

ZnBr₂-Catalyzed Chemical Effects in Poly(acrylonitrile-co-butadiene)

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ABSTRACT: The excellent chemical properties and resistance to oil of poly(acrylonitrile-co-butadiene), or nitrile-butadiene rubber (NBR), has led to the extensive use of these elastomers as O-ring material in the oil extraction industry. The degradation of NBR gaskets is known to occur during the well completion and oil extraction process when they are exposed to bromide fluids such as ZnBr₂-based completion fluid. Samples of NBR, polyacrylonitrile, and polybutadiene were exposed to ZnBr₂-based completion fluid and analyzed by attenuated total reflectance (ATR) and diffuse reflectance

IR. These analyses showed that the ZnBr₂ completion fluid promoted the hydrolysis of the nitrile group to form amides and carboxylic groups. The carbon-carbon double bonds in NBR were unaffected after short exposure to ZnBr₂-based completion fluid but were quickly hydrated in acidic bromide mixtures. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1250–1257, 2003

Key words: elastomers; degradation; FTIR

INTRODUCTION

Chemical resistance to oils, solvents, alkali, and aqueous salt solutions has led to the wide-scale use of nitrile rubbers [acrylonitrile-butadiene copolymers, or poly(acrylonitrile-co-butadiene) (NBR)] in seals, gaskets, O-rings, packers, and hoses. The high nitrile content of the copolymer also increases its resistance to swelling.^{1,2} Serious degradation occurs, however, when the elastomer comes into contact with certain materials that are used in the extraction process. Degradation is usually associated with chain cleavage and a decrease in molecular weight. Exposure to oxygen, ozone, heat, and light is also known to cause polymer degradation.^{3,4} Although the thermal and oxidative degradation of nitrile rubbers has been reviewed extensively in the literature,^{5–12} the chemical effects of many substances on NBR are not well known. Because the mechanical properties of polymers depend on molecular weight and chain entanglement, the chemical degradation of a polymer may lead to mechanical failure.⁴

During oil-well drilling, completion and oil extraction process fluids are in contact with NBR elastomer seals. ZnBr₂ brine is an important fluid, which is used as a completion fluid in the oil-well building and completion processes. Although literature reports in-

dicating that nitrile rubber is very resistant to zinc salts,¹³ studies on the chemical effects of ZnBr₂ have not been reported. NBR packers fail frequently during well completion and oil extraction when exposed to different completion fluids at elevated temperatures.

In this article, we present the results of chemical interactions of ZnBr₂ brine with uncrosslinked NBR, vulcanized carbon-filled NBR elastomer, polybutadiene (PB), and polyacrylonitrile (PAN).

EXPERIMENTAL

Materials

ZnBr₂ brine blend [19.2 pounds per gallon (ppg; 2.3 g/mL)] composed of 50 wt % ZnBr₂, 18 wt % CaBr₂, and 18 wt % NaBr; CaBr₂ [14.2 ppg (1.7 g/mL)]; and CaCl₂ [11.6 ppg (1.4 g/mL)] completion fluids were provided by Baroid Drilling (Houston, TX). Raw NBR was provided by Halliburton Energy Services (Duncan, OK) and was used as received. Solutions of ZnCl₂ and NaBr were prepared from technical-grade (Fisher Scientific, Pittsburgh, PA) reagents. Anhydrous ZnBr₂ and CuCl₂ (Alfa Aesar, Ward Hill, MA), and NiCl₂ (Aldrich, Milwaukee, WI) were used as received. Sulfuric acid and hydrochloric acid were obtained from Fisher Scientific. Hydrobromic acid (62%) was from Alfa Aesar. PAN and PB (36% cis, 55% trans), from Aldrich, were used without any further treatment. NBR O-ring cord (durometer 70 ± 5), 0.635 cm (1/4 in) in diameter (from American Packing and Gasket Company, Houston, TX), was cut into 1/4-in. slices. Water was deionized.

