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Some Properties of Nitroso Rubbers in Fluorine at Ambient and Cryogenic Temperatures

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SUMMARY

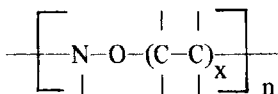
The effects of fluorine exposure between 1 and 2 atm pressure at ambient temperature and in liquid fluorine at cryogenic temperature on some properties of nitroso rubbers (the $\text{CF}_3\text{NO}/\text{CF}_2=\text{CF}_2$ copolymer and the $\text{CF}_3\text{NO}/\text{CF}_2=\text{CF}_2/\text{ON}(\text{CF}_2)_3\text{COOH}$ terpolymer systems and the compounded terpolymers) are described.

The apparatus, testing methods, and results on permeation of fluorine through a compounded CNR terpolymer and the ABMA open-cup drop-weight impact sensitivities of various compounded and unvulcanized CNR terpolymer were reported.

Based on the infrared analysis, it was concluded that the one-to-one copolymer representing the nitroso rubber polymer backbone is more stable to fluorine than the CNR terpolymer due to the carboxyl pendant groups.

INTRODUCTION

Nitroso rubbers represent the class of polymeric structures having the repeating nitrogen-oxygen-carbon linkage of the following structure:



Many structures containing this repeating unit have been reported, but only two systems have been studied intensively. These are the one-to-one copolymer of trifluoronitrosomethane and tetrafluoroethylene, and the carboxyl-nitroso rubber terpolymer [1]. Griffis and Henry have reported the chemical and physical properties of the $\text{CF}_3\text{NO}/\text{CF}_2=\text{CF}_2$ copolymer and $\text{CF}_3\text{NO}/\text{CF}_2=\text{CF}_2/\text{ON}(\text{CF}_2)_3\text{COOH}$ terpolymer systems [2, 3].

This paper describes the effects of the exposure to gaseous fluorine at 1 atm and ambient temperature and to liquid fluorine at cryogenic temperature on some properties of the nitroso rubber co- and terpolymers and the compounded terpolymers. Table 1 is a list of the materials used in this study.

RATE OF PERMEATION BY GASEOUS FLUORINE

Figure 1 shows the permeation cell. A specimen of CNR terpolymer A, 207 cm in diam by 0.2 cm thick, was placed between a 2.22-cm-diam poppet and a seat seal with a 1.58-cm-diam 316 stainless-steel by 0.159-cm-thick sintered $10\text{-}\mu$ filter disk insert. The specimen between the poppet and

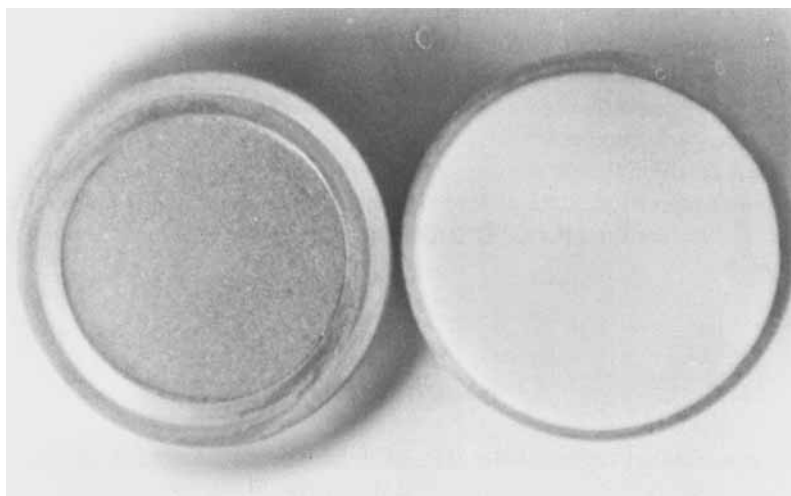


Fig. 1. Permeation test cell. (a) Metal seat with chevron seal and 5/8-in.-diam filter support. (b) Test sample placed on mating poppet seal.

