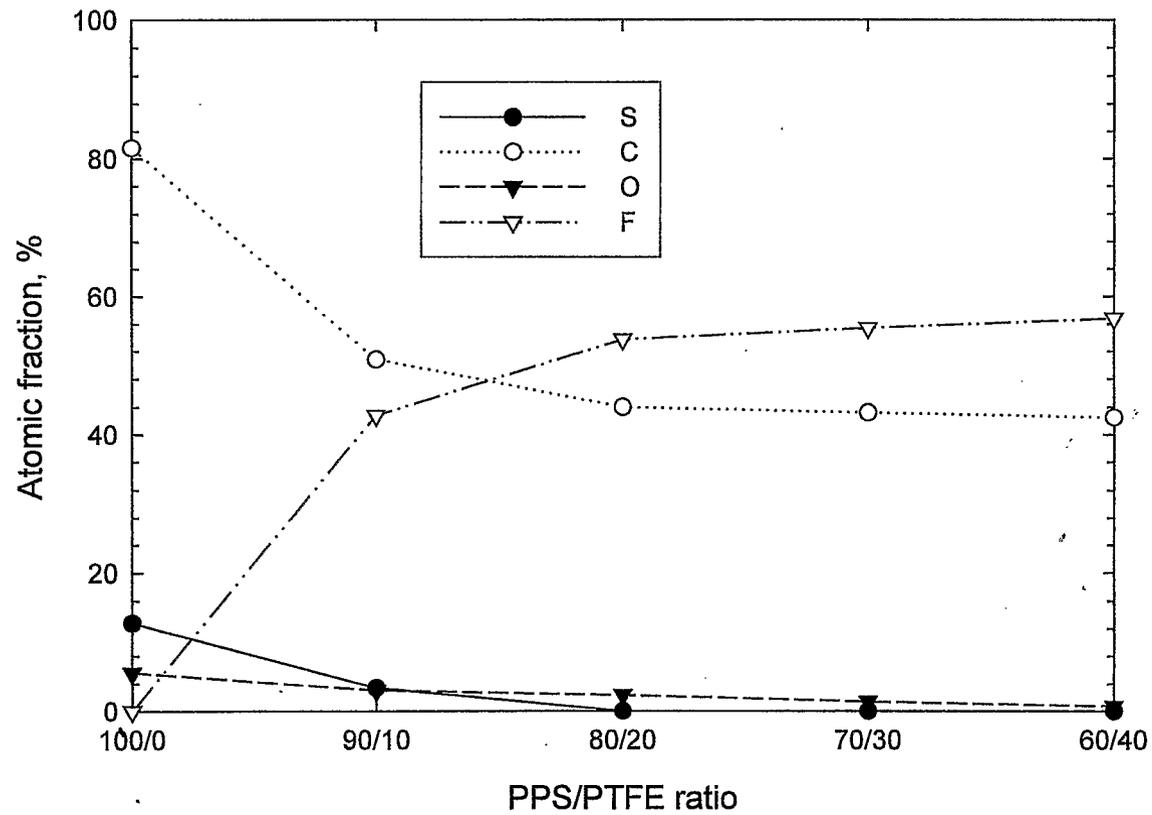


Figure 1. Atomic fraction of coatings' surfaces made with 100/0, 90/10, 80/20, 70/30, and 60/40 PPS/PTFE ratios.