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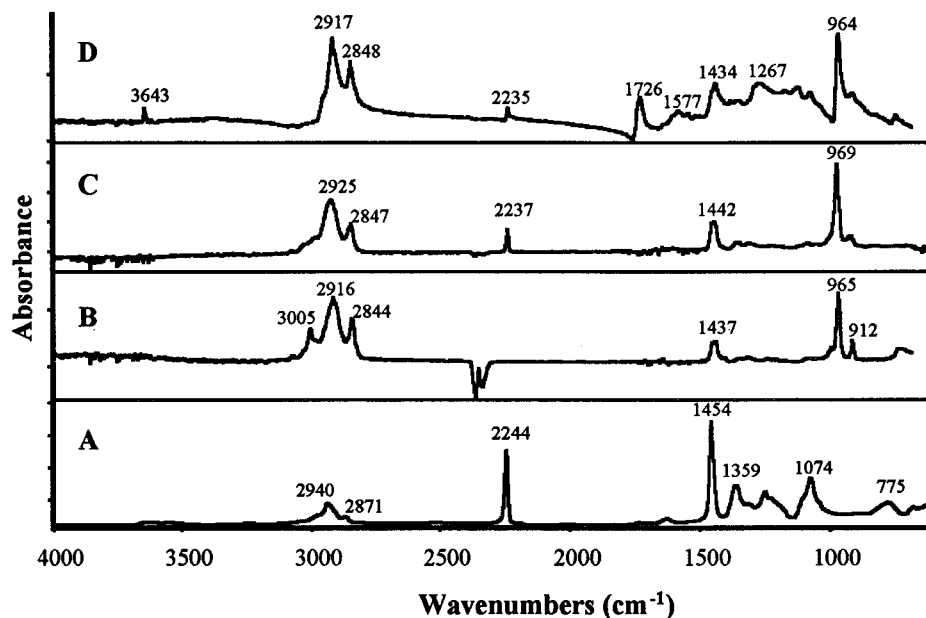


Figure 1 IR spectra of untreated samples: (A) PAN, (B) PB, (C) raw NBR, and (D) NBR O-ring.

Chemical treatments

Experiments were carried out at 85–90°C for 72 h. Pieces of 0.5-cm NBR and PB, or samples of about 0.1 g of PAN, were placed into a 100-mL beaker with about 30 mL of completion fluid or salt solution. The beaker was covered with parafilm and heated over a hot plate while it was stirred with a magnetic bar. Experiments under argon were carried out in a closed stainless steel chamber wrapped with heating tape. We degassed the ZnBr₂ fluid by bubbling argon through the solution for several hours. Reactions of PAN in acid solutions were carried out in a round-bottomed flask equipped with a condenser. The mixtures were refluxed for 72 h at 90°C. After exposure to the completion fluid, the samples were washed several times with water. NBR and PB samples were dried at room temperature. PAN samples were dried in a vacuum oven at 80°C.

Measurements

IR spectra were collected with a Nicolet (Madison, WI) Magna-FTIR 760 spectrometer with a deuterated triglycine sulfate pyroelectric (DTGS) detector and a KBr beam splitter. The IR spectra of NBR and PB were collected with a Pike Technologies (Madison, WI) Miracle ATR accessory equipped with a single-bounce Ge crystal. The IR spectra of PAN were collected with a diffuse reflectance unit from Spectra-Tech (Nicolet, Madison, WI) International. The spectra of PAN treated with acid under an argon atmosphere were collected by ATR. For acid-treated PAN, all spectra were obtained with 64 scans and a resolution of 8 cm⁻¹. The diffusion of ions into the rubber samples

was measured in a transverse slice taken from the center of the treated sample. Ion diffusion was measured from the surface to the center of the cut by energy-dispersive X-ray analysis (EDAX) with a Philips Electroscan XL 30 Environmental Scanning Electron Microscope-Field Emission Gun (FEI Company, Hillsboro, OR) equipped with an EDAX unit.

RESULTS AND DISCUSSION

We carried out preliminary experiments by treating raw NBR with ZnBr₂ completion fluid under a variety of conditions. The same experiments were also carried out with PAN and PB to study the chemical effects that ZnBr₂ had on each functional group. The IR spectra of the three polymers, along with the IR spectrum of an NBR O-ring, are displayed in Figure 1.

