Enhancement of the Chemical Resistance of Nitrile Rubber by Direct Fluorination

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ABSTRACT: Nitrile rubber (NBR), poly(acrylonitrile-*co*-butadiene) or NBR packers, are used to seal oil-well tubing, where they often come into contact with $ZnBr_2$ brines at high temperatures and pressures. Under these conditions, NBR exhibits accelerated chemical degradation, which results in embrittlement and cracking. Although alternative fluoropolymers exhibit excellent chemical resistance, their strength is less than NBR, and replacement of the usual gasket materials with fluoroelastomers is expensive. We have demonstrated that a fluoropolymer surface on a nitrile elastomer provides the necessary chemical resistance while the elastomer retains strength. This can be achieved by direct fluorination, a rather easy and inexpensive process. Samples of NBR O-rings were fluorinated by exposure to F_2 and F_2/HF mixtures at various temperatures. Although fluorination by F_2 produced the desired fluoropolymer layer, fluorination by F_2/HF (hydrofluoric acid) mixtures gave a smoother fluorinated layer at lower temperatures and shorter reaction times. Elemental analysis showed that the fluorinated layer eliminated $ZnBr_2$ diffusion into the NBR polymeric matrix. Surface fluorination also significantly retarded the loss of the mechanical properties of NBR when it was exposed to zinc bromide fluid. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 971–979, 2003

Key words: elastomers; fluoropolymers; mechanical properties

INTRODUCTION

Because of its chemical resistance to oil and solvents,[1–3] nitrile rubber (acrylonitrile–butadiene copolymer, or NBR) is often used for gaskets, O-rings, and packers in oil-well completion and production. During this process, the rubber is often in contact with fluids other than oil. One is $ZnBr_2$ brine, which because of its high density, is used to balance internal pressures. In a previous study,[4] it was shown that the $ZnBr_2$ degrades the NBR by hydrolysis of the nitrile group. The hydrolysis causes hardening and a loss of the mechanical properties of the rubber, which leads to failure of the seals, with an economic impact estimated at millions of dollars.

It is well known that fluoropolymers have outstanding chemical resistance and superior thermal and mechanical properties.[5] These materials can be used when rubber-like elasticity is needed in severe environments;[6,7] however, the fabrication of fluoromonomers and their polymerization is difficult and expensive.[8,9] Literature reports have indicated that the characteristic chemical resistance properties of fluoropolymers can be largely achieved with a fluoropolymer surface.[6] It is known that fluorination improves chemical and mechanical properties by crosslinking and increasing the molecular weight at the surface.[10] Fluorinated surfaces can be produced by different methods. Direct fluorination by F_2 diluted in He has been used to fluorinate a wide variety of polymers.[11–14] In this article, we discuss the surface fluorination of NBR as a route to the production of materials that exhibit improved resistance to zinc bromide fluids as determined by standard chemical and mechanical tests.

EXPERIMENTAL

Materials

$ZnBr_2$ brine blend (2.3 kg/L), $CaCl_2$ (1.4 kg/L), and $CaBr_2$ (1.7 kg/L) completion fluids from Baroid Drilling Fluids (Houston, TX) were used as received. Helium (technical grade) was obtained from Matherson Tri-Gas (Irving, TX). Fluorine (98%) was obtained from Air Products (Houston, TX), and anhydrous HF was received from Matheson Gas Products (Laporte, TX). Toluene (technical grade) was obtained from Fisher Scientific (Pittsburgh, PA) and was used without any further purification. NBR O-ring cord, 0.635 cm (0.25 in.) in diameter; a 70 ± 5 durometer; and 0.635 cm (0.25 in.) thick NBR flat sheets were obtained from American Packing and Gasket Co. (Houston, TX). NBR-90-214 O-rings were obtained from Parker
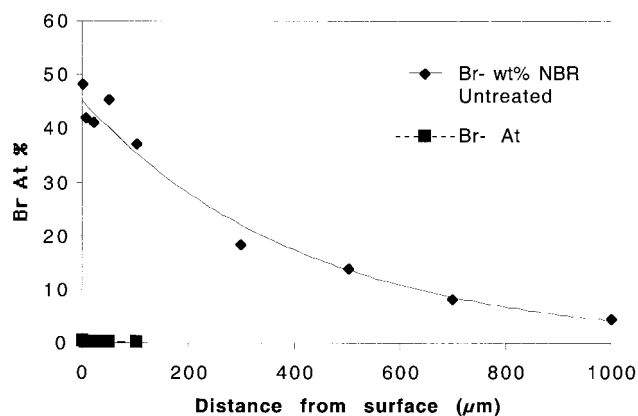
Figure 1 Bromide diffusion into NBR treated with ZnBr2 and CaBr2 completion fluids at 85–90°C for 72 h. At%, Atomic percentage.

Seals (Houston, TX) and American Packing and Gasket Co.

Fluorination

The fluorination mixture was passed through a temperature-controlled Monel alloy flow reactor containing the NBR samples. Experiments were carried out at 25, 50, and 100°C with either F_2/He or a mixture of $F_2/HF/He$ or $F_2/H_2/He$. Fluorination experiments were carried out for 5 or 24 h. A flow rate of 20 sccm was used.