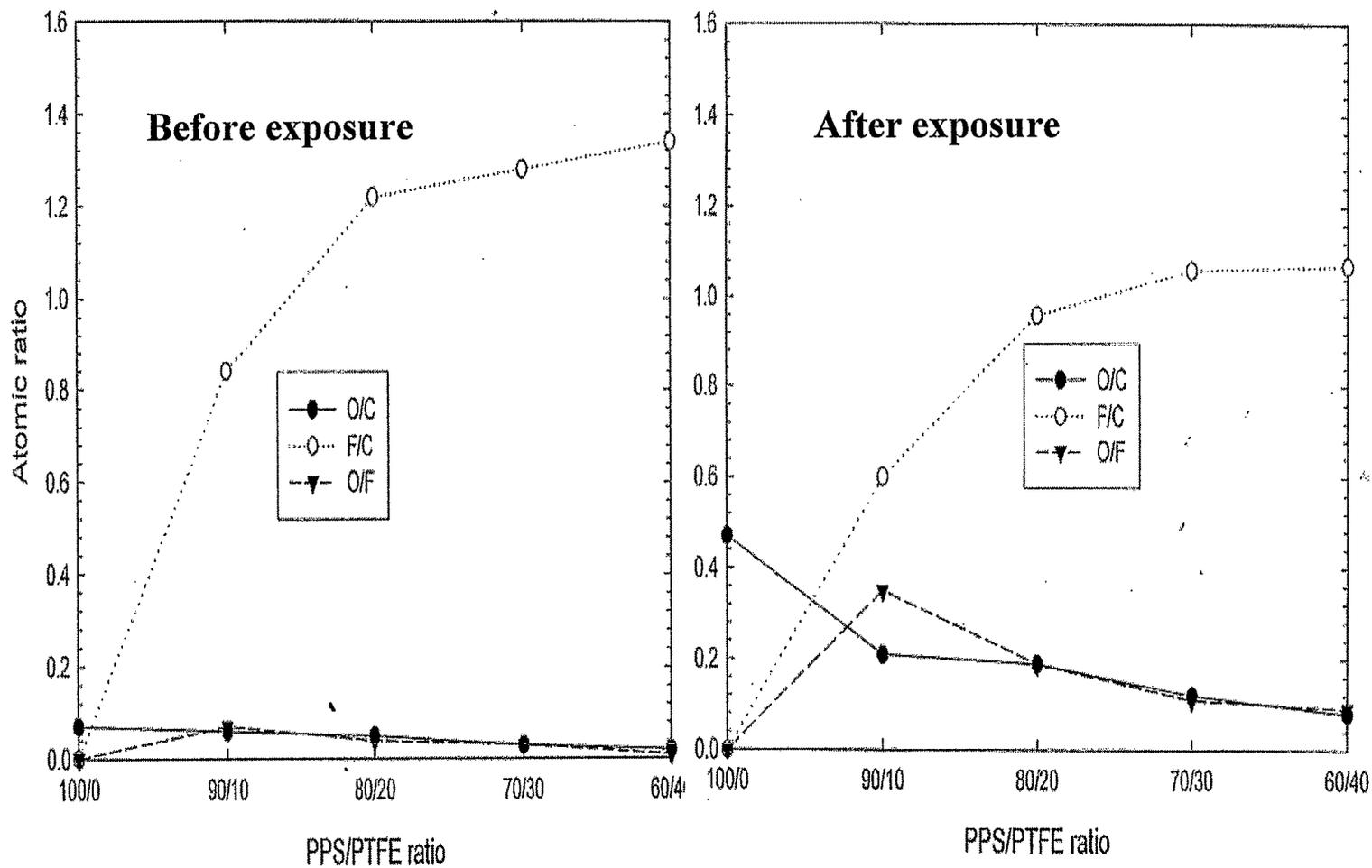


Figure 2. Comparison of O/C, F/C, and O/F atomic ratios before exposure and after exposure to hot brine for various PPS/PTFE ratio coatings' surfaces.