Chemical effects of ZnBr₂ on NBR

NBR samples changed from a clear yellow color to an opaque dark brown after exposure to ZnBr₂ solution. Samples were also harder and less flexible than the untreated polymer; however, the samples did not exhibit a weight change during exposure to the ZnBr₂ solution.

The IR spectra of nitrile rubber recorded before [Fig. 2(A)] and after various treatments at 85–90°C for 72 h are illustrated in Figure 2. Small changes were observed when the NBR was heated in H₂O [Fig. 2(B)]. In contrast, when the elastomer was treated with ZnBr₂ completion fluid [Fig. 2(C,D)], extensive spectral changes were observed. In the presence of air [Fig.

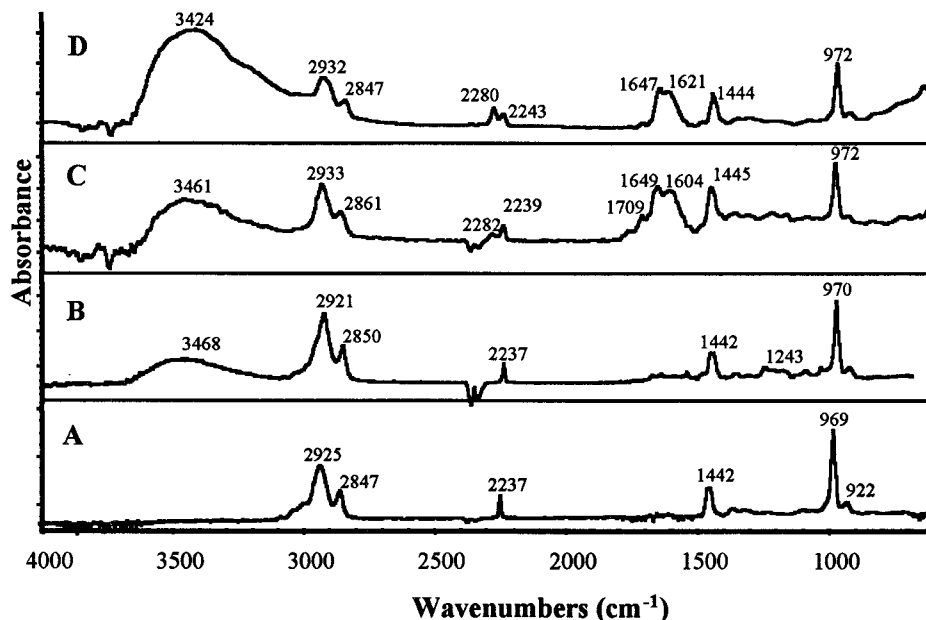


Figure 2 IR spectra of uncrosslinked NBR treated at 85–90°C for 72 h: (A) untreated, (B) treated with H₂O, (C) treated with ZnBr₂ completion fluid, and (D) treated with deoxygenated ZnBr₂ fluid.

2(C)], the C≡N absorption at 2239 cm⁻¹ diminished in intensity, and new features appeared in the 1630-cm⁻¹ region. The broad peak at 3461 cm⁻¹ was attributed to adsorbed water. When the experiment was carried out under argon [Fig. 2(D)], two new absorptions at 2243 and 2280 cm⁻¹ were observed. These new features were assigned to a complex of zinc with the nitrile group.¹⁴

The appearance of new absorptions at 1647 cm⁻¹ (C—O stretch from R—CO—NH₂) and 1621 cm⁻¹ (NH₂ scissors, R—CO—NH₂), along with the absence of the nitrile peak, indicated that the C≡N group was hydrolyzed to yield an amide. Under these conditions, no further reaction occurred. These results indicated that a complex between a zinc ion and a nitrile group was the initial step in the catalyzed hydrolysis of the nitrile group to yield an amide.

In nondegassed brine, further oxidation to carboxylic acids was observed, as shown by the appearance of a weak peak at 1709 cm⁻¹ [Fig. 2(C)], which was assigned to the carbonyl stretch of a carboxylic acid.¹⁵ Because the corresponding stretching signal of the C—O bond at 1320–1210 cm⁻¹ was also weak, we concluded that only a partial conversion to the carboxylic acid occurred.