Chemical treatments

$ZnBr_2$ and fluorine diffusion experiments were performed with 0.5-cm slices of NBR O-ring cord. All experiments were carried out at 85–90°C for 72 h. Samples were placed in a beaker containing a completion fluid. The beaker was covered and heated by a hot plate while the solution was stirred. The samples were then washed several times with deionized water and dried at room temperature.

Compression set measurements

This test was performed according to the ASTM method D 395-98. NBR-90 O-rings were placed between steel plates without the use of a lubricant. The plates were then bolted together. Steel spacers [0.269 cm (0.106 in.) thick], in the form of rings around each bolt, were placed between the plates to control the compression of the samples. Tests were carried out in argon and air by enclosure of the sample assembly in a closed stainless steel chamber at ambient pressure.
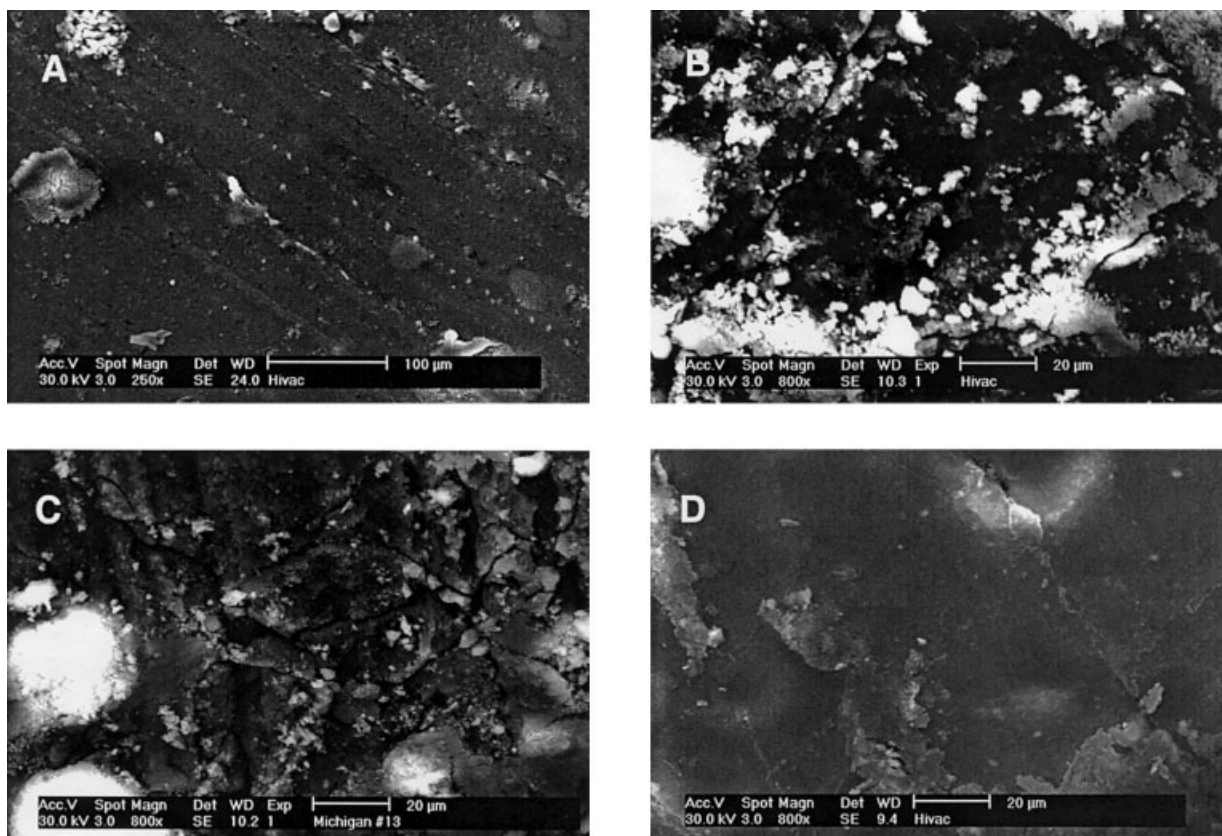
Figure 2 SEM images of NBR samples fluorinated under diverse conditions with fluorine in helium: (A) untreated NBR, (B) NBR fluorinated at room temperature for 24 h, (C) NBR fluorinated at 50°C for 5 h, and (D) NBR fluorinated at 100°C for 5 h.
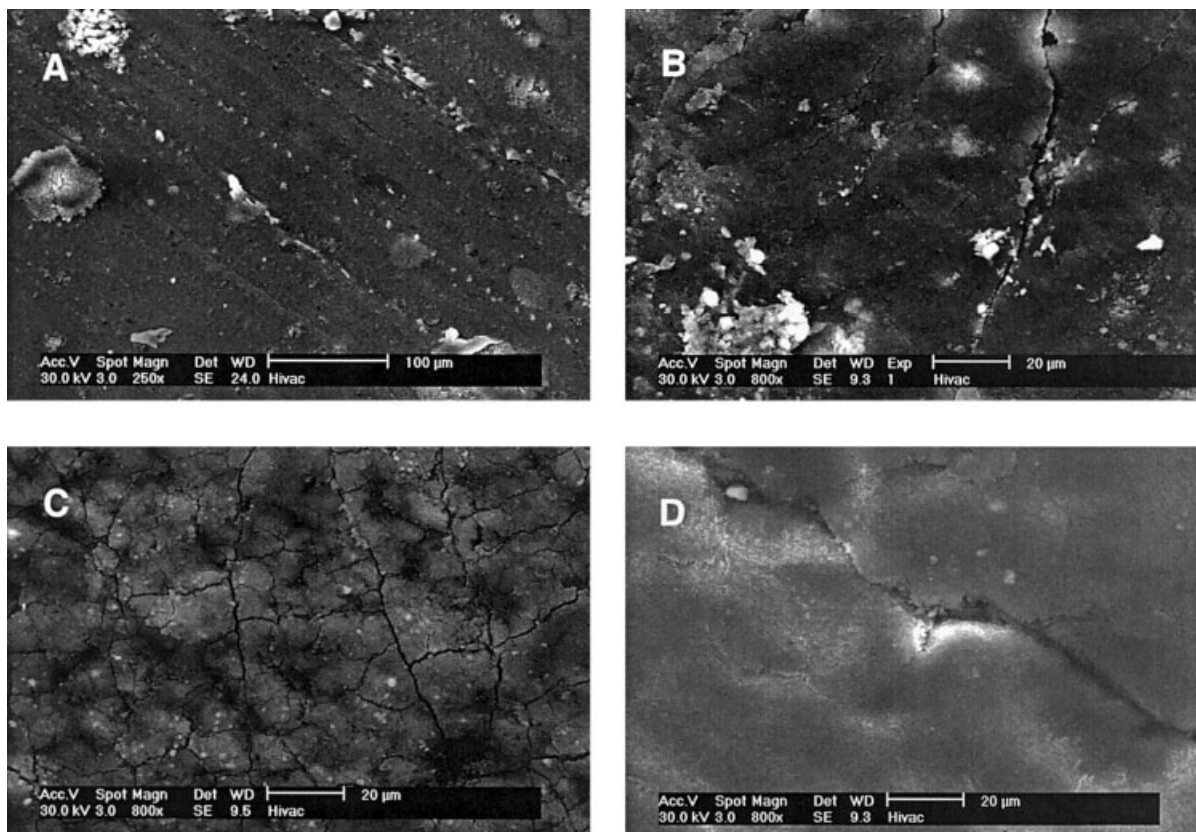
Figure 3 SEM images of NBR fluorinated with 50% F2/HF (1:1) in helium: (A) untreated NBR, (B) NBR fluorinated at room temperature for 24 h, (C) NBR fluorinated at 50°C for 5 h, and (D) NBR fluorinated at 100°C for 5 h.