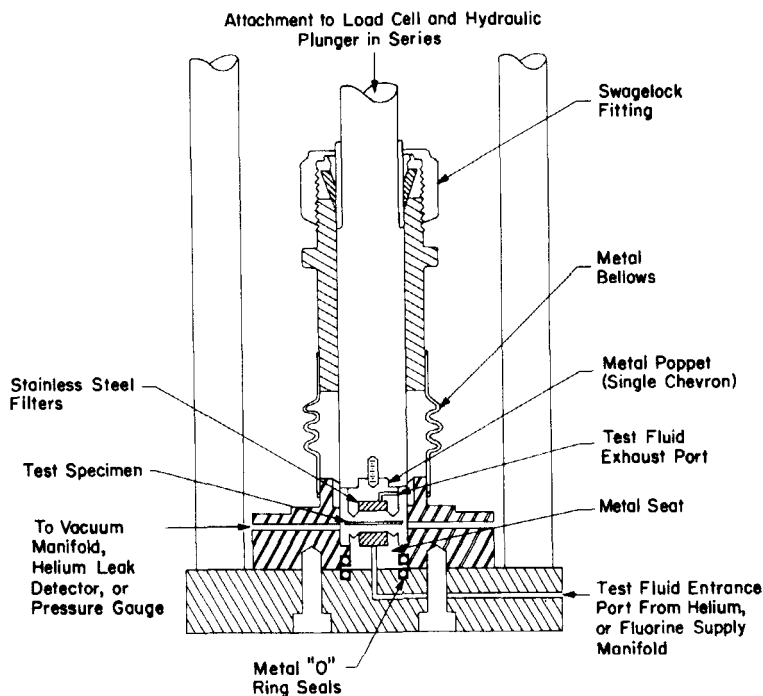


Fig. 2. Permeation test fixture.

the seat formed a seal as it was compressed under a 30-lb load and helium leak-checked at 1 atm. The poppet and seat have a single mating chevron seal. The chevron compresses 0.00508 cm into the terpolymer specimen.

The poppet-and-seat test chamber (Fig. 2) consists of a 1-in-diam plunger connected to a Swagelok feed-through which is welded to a metal bellows welded to the top flange, which contains an exit port. Copper-coated stainless-steel "O" rings seal the poppet seat to the top and bottom flanges. This test chamber is attached to a stainless-steel vacuum manifold for evacuation, introduction of fluorine, helium pressurization, and venting.

The test chamber was closed after it had been evacuated to less than 10^{-5} Torr of helium pressure by a Veeco helium detector vacuum pump unit. The seat side chamber was pressurized to 1 atm with helium and the helium leak rate was measured by the rise in pressure on the vacuum side with a Seegers gauge at 15-min intervals. If no rise in pressure was observed on the Seegers gauge, the vacuum chamber side was opened to the Veeco

Table 1. Formulation and Cure Cycle of Carboxyl-Nitroso Rubber Terpolymer Samples

A. Filled with calcium fluoride	
Formulation	Material, parts by weight CNR terpolymer gum, 100.00 CaF ₂ reagent-grade powder, 70.00 Chromium trifluoroacetate, 5.00
Cure cycle	Press cure, 60 min @ 200°F Oven postcure of total 9 hr by stepwise manner, 1.5 hr @ 225°F 1.5 hr @ 225°F 1.5 hr @ 250°F 1.5 hr @ 275°F 1.5 hr @ 300°F 1.5 hr @ 325°F 1.5 hr @ 350°F

B. Filled with silstone 115

Material, parts by weight
 CNR terpolymer gum, 100.00
 Chromium trifluoroacetate, 50.00
 Silstone 115, 25.00

Cure cycle
 Press cure, 60 min @ 200°F
 Oven postcure of
 total 9 hr by
 stepwise manner

3 hr @ 250°F
 3 hr @ 300°F
 3 hr @ 350°F

C. Unfilled

Material, parts by weight
 CNR terpolymer gum, 100.00
 Chromium trifluoroacetate, 5.00

Cure cycle
 Press cure, 60 min @ 200°F
 Oven postcure, 16 hr @ 250°F

helium leak detector. The Vecco units were recorded and converted to standard cc/sec by calibrating the Vecco units to a standard helium leak rate reference source. (Vecco sensitivity calibrator Type SC-4). For these test runs,