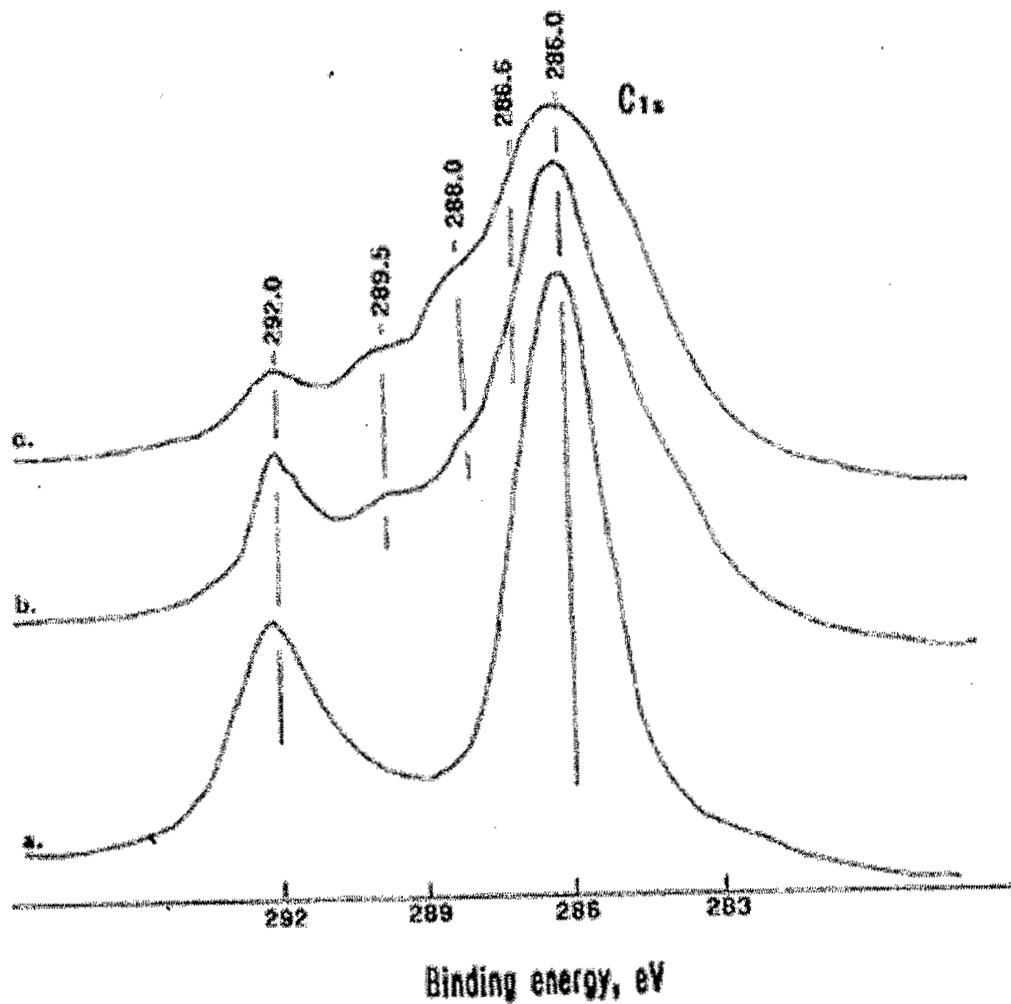


Figure 3. XPS C_{1s} core-level excitations for (a) “as-received” PTFE powder, (b) PTFE film after melt-flowing at 320°C , and (c) PTFE film after exposure for 14 days to 300°C brine.