Compression set tests were also made with the sample assembly immersed in $ZnBr_2$ brine. The tests were carried out at 85–90°C for 72 h. The samples were then removed and allowed to recover at room temperature for 30 min before the change in thickness was measured. The compression set measurement is the difference between the original thickness (t_0) of the O-ring sample and the thickness after recovery (t_r):[15]

$$Compression\ set\ (\%) = (t_0 - t_r)/(t_0 - t_s) \times 100$$

where t_s is the thickness of the spacer.

Chemical resistance (swelling)

O-rings were placed in a beaker with toluene to evaluate resistance to swelling in hydrocarbons. The beaker was covered with aluminum foil and left at room temperature. The thickness of each sample was measured periodically, and then the sample was placed immediately back into the toluene.

Tensile properties

The stress–strain properties were determined with an Instron 4505 Universal Electromechanical Testing Ma-
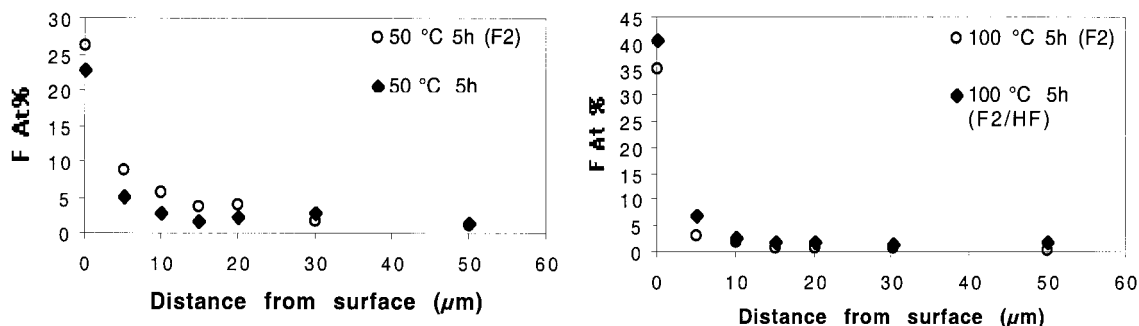
Figure 4 Comparison of fluorine penetration in NBR fluorinated with F_2 in He or with 50% F2/FE in He at (A) 50 and (B) 100°C. At%, Atomic percentage.
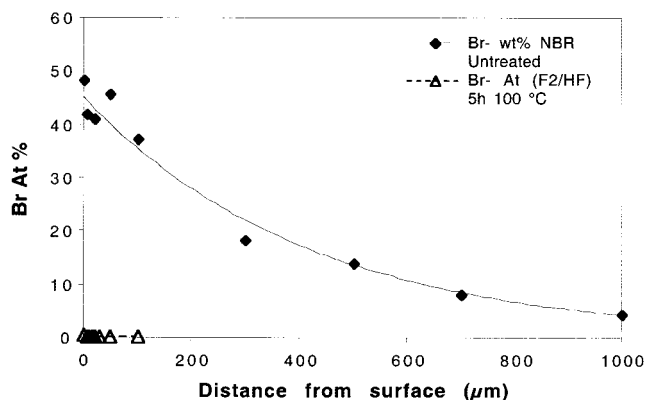
Figure 5 Bromine diffusion in NBR fluorinated at 100°C and treated with zinc bromide completion fluid at 85–90°C for 72 h. At, Atomic.