$$1 \text{ Vecco unit} = 3.23 \times 10^{-8} \text{ std cc/sec of helium}$$

The helium permeation rate was determined to be 4.0×10^{-6} atm cc/sec for 1 atm helium upstream pressure at 35°C . After helium had been replaced by fluorine at the same pressure and temperature, the fluorine upstream pressure dropped 0.22 atm in 17 hr. There was no downstream pressure change to an accuracy of 0.13 Torr, indicating that GF_2 was not passing through the terpolymer disk. Hence the upstream pressure drop was due to reaction of fluorine with the polymer at a reaction rate calculated to be 5×10^{-6} g of F_2 per cm^2/sec initially, and 0.5×10^{-6} g of F_2 per cm^2/sec after 17 hr. Figure 3 shows the slimy surface of the upstream fluorine side of a CNR nitro rubber specimen after fluorine exposure. The fluorine was evacuated from the upstream side, and the system was repressurized to the same pressure of 1 atm helium. The helium permeation rate through the sample was remeasured. It had increased to 4.4×10^{-6} atm cc/sec for a period of 2 hr.

IMPACT SENSITIVITY IN LIQUID FLUORINE

The ABMA open-cup drop-weight impact sensitivities in liquid fluorine at -196°C of the three cured samples, A, B, and C, and of unvulcanized gum stock were tested in the impact tester shown in Fig. 4 [4].

The three cured samples were in the form of $4.5 \times 2 \times 0.07$ -in.-thick sheets. See Table 1 for details of the curing mix and postcure cycle. Impact test coupons of specimens A, B, and C were cut from the sheets using a cork borer. The disks were $5/8$ in. in diam. The edges of the disks were deburred using an Xacto knife. The disks were cleaned by vapor degreasing for 1 hr in Genesolv D. The cleansed specimens were then vacuum-baked for 24 hr at 105°C , 1 Torr pressure.

The specimens were then placed in standard ABMA sample cups made of 1100 aluminum. Disks of 347 stainless steel were placed between the samples and the cup bottom. Stainless-steel (17-4 PH) striker pins were used for the tests. Standard LF_2 -ABMA impact tests were conducted on these specimens and on blanks with only the stainless-steel disks present.

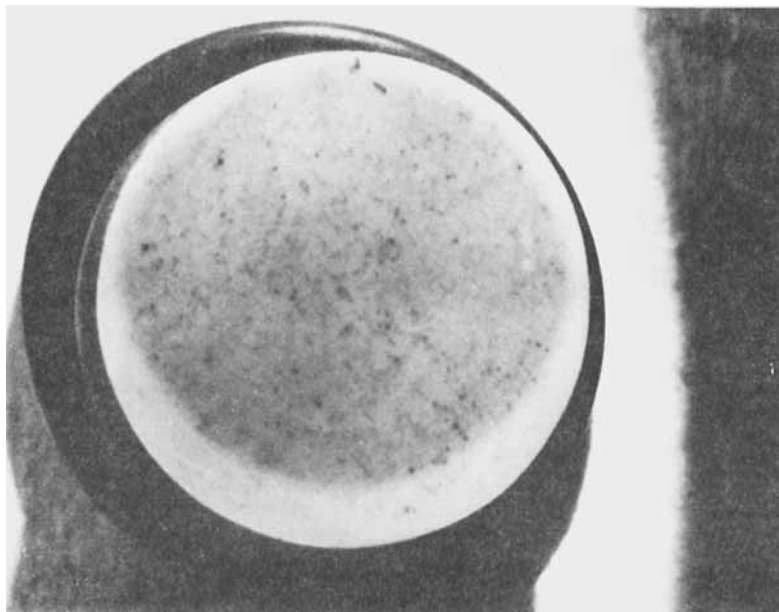


Fig. 3. Upstream fluorine side of nitroso rubber gasket, 13/16 in. in diam, illustrating surface slime product.

Test conditions included working in a moisture-free GN_2 atmosphere to avoid false positives due to frost; prechilling the sample, cup, and striker pin to -196°C ; and use of 4 ml of LF_2 at -196°C in the test. The plummet used weighs 20 lb and drops through a distance of 43.3 in. to deliver 72 ft lb of energy at impact.

To prepare specimens for the impact tests of unvulcanized CNR terpolymer, small pea-sized portions of the gum were cut from the sticky and transparent mass of material. LF_2 -clean, stainless-steel spatulas with the blades warmed to about 60°C were used to cut the gum. The small portions were placed on LF_2 -clean, 0.5-in.-diam, 0.025-in.-thick disks of 304 stainless steel, and the disks were placed in clean 1100 aluminum cups.