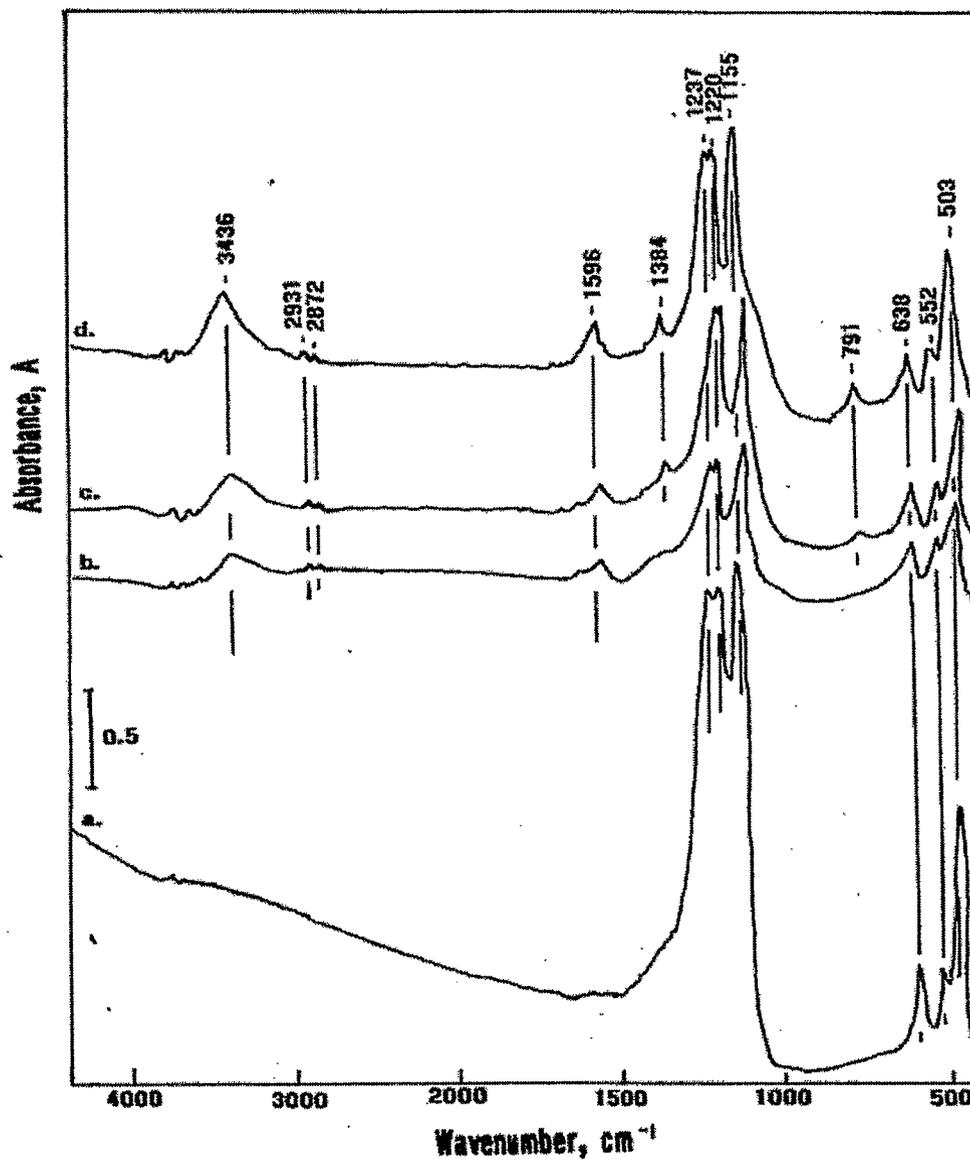


Figure 4. FT-IR spectra for (a) “as-received” PTFE, (b) PTFE after melt-flowing at 320°C, (c) 7-day and (d) 14-day exposed PTFE.

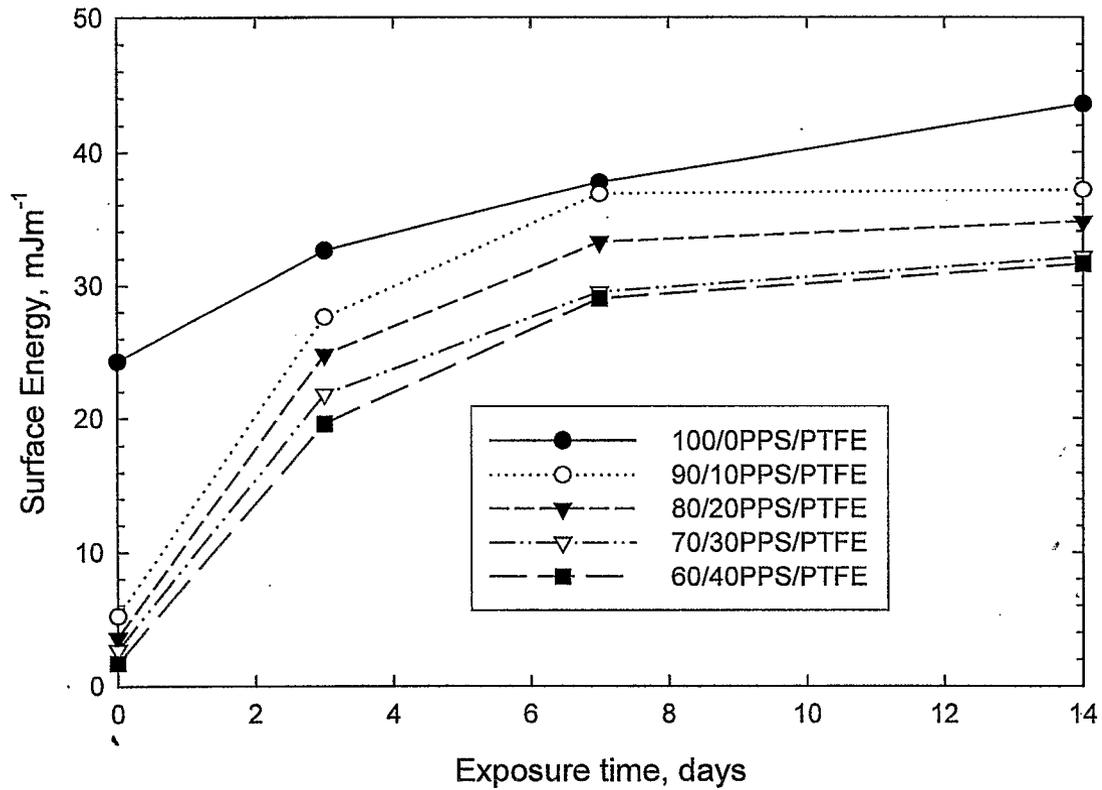


Figure 5. Changes in surface energy of 100/0, 90/10, 80/20, 70/30, and 60/40 PPS/PTFE ratio coatings as a function of exposure time.