chine (Canton, MA) with a Series IX Automated Materials Tester Version 8.09.00 software. The measurements were made at room temperature according to ASTM D 412 for dumbbell and straight specimens with a crosshead speed of 500 mm/min. The dumbbell-shaped specimens (gauge length = 7.5 mm, width = 3.1 mm, and thickness = 3.38 mm) were cut out of NBR flat sheets.

Electronic microscopy and elemental analysis

A Philips Electroscan XL 30 ESENI-FEG scanning electron microscope (FEI Company, Hillsborough, OR) in high vacuum mode was used to obtain scanning electron micrographs. Elemental analyses were performed with energy-dispersive X-ray analysis unit (EDAX model ES-3030, Mahwah, NJ) attached to the electron microscope. The amount of bromide at different depths of the sample was taken as a measurement of the resistance to attack and penetration by the zinc bromide solution. Images of the fracture surfaces were obtained from a cut of the tensile test specimens.

Contact angle measurements

Contact angles were measured with a Krss DSA 10 (Hamburg, Germany) instrument. A drop of a liquid (30 wt % $ZnBr_2$ in H_2O) was placed on the rubber surfaces in air. The contact angle was obtained from a drop-shape (profile) analysis. All contact angles were measured immediately after the drop was placed onto the sample surface, corresponding to static advancing contact angles.

RESULTS AND DISCUSSION

Bromide diffusion into the NBR samples

The diffusion of bromide into NBR treated with zinc and calcium bromide fluids at 85–90°C is illustrated in Figure 1. The corresponding determination of Zn at different depths is not shown because the NBR contained both traces of an initiator and fillers containing zinc and sometimes a clear trend could not be observed; however, the diffusion of bromide ion was accompanied by Zn^{2+} when $ZnBr_2$ was used. As we observed, the bromide ion from $ZnBr_2$ diffused readily into NBR, whereas bromide from $CaBr_2$ did not. Clearly, the interaction of Zn^{2+} with NBR was responsible for the rapid diffusion of the bromide ion. We believe that the high Lewis acidity of Zn^{2+} facilitated this rapid diffusion because of the complexation of Zn^{2+} with either the lone pair of electrons on nitrogen or the π bonds in the polymer chain.

Bromide diffusion into fluorinated NBR samples

Scanning electron microscopy (SEM) images of samples fluorinated by F_2/He (Fig. 2) showed that surfaces fluorinated at low temperatures [Fig. 2(B)] developed a considerable number of cracks on the surface. As the temperature increased, the fluorine appeared to etch away loose particles, and the surface

TABLE I
Bromide At Percentage 20 μm from the Surface of the Fluorinated NBR

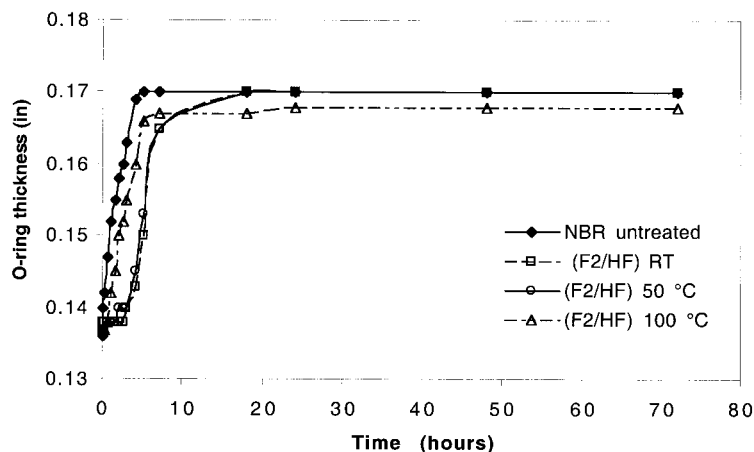| Fluorinating gas	Fluorinating gas concentration (%)	Temperature (°C)	Time (h)	Br At at 20 μm from the surface (%)
F_2	10	Room temperature	24	2.7
F_2	10	50	5	2.0
F_2	10	100	5	<0.1
F_2	50	Room temperature	24	<0.1
F_2	50	50	5	4.8
F_2	50	100	5	<0.1
F_2/HF	10	Room temperature	24	<0.1
F_2/HF	10	50	5	2.3
F_2/HF	10	100	5	<0.1
F_2/HF	50	Room temperature	24	<0.1
F_2/HF	50	50	5	<0.1
F_2/HF	50	100	5	<0.1

At%, Atomic percentage.