Other workers have reported that the thermal oxidation of nitrile elastomers leads to carbonyl compounds at higher temperatures.^{4–6,16,17} Lee et al.¹² reported that the presence of metallic impurities such as iron, copper, nickel, and manganese accelerate oxidation by a redox mechanism. In their study, however, zinc was shown to exhibit weak catalytic activity. The enhanced activity of zinc found in this work was due to the low pH of the ZnBr₂ completion fluid.

Treatment with laboratory-prepared ZnCl₂ and ZnBr₂ solutions

When samples of unvulcanized raw NBR were heated in either 10 wt % ZnCl₂ [Fig. 3(A)] or 10 wt % ZnBr₂ [Fig. 3(B)] in the presence of air, hydrolysis of the nitrile group was observed, as shown by the appearance of carbonyl peaks in the 1600–1650-cm⁻¹ region. More extensive hydrolysis was observed when the copolymer was treated with a 50 wt % ZnBr₂ solution [Fig. 3(C)], as indicated by the higher intensity of the 1712- and 1764-cm⁻¹ peaks. It was clear that a higher concentration of Zn²⁺ produced a more acidic solution, leading to a more extensive hydrolysis of NBR and thus providing further confirmation of the catalytic effect of Zn²⁺. The IR spectrum of the products resulting from treating unvulcanized raw NBR with ZnBr₂ completion fluid is presented in Figure 3(D) for comparison.

Analogous behavior was found when vulcanized carbon-filled NBR O-rings were exposed to ZnBr₂ fluid. Hydrolysis of the nitrile group is thought to affect the physical properties of elastomers because the resulting amides and carboxyl groups can act as initiation points for thermal degradation.⁹

Treatment of PAN and PB with ZnBr₂ completion fluid

ZnBr₂-catalyzed reaction of nitrile and double-bond groups

The exposure of NBR, PAN, and PB to ZnBr₂ solution was carried out to determine the catalytic effect that ZnBr₂ had on the respective functional groups. A so-

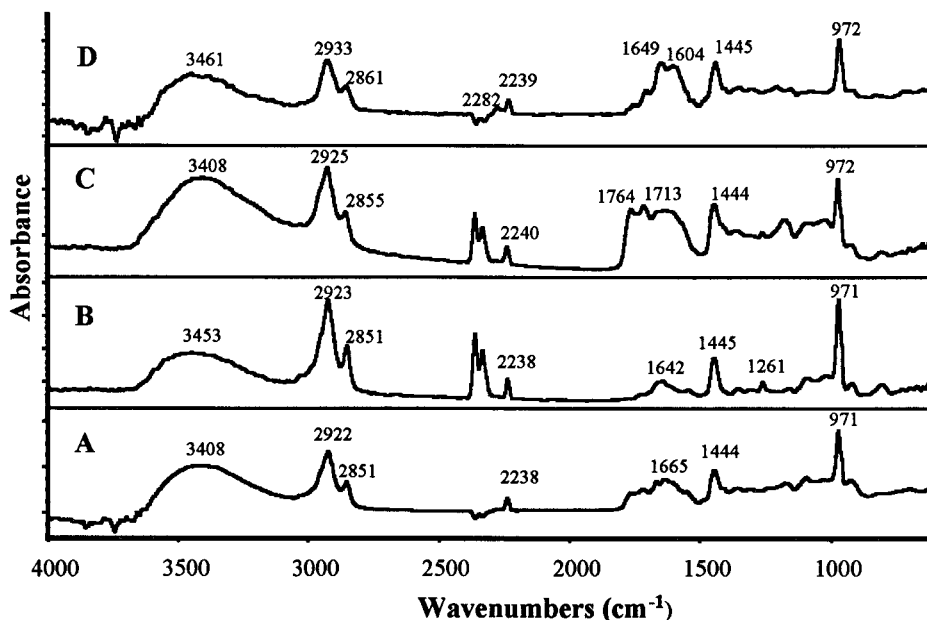


Figure 3 IR spectra of uncrosslinked NBR treated with Zn²⁺ solutions at 85–90°C for 72 h: (A) treated with 10 wt % ZnCl₂, (B) treated with laboratory-prepared 10 wt % ZnBr₂, (C) treated with laboratory-prepared 50 wt % ZnBr₂, and (D) treated with ZnBr₂ completion fluid.

lution of PAN was formed when the polymer was heated in ZnBr₂ brine for a few hours. The polymer remained in solution even after the mixture was cooled to room temperature but precipitated when water was added. The color of the recovered PAN changed from white to slightly yellow, and the consistency changed from a powder to a solid that agglomerated, forming irregular particles.