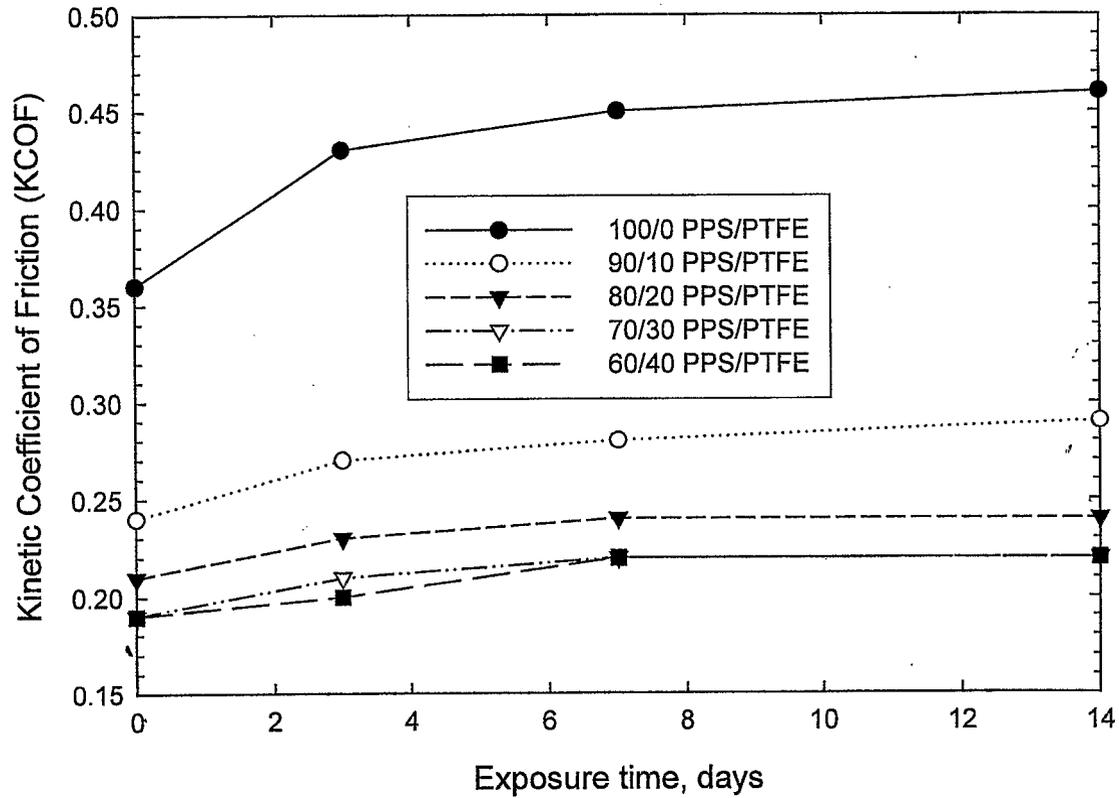


Figure 6. Changes in KCOF value of 100/0, 90/10, 80/20, 70/30, and 60/40 PPS/PTFE ratio coatings as a function of exposure time.