Figure 6 Swelling versus time for NBR fluorinated with 50% F_2/HF in helium at 100°C for 5 h.

became smoother [Fig. 2(D)]. The same behavior was observed when samples were fluorinated with F_2/HF/He, as illustrated in Figure 3. However, samples fluorinated at low temperatures with the F_2/HF/He reagent [Fig. 3(B)] exhibited less cracking on the surface than samples fluorinated with fluorine alone.

The depth of fluorination was the same for the various reagents. There was also no significant difference in the depth of fluorination with different ratios of F_2/HF. The fluorination results are shown in Figure 4 for samples treated with F_2 and F_2/HF at 50 and 100°C for 5 h.

Figure 5 shows a comparison of bromide diffusion into untreated rubber and NBR fluorinated by F_2/HF (hydrofluoric acid) at 100°C for 5 h. The results for different fluorination conditions are summarized in Table I, where the bromide concentrations in the NBR samples at 20 μm from the surface are given. This depth is considered to be representative of the effectiveness of the fluorine treatment to stop the diffusion of bromide. Clearly, samples fluorinated by the F_2/HF/He reagent appeared to be somewhat more effective in stopping zinc bromide diffusion than samples fluorinated by fluorine alone.

Chemical resistance to toluene (swelling)

Figure 6 shows swelling versus time curves for fluorinated materials in toluene. Fluorinated samples absorbed toluene more slowly than the untreated sample at the beginning of the experiment; however, after 72 h, all of the samples exhibited the same level of swelling. After 72 h, the NBR O-rings were removed from toluene, and their thicknesses and weights were measured. The amount of toluene absorbed by untreated NBR was slightly higher than the amount absorbed by the fluorinated samples (Table II). The weights and thicknesses were measured again 48 h after the O-rings were removed from the toluene bath.

Although the thickness recovered to the original value after this period of time, the final weight was lower than the initial weight (Table II). This indicates that either some of the NBR or the organic material that was used in the formulation of the rubber composite dissolved during the experiment. However, fluorination of the O-ring surfaces clearly reduced the solubility of the samples.
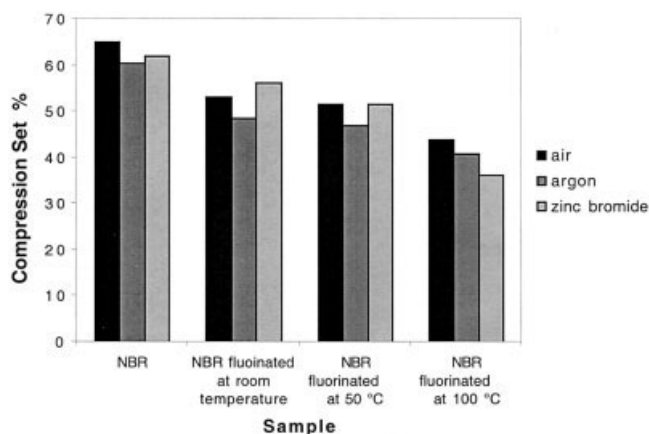
Compression set

Figure 7 shows the compression set results for O-rings fluorinated at room temperature and 50 and 100°C. Samples were exposed to $ZnBr_2$, air, or argon at 85–90°C for 72 h.

Compression set data measures the ability of a sample to recover from compression and provides information regarding the degree of crosslinking that has taken place during compression: a lower result indicates less crosslinking (hardening) during compression. As shown in Figure 7, fluorination not only improved the chemical properties of the surface but also improved the overall resistance to the deformation of the O-ring. This may indicate that additional crosslinking occurred during fluorination, decreasing the potential for hardening afterward.

TABLE II
Resistance to Toluene (Swelling) at Room Temperature for 72 h

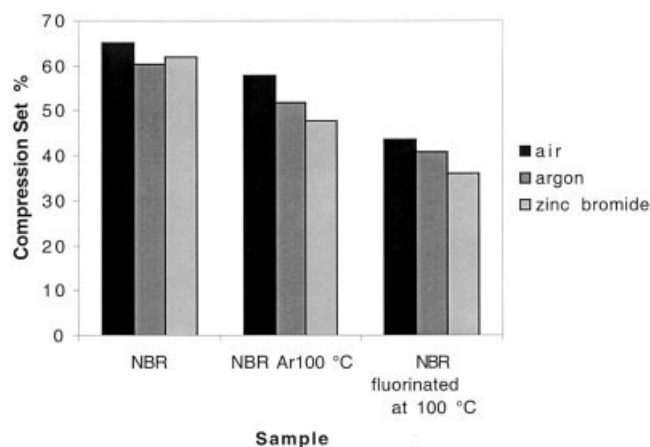| NBR sample	Weight increment (%) after 72 h	Total weight loss (%)
Untreated	38	2.4
Fluorinated		
25°C	35	1.3
50°C	36	1.9
100°C	35	2.2

**Figure 7** Compression set of fluorinated NBR in air, argon, and zinc bromide fluid at 85–90°C for 72 h.

Figure 8 Compression set in air, argon, and zinc bromide fluid at 85–90°C for 72 h for untreated NBR, NBR preheated in argon at 100°C, and NBR fluorinated at 100°C.