Figure 4 shows the diffuse reflectance IR of PAN treated with various Zn²⁺ solutions. The spectrum of the untreated polymer is presented in Figure 2(A). Exposure of the polymer to the ZnBr₂ brine led to the appearance of new absorptions at 1693 and 1619 cm⁻¹, indicating that hydrolysis to amides occurred [Fig. 2(D)]. The C≡N peak decreased as the new features appear. The zinc fluid had a similar effect on PAN.

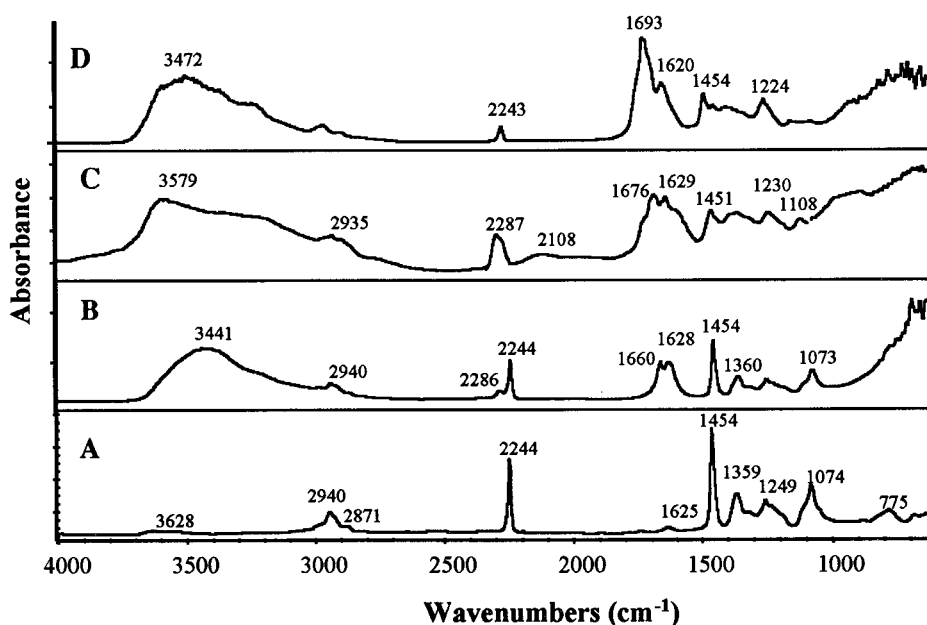


Figure 4 Diffuse reflectance IR of PAN: (A) untreated, (B) treated with 60 wt % ZnCl₂ solution, (C) treated with ZnBr₂ fluid under an argon atmosphere, and (D) treated with ZnBr₂ completion fluid.

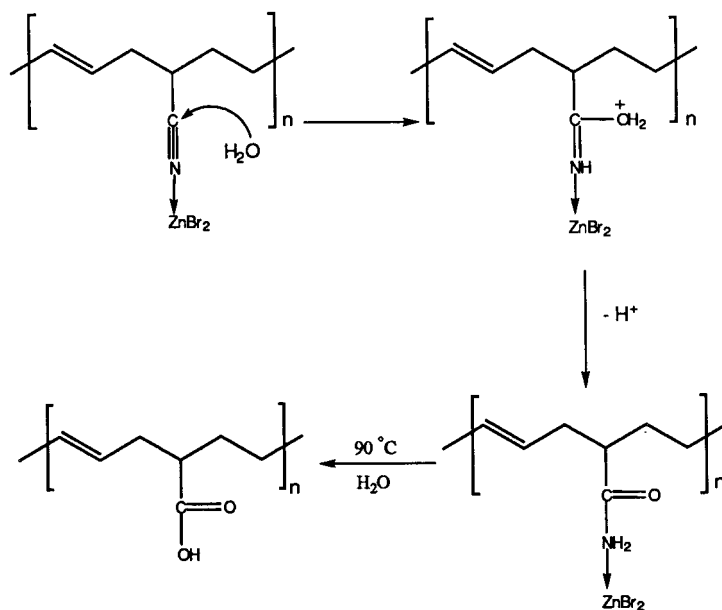


Figure 5 Hydrolysis of the nitrile group catalyzed by ZnBr_2 .