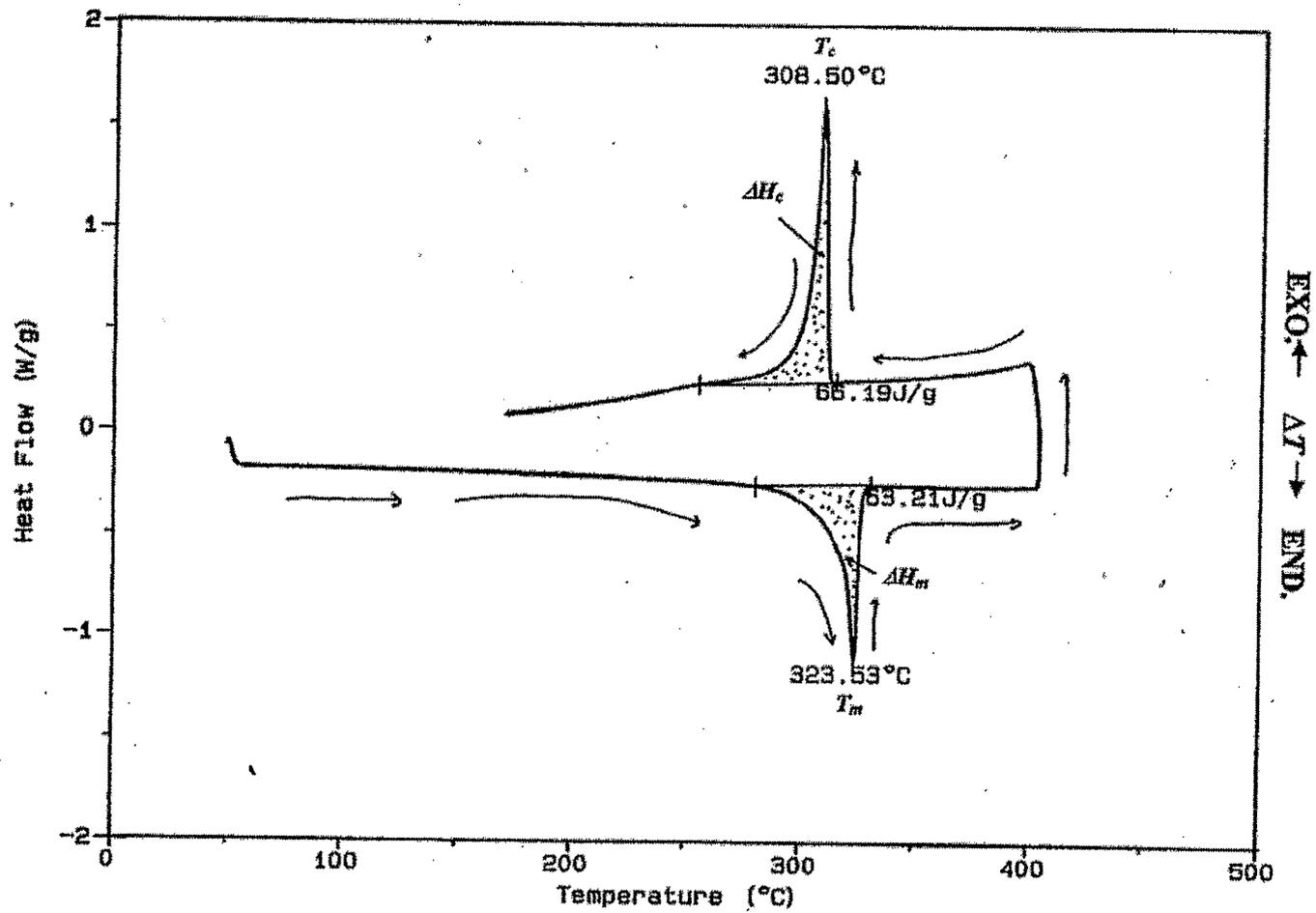


Figure 7. Typical cyclic DSC curve of unexposed PTFE.