The fluorinated samples were significantly harder after the fluorination process. Increased crosslinking may have occurred from fluorine free radicals or from remaining vulcanization agents activated by heating. To prove that this was not just an effect of heating during the treatments, the experiments were repeated with unfluorinated samples that were heated in argon at 100°C for 24 h (Fig. 8). The results suggest there was a temperature effect; however, it was also clear that fluorination also decreased the compression set of the surface-fluorinated NBR.

Tensile properties

Figure 9 shows the stress–strain plots of NBR samples treated with completion fluids for 72 h at 85–90°C. Moduli and maximum stress values are summarized in Table III. $CaCl_2$ and $CaBr_2$ completion fluids did not

affect the mechanical properties of NBR; however, after contact with $ZnBr_2$ fluid, NBR lost elasticity, and its mechanical properties decreased.

Figure 9 suggests that NBR became brittle after exposure to zinc bromide fluid as the energy required to break it was significantly lower than the energy required to break the untreated rubber or the rubber exposed to either calcium bromide or calcium chloride fluids. This is in agreement with a previous study where it was found that $CaCl_2$ and $CaBr_2$ did not diffuse into NBR although $ZnBr_2$ did.[4]

The tensile curves of untreated NBR samples and NBR samples fluorinated before and after being treated with $ZnBr_2$ brine are presented in Figure 10. These results suggest that fluorination reduced the elasticity of NBR but protected it from zinc-bromide-catalyzed hardening. As shown in Table III, the elas-
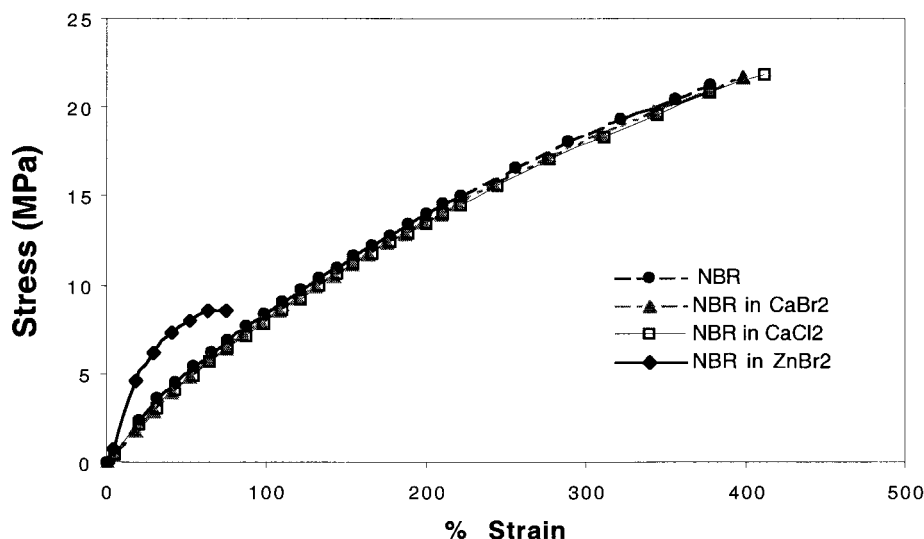

Figure 9 Stress versus percentage strain of NBR samples treated with calcium bromide, calcium chloride, and zinc bromide completion fluids at 85–90°C for 72 h.

TABLE III
Maximum Stress and Moduli of NBR Samples Treated with Completion Fluids

Sample	Young modulus (E_0; MPa)	Maximum stress (MPa)	Elongation at break (%)
NBR			
Untreated	11.7	21.1	376.1
Treated with $ZnBr_2$	22.4	9.6	74.4
Treated with $CaBr_2$	10.7	21.6	390.0
Treated with $CaCl_2$	10.3	21.9	365.7
Preheated in argon at			
50°C	12.2	20.8	376.1
100°C	11.8	22.0	388.7
Fluorinated at			
Room temperature	10.7	15.1	210.0
50°C	12.4	16.1	244.2
100°C	12.4	16.1	176.2
Treated with $ZnBr_2$ after fluorination at			
Room temperature	13.2	15.0	169.5
50°C	12.4	13.8	168.4
100°C	11.2	17.5	175.1

ticity modulus of NBR increased more than twice after exposure to zinc bromide fluid. This did not occur with the fluorinated samples.