A shoulder near the nitrile group frequency is shown in Figure 4(B); and it was much more evident when PAN was treated with the completion fluid under an argon atmosphere [Fig. 4(C)]. This suggested the formation of a complex between zinc and the nitrile group, as in the case for NBR. This is also in agreement with the reports of Bajaj et al.¹⁸ and Stelzer et al.,¹⁹ who reported the formation of metal complexes of PAN.

The formation of this complex was also much more evident when oxygen was excluded from the reaction.

The loss of intensity of the 2940, 1074, and 1454 cm^{-1} features evident in Figure 4(B,D) suggested that the CH and CH_2 groups were also undergoing redox-type chemistry. The broad peak in the 3500- cm^{-1} region of Figure 4 may have been due to hydroxyl groups formed in hydrolysis; however, residual adsorbed water was also likely to be present.

IR spectra of PB before and after treatment with the ZnBr_2 fluid and 60 wt % ZnCl_2 solution indicated that the PB experienced no significant chemical changes.

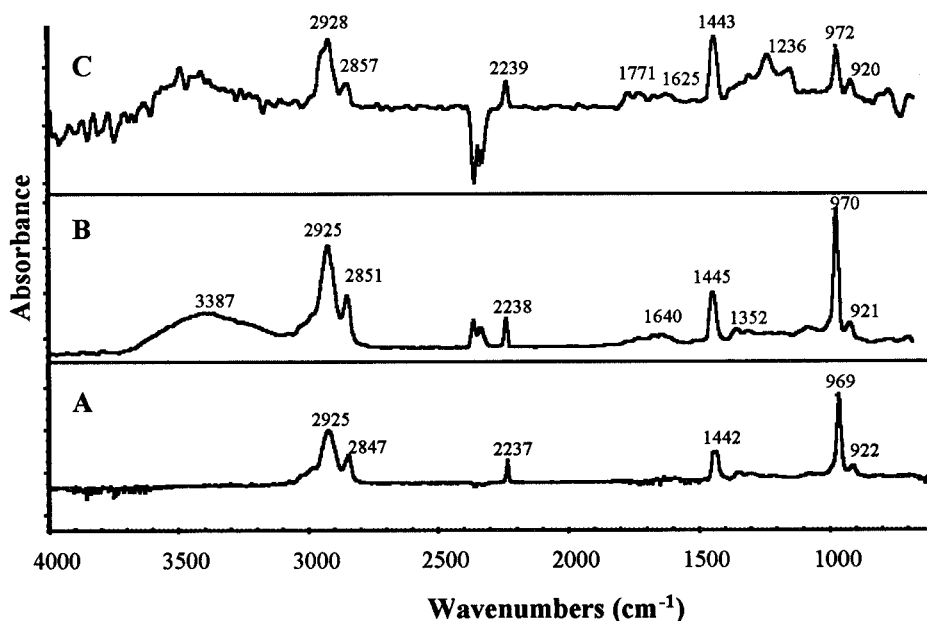


Figure 6 IR spectra of NBR after treatment with 30% acid solutions at 85–90°C for 72 h: (A) untreated, (B) treated with HCl, and (C) treated with HBr.