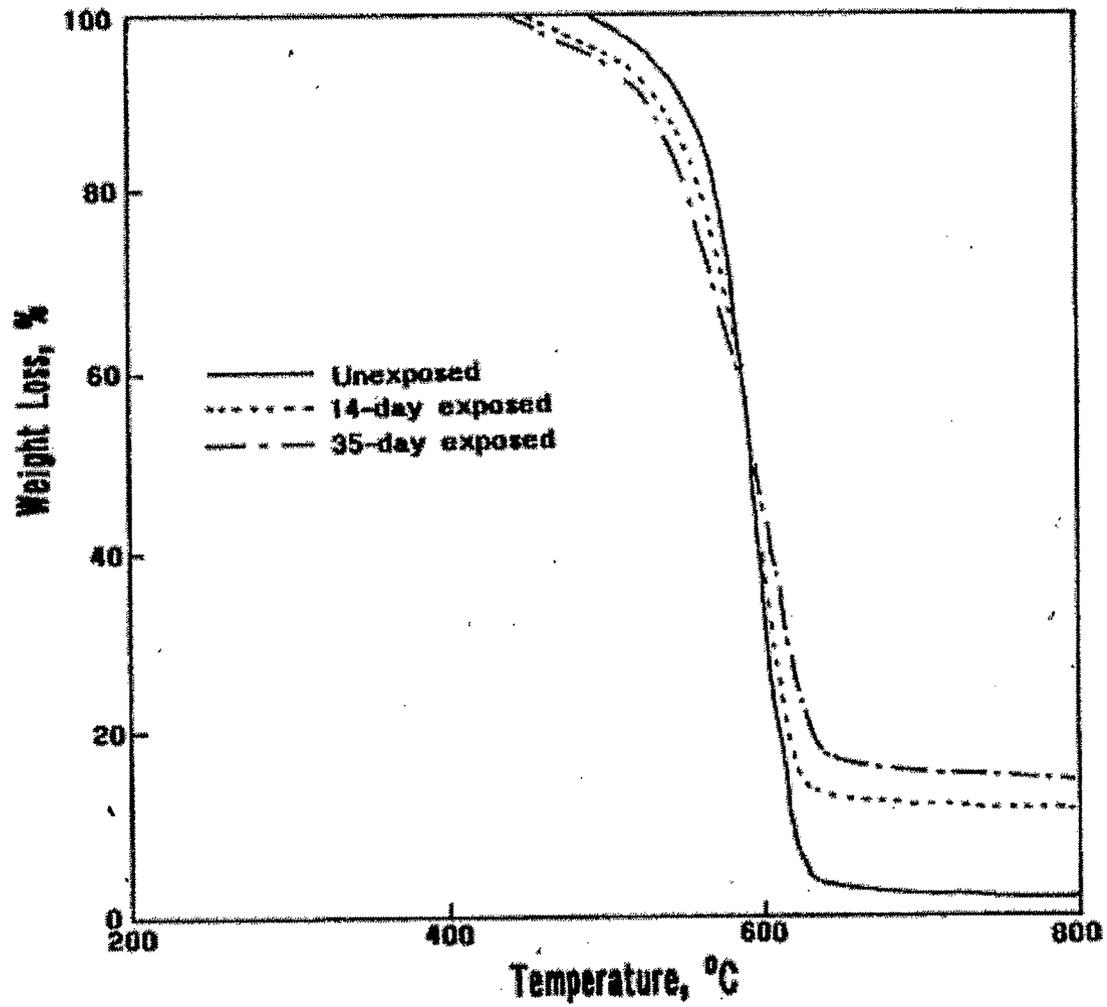


Figure 8. TGA curves for unexposed PTFE, and 14 and 35 days exposed PTFE.