Several authors have attributed the increase in Young's modulus, hardness, and compression set and a decline in the elongation at break to an increase in the degree of crosslinking, whereas tensile strength depends also on the nature of the crosslinks.[16–20] Therefore, tensile stress–strain tests suggested, but did not prove, that exposure to zinc bromide fluid at 85–90°C induced crosslinking and hydrolysis on the backbone polymer chain. The tensile strength and the elongation at break of the fluorinated samples were lower than those of the original NBR. Joseph et al.[16] suggested that a decease in tensile strength probably means that polymer chains have been broken at the
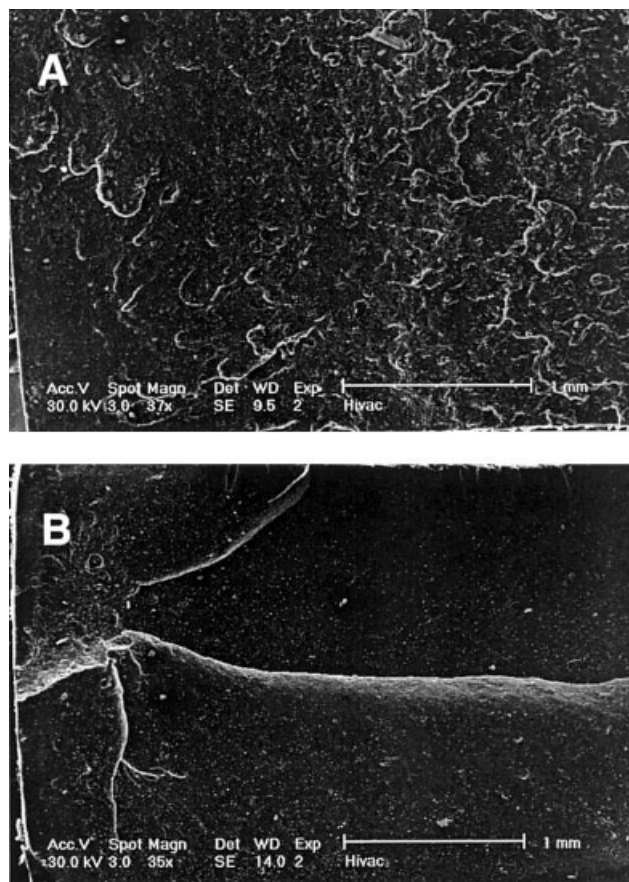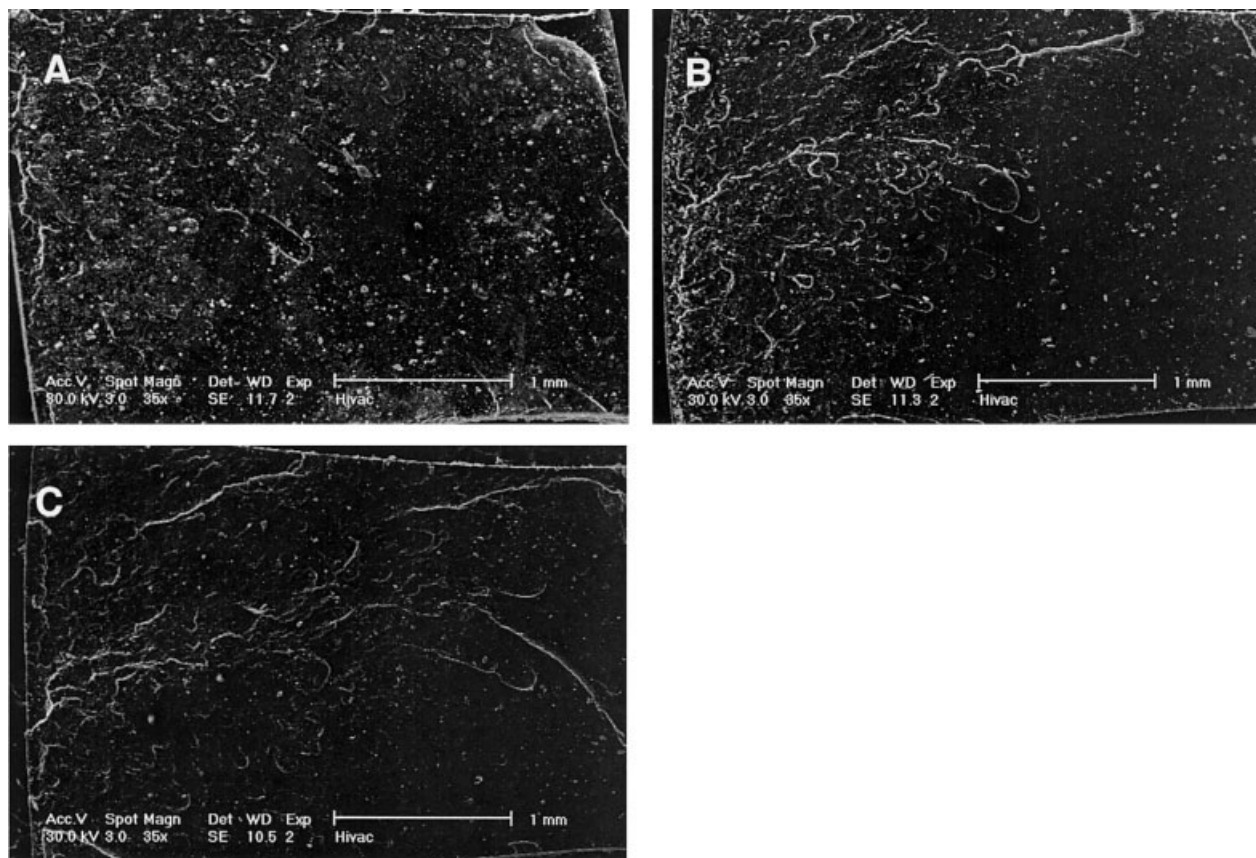

Figure 11 SEM images of the tensile fracture surfaces of NBR: (A) original and (B) after exposure to zinc bromide fluid.

surface or that the nature of the crosslinked bonds have been altered (from polysufidic to disulfidic or monosulfidic); however, the effect that fluorination has on crosslinking requires additional investigation.