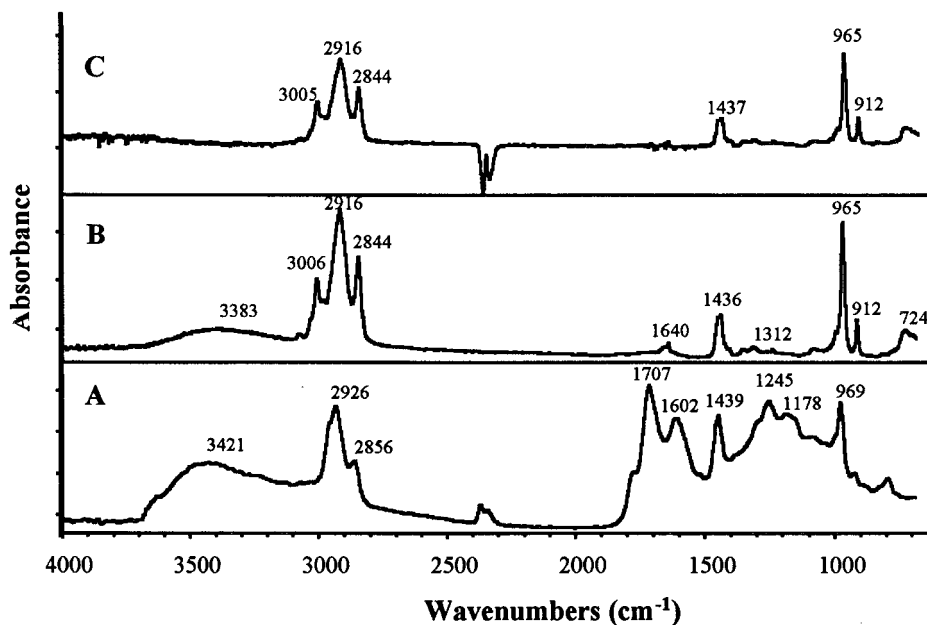


Figure 7 IR spectra of PB after treatment with 30% acid solutions at 85–90°C for 72 h: (A) treated with HBr, (B) treated with HCl, and (C) untreated.

These results confirmed that ZnBr₂ solutions interacted with the acrylonitrile part of the NBR. A suggested mechanism is shown in Figure 5, where the initial complexation of the nitrile followed by a series of hydrolysis reactions to produce a carboxylic amide and ultimately carboxylic acids is presented.²⁰

Acid hydrolysis

NBR, PAN, and PB were heated at 85–90°C in acid solutions to compare acid hydrolysis with hydrolysis

induced by the ZnBr₂ fluid. The IR spectrum of untreated NBR is presented in Figure 6(A). IR spectra of NBR treated with 30% HCl and 30% HBr solutions are presented in Figures 6(B) and 6(C), respectively. A major change occurred when NBR was treated with HBr. The absorption at 969 cm⁻¹, which corresponded to an H wagging mode for the C=CH group decreased significantly, and new peaks appeared in the 1230–1200-cm⁻¹ region, suggesting, as expected, that an electrophilic addition to the carbon–carbon double bond occurred.

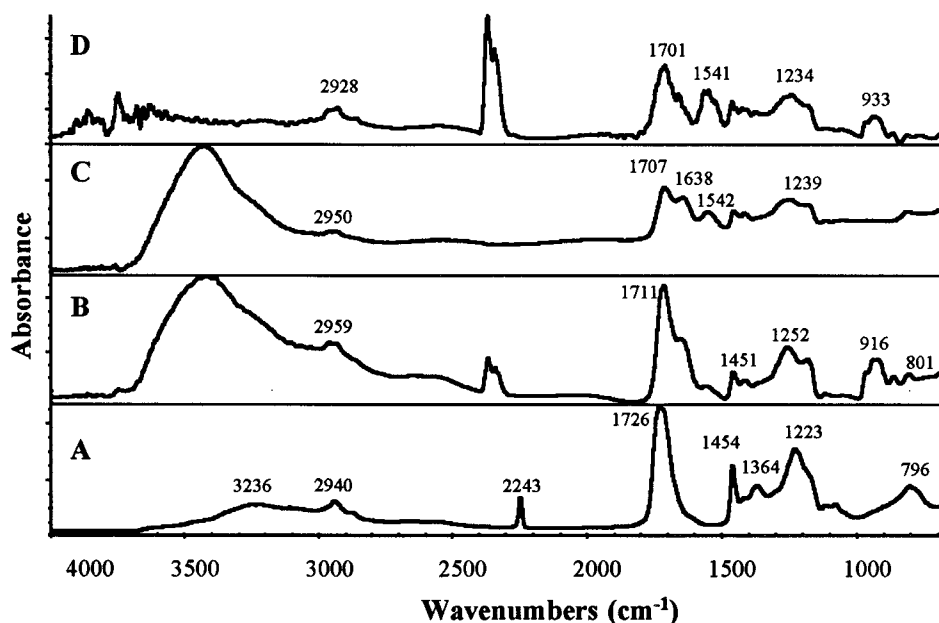


Figure 8 IR spectra of PAN after treatment with 30% acid solutions at 85–90°C for 72 h: (A) HCl under air, (B) HCl under argon, (C) HBr under air, and (D) HBr under argon.