The cups were placed in a vacuum oven and heated at 105°C , 1 Torr, overnight. Under these conditions, the gum softened and flowed sufficiently to form a coating about 0.1 in. thick on the disks. A small amount of gum flowed off the disk and onto the base of the cup in a few instances.

The specimens in the cups were removed from the oven and allowed

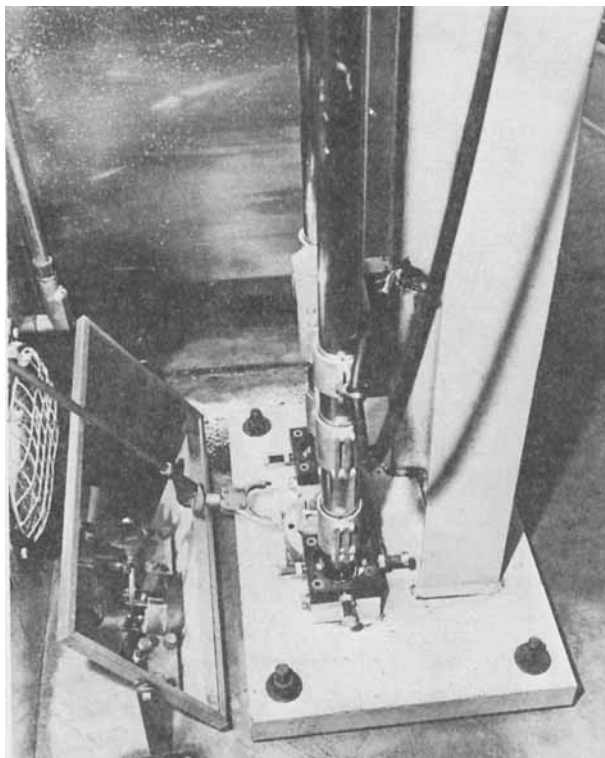


Fig. 4. Open-cups ABMA-type impact tester designed by Douglas Aircraft, Astropower Laboratory.

to cool to room temperature in a clean area. The cooled specimens in the cups were placed in covered stainless-steel trays, together with the striker pins and guide bars for impact testing. These were placed in the tester enclosure and the enclosure was swept dry with GN_2 before initiating cool-down and testing (Fig. 4).

Tests were carried out in the same manner as for the cured specimens at 72-ft lb input with precooled (-196°C) anvil, sample, cup, and striker pin and using 4 ml of liquid oxidizer. The observations of the unvulcanized CNR terpolymer and the cured samples A, B, and C are summarized in Table 2.

The results indicate that the cured samples B and C, and the uncured gum stock, were very impact sensitive in liquid fluorine at 72-ft lb input