The results show that the elasticity modulus of fluorinated NBR did not increase and that the toughness was
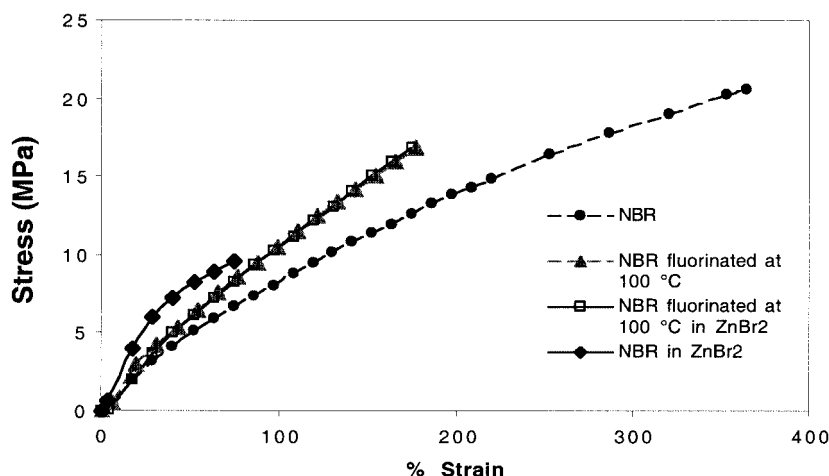
Figure 10 Stress versus percentage strain of unfluorinated and fluorinated NBR samples with $F_2/HF/He$ and treated in zinc bromide fluid at 85–90°C for 72 h.

Figure 12 SEM images of the tensile fracture surfaces of fluorinated NBR at (A) room temperature, (B) 50°C, and (C) 100°C after exposure to zinc bromide fluid.

retained after exposure to zinc bromide brine. This indicates that fluorination of the NBR surfaces effectively blocked zinc bromide diffusion, disabling the catalyzed hydrolysis reaction of the nitrile group and crosslinking reactions resulting from exposure to $ZnBr_2$ fluid.

Fractography

SEM has been used extensively to understand the failure mechanism of rubbers and elastomers.[18,19,21–24] As discussed previously, fluorination can produce cracks on the surface (Figs. 2 and 3) and induce crosslinking in NBR. It is known that surface damage can lead to failure during stress situations.[25] Thus, crack formation and propagation during loading may affect the life of a packer. SEM surface tensile fracture images were taken to determine the kind of failure that each sample underwent.

Figure 11 shows the tensile fracture surfaces of NBR before and after exposure to zinc bromide fluid. The untreated NBR showed a homogeneous fracture as indicated by the rough surface. The discontinuous fracture paths suggest that the stress was homogeneously distributed, causing failure in different spots at the same time during the application of load and that the fracture was proceeded by a tearing ac-

tion.[22,24] In contrast, the exposure of untreated NBR to zinc bromide fluid resulted in a brittle failure, as shown by the continuous fracture path and the absence of fibrils on the surface.

Figure 12 shows the SEM tensile fracture surface images of NBR exposed to zinc bromide fluid after fluorination with F_2/HF (1:1) in helium at room temperature at 50 and 100°C. Although all of the samples showed evidence of brittle fracture, Figure 12(A) shows more brittle fracture than either Figure 12(B) or 12(C). This is in agreement with the EDX results of bromide diffusion, which demonstrate that fluorination at room temperature provided a polymer that was less effective at blocking the diffusion of bromide.

Wettability (contact angle)

The results of the contact angle experiments are presented in Table IV. The higher value for the sample fluorinated at room temperature may have been due to the nonuniform surface that resulted from fluorination at this temperature. The values for samples prepared at higher temperatures were the same and showed that fluorination led to an increase in the hydrophobicity of the surface. Increased hydrophobicity accounted for the resistance to zinc bromide fluid diffusion.

TABLE IV
Contact Angle of ZnBr$_2$ Fluid on NBR Samples

Sample	Contact angle (θ)
Untreated NBR	105.9
Fluorinated NBR	
Room temperature	130.1
50°C	112.3
100°C	115.5

CONCLUSIONS

Fluorination of NBR with either F$_2$/He or F$_2$/HF/He created a highly fluorinated layer on the surface of the polymer. The samples treated with the F$_2$/HF/He reagent had less cracking on the surface than samples fluorinated with fluorine alone. Elemental analysis confirmed that the fluorinated rubber was resistant to diffusion by zinc bromide completion fluid. Compression set experiments and tensile behavior measurements indicated that treatment with ZnBr$_2$ fluid negatively affected the mechanical properties, such as the modulus of elasticity and resistance to permanent deformation by compression, of untreated NBR. Surface-fluorinated samples exhibited considerably less degradation of mechanical properties when they were treated with zinc bromide fluid.

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