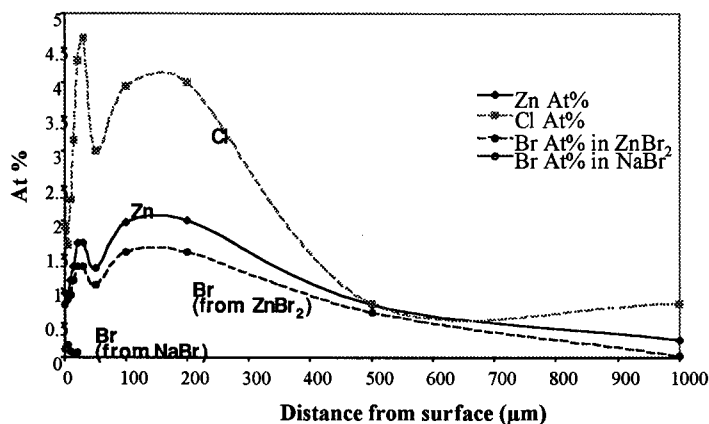


Figure 9 Zn^{2+} , Cl^- , and Br^- diffusion into NBR O-ring treated with NaBr and $ZnCl_2/ZnBr_2$ solutions at 85–90°C.

More pronounced effects were observed when PB was treated with HBr [Fig. 7(A)]. Strong new peaks were observed at 1707 and 1602 cm^{-1} , indicating that the oxidation of the carbon–carbon double bond to form carbonyl compounds occurred. The IR spectrum after treatment with HCl is illustrated in Figure 7(B), demonstrating a much lower degree of reaction. The IR spectra of PAN treated with 30% acid solutions at 85°C for 72 h are presented on Figure 8. Both HCl and HBr reacted, but treatment with HBr resulted in the complete disappearance of the nitrile peak at 2243 cm^{-1} . These observations indicated the higher reactivity of the $C\equiv N$ group compared to the carbon–carbon double bond.

Ion diffusion into NBR

The results of a study on the diffusion of $ZnBr_2$, $ZnCl_2$, and NaBr into NBR are presented in Figure 9. These observations indicate that a complex of the zinc ion with the nitrile group was an important driving force for diffusion of zinc halide salts because sodium bromide did not diffuse into the NBR. The enhanced catalytic behavior found for $ZnBr_2$ fluids was attributed to their low pH (≈ 1).

CONCLUSIONS

NBR samples lost flexibility after exposure to $ZnBr_2$ solution. Zn^{2+} solutions were shown to promote the hydrolysis of nitrile groups through formation of an initial complex between the $C\equiv N$ group and Zn^{2+} . This complex was sensitive to the presence of oxygen, which suggests that it played a role in catalyzing the reaction of oxygen with the nitrile group. Hydrolysis of this complex led to the formation of amides and carboxyl acids. Hydrolysis was not observed when a deoxygenated solution of $ZnBr_2$ in deionized water was used.

Attack of the nitrile group by Zn^{2+} was confirmed by the effects that the fluid had on PAN and PB and from the results of treatment with 10 and 60 wt % $ZnCl_2$ solution. $ZnBr_2$ had the same effect on NBR O-rings. The effect that $ZnBr_2$ completion solutions had on the double bond of the butadiene group appeared to be negligible; however, the IR spectra of NBR and PB treated with HBr solution provided support for the hydration of the $CH=CH$ group.

NBR was not affected substantially by other metal bromide and chloride solutions. These results suggest the stronger reactivity of $ZnBr_2$ with nitrile rubber may have been due to the higher acidity and to its diffusion through the polymer matrix via complexation with the nitrile group.

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