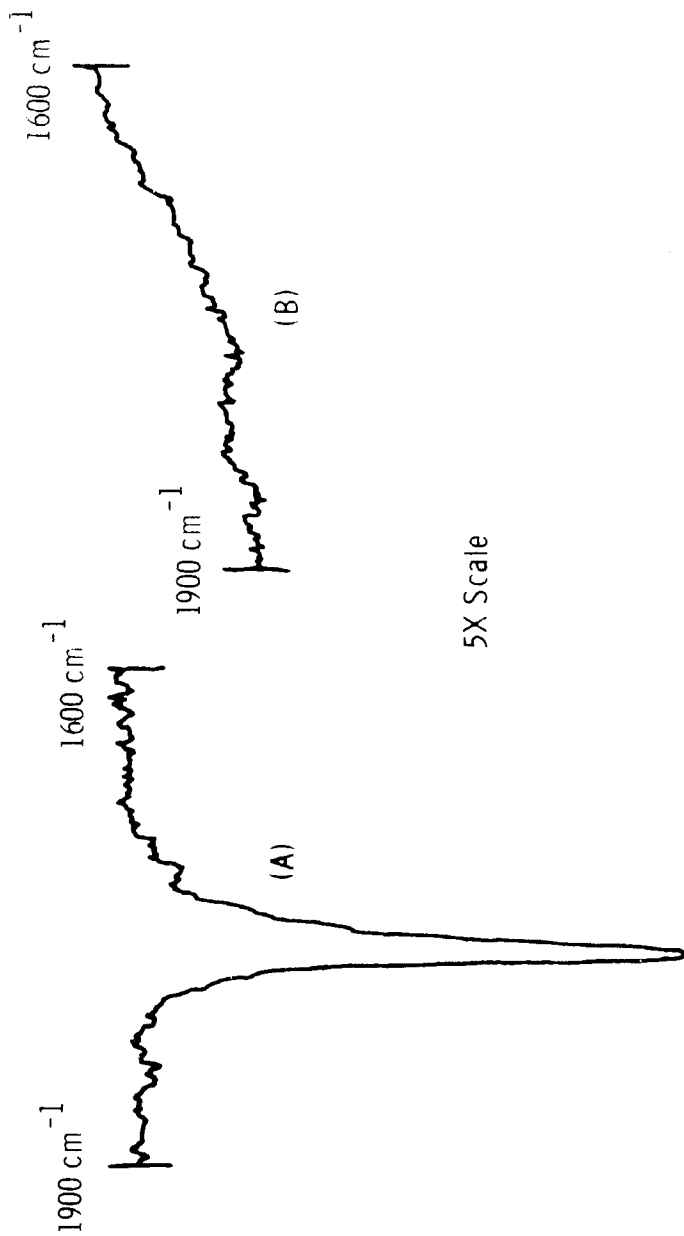


Fig. 5. Infrared spectrum of nitroso rubber terpolymer (CNR) before (A) and after (B) exposure to fluorine for 88 hr.

Table 2. ABMA Open-Cup Drop-Weight Impact Sensitivities of Unvulcanized and Compounded CNR Terpolymers in Liquid Fluorine

Samples ^a	No. of drops ^b	No. of reactions
Specimen A	16	4 (2 of these on rebound)
Specimen B	2	2
Specimen C	5	5
Unvulcanized		
CNR-terpolymer	9	5
Stainless-steel 304 blank	4	0

^aSee Table 1 for details of curing mix and fast cure cycle of specimens A, B, and C.

^bEquivalent to 72 ft lb of energy at impact in LF_2 at -196°C .

and -196°C , while the sensitivity under identical conditions was greatly reduced for the cured sample A.

INFRARED ABSORPTION AFTER FLUORINE EXPOSURE

The infrared spectrum of unvulcanized CNR terpolymer before and after exposure to fluorine at 1 atm and ambient temperature for 88 hr indicates the disappearance of the



group, as shown in Fig. 5 (through the courtesy of D. D. Lawson, Jet Propulsion Laboratory, Pasadena, California); no obvious changes occurred in the infrared spectra of the one-to-one copolymer after either exposure to gas fluorine at 1 atm and ambient temperature for 48 hr or to liquid fluorine for 1 hr at -196°C .

CONCLUSIONS

Based on the infrared analysis, it was concluded that the one-to-one

copolymer representing the nitroso rubber polymer backbone is more stable to fluorine than the CNR terpolymer due to the carboxyl pendent groups.

The results from permeation rate of fluorine through a specimen of CNR terpolymer A indicate no permeation as a result of fluorine reaction with the CNR terpolymer.

The ABMA open-cup drop-weight impact sensitivities of various compounded terpolymers and the unvulcanized CNR terpolymers indicate that nitroso rubber for fluorine service cannot be based on CNR terpolymer, although chemical reactivity can be reduced by CaF_2 as the filler.

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Discussion of Paper by S. M. Toy et al.

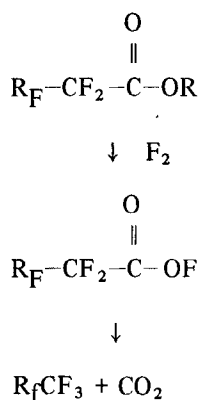
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R. F. Landel: Were the permeation tests made on the unfilled material or on the filled rubber? What is the effect of filler on permeation?

S. M. Toy: The tests were run on the CaF_2 -filled sample A; the others were too reactive. We have no data from specimens with other fillers for comparison.

R. Kratzer: In the tests with gaseous fluorine you found a pressure drop of 0.22 atm. Was this occurrence paired by a corresponding increase in the weight of the test sample?

- S. M. Toy: No samples were weighted in these studies. Cross sections of the specimens after GF_2 exposure showed reaction zones moving progressively through the thickness of the specimens.
- A. A. Volpe: What reactions are taking place which cause the disappearance of the $\text{C}=\text{O}$ absorption band upon exposure of the nitroso rubber to fluorine?
- S. M. Toy: Probably



Also, please refer to the work of George Cady at the University of Washington.