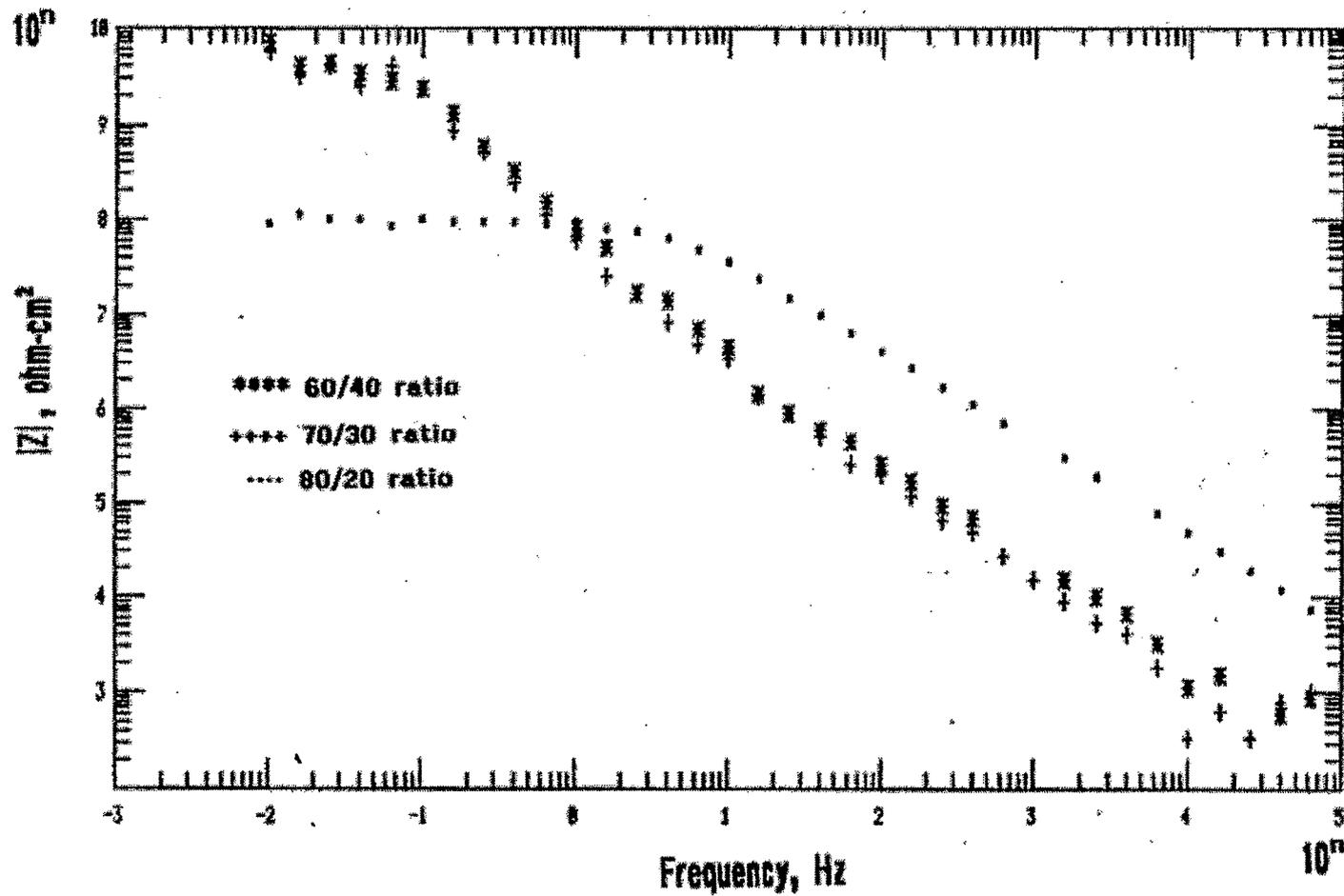


Figure 9. Bode-plot features for 80/20, 70/30, and 60/40 ratio-coated carbon steel coupons after 35 days exposure.

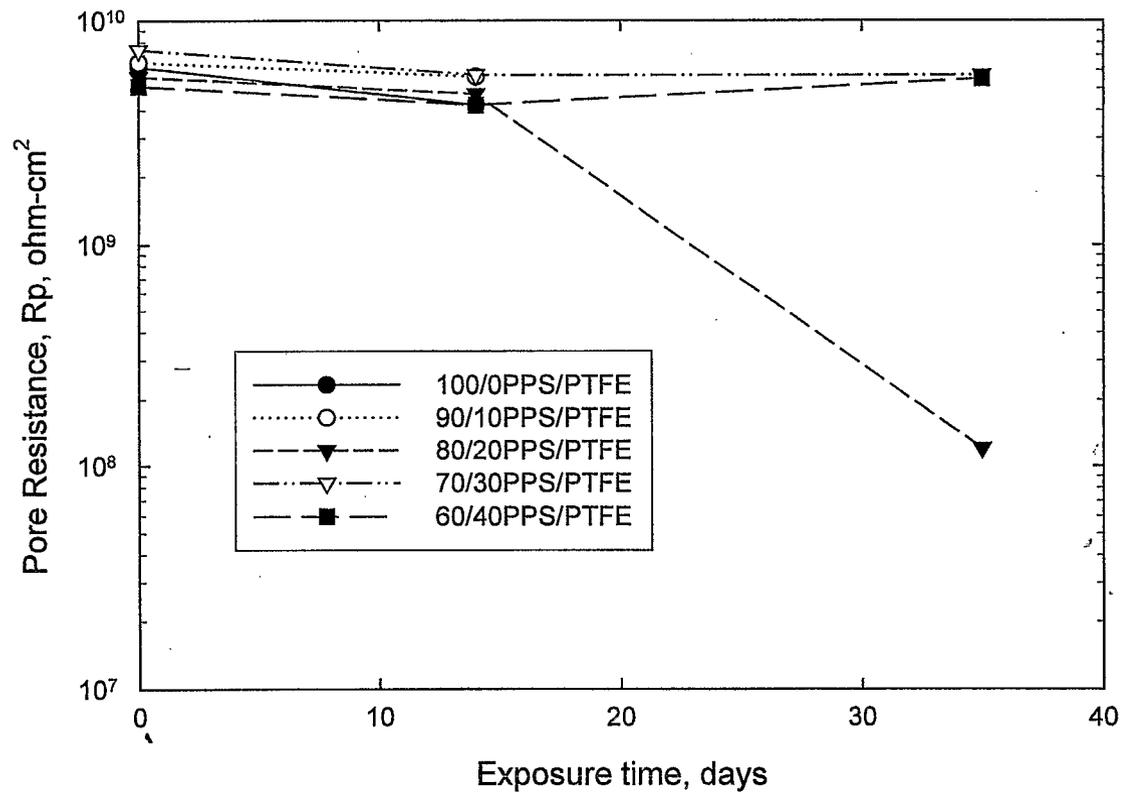


Figure 10. Changes in pore resistance, R_p , of 100/0, 90/10, 80/20, 70/30 and 60/40 PPS/PTFE ratio coatings as a function of exposure time.