

# Effects of nitrogen tetroxide exposure on DuPont Kalrez 1045

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Chemical and physical tests were conducted to determine the effects of long-term exposure to nitrogen tetroxide on Kalrez 1045, a perfluorinated copolymer. The weight and Shore A hardness of samples from two different lots were determined after exposure at two different pressures, 7320 kPa (72.5 atm) and 101 kPa (1 atm), for times ranging between 1 and 80 days and for periods up to 21 days following their exposure. The largest changes occurred in the first 8 to 10 days of exposure. The weight increased between 15 and 30% and the Shore A hardness declined from 83 to 60. Both weight and hardness partially recovered to their original values after removal from liquid  $N_2O_4$ . However, samples exposed for more than 1 day never fully recovered. The chemical stability of the Kalrez as a function of time exposed to  $N_2O_4$  was monitored with solid probe-mass spectrometry. The results indicated that there was no main chain scission for the first 30 days of exposure. Loss of the pendant groups from the main chain was observed within 16 h. Loss of the pendant group from the crosslink site monomer, and loss of the crosslink itself occurred after 150 h of exposure to  $N_2O_4$ . The overall results indicated that Kalrez 1045 exhibited exceptional stability to  $N_2O_4$ , and seals manufactured from this material should be superior to the butyl rubber currently employed in oxidizer vessels of launch systems.

**(Keywords: chemical compatibility; Kalrez; nitrogen tetroxide; elastomers)**

## INTRODUCTION

The Parker Seals Company has for many years manufactured O-rings from a type of butyl rubber designated B591-80 for use with oxidizing materials. When subjected to  $N_2O_4$ , the material is known to irreversibly swell and soften, indicating that chemical changes are occurring. Despite these well known effects, butyl rubber type B591-80 has continued in use in the solid rocket boosters of Titan IV launch vehicles for over two decades. The wet life — the total time from initial elastomer exposure to the end of life — is qualified for a maximum of 75 days.

Despite having to pass acceptance tests and conform to manufacturing and installation controls, seals of B591-80 have been known to fail prior to launch, resulting in flight delays and rebuilding expense. As a result of these failures and the wet-life restrictions, alternative materials were investigated for use in these seals. A prime candidate for this purpose was Kalrez 1045, manufactured by the DuPont Chemical Company. It is a copolymer of tetrafluoroethylene and perfluoromethyl vinyl ether containing titanium dioxide filler and is expected to be much more inert to oxidizer exposures than butyl rubber.

Previous investigations have evaluated the effectiveness of Kalrez in high-vacuum seals. These studies determined that the material shows very low outgassing rates<sup>1</sup> and is thermally stable<sup>2</sup> up to 175°C. A survey of elastomer materials for vacuum seals<sup>3</sup> lists Kalrez as having excellent resistance to ozone, oils, esters, ketones, acids and alkalis, but only fair resistance to freons. An

unpublished, anonymous manuscript describing tests conducted by the Aerojet Corporation<sup>4</sup> on this material reports the effect of  $N_2O_4$  exposure for periods up to 29 days at a temperature of 37.8°C (100°F). The properties of hardness, tensile strength, modulus, elongation and volume swell were measured after various exposure times. Exceptional changes included a volume swell of 32%, a decrease in the modulus of 65%, and a loss of tensile strength of 80%. The other properties were retained fairly well. In addition, all of the properties recovered nearly to their original values within a few days after the samples were removed from the oxidizer and subjected to air drying. Chemical degradation was suspected but not studied.

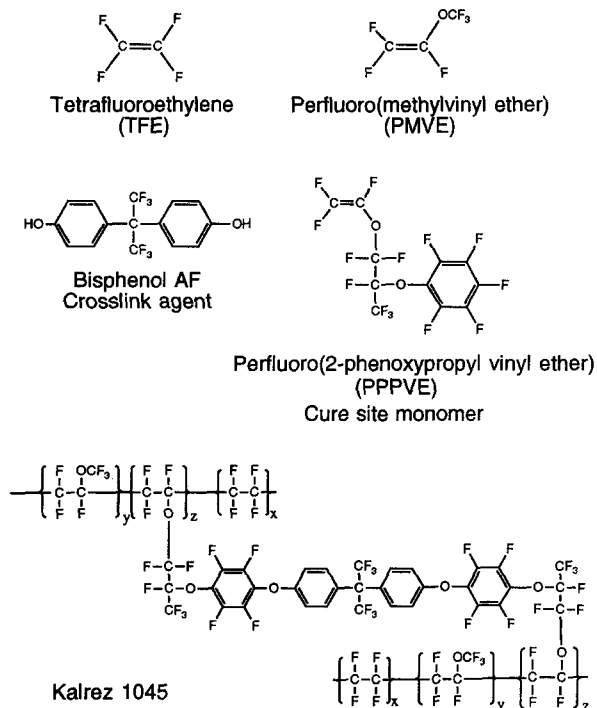
The work described here was conducted to determine the effect of  $N_2O_4$  on the physical and chemical properties of Kalrez 1045. Samples of Kalrez 1045 were exposed to  $N_2O_4$  for up to 80 days at ambient and elevated pressures. Recovery measurements were made by storing the specimens in an enclosed container after removal from the immersion vessels. The properties determined were Shore A hardness, weight gain and physical appearance, as well as the chemical decomposition as determined by solid probe-mass spectrometric analysis.

## EXPERIMENTAL

### *Kalrez samples*

Kalrez 1045 is a perfluorinated elastomer based on the copolymer of tetrafluoroethylene (TFE) and perfluoromethyl vinyl ether (PMVE)<sup>5</sup>. This copolymer is

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**Figure 1** Chemical structures of monomers, crosslink agent and Kalrez polymer

linear and chemically inert. A third monomer with a reactive crosslinking site is added to the system. This, together with the crosslinking agent, results in a crosslinked polymer. There are different Kalrez formulations depending on the cure site monomer and the crosslinking agent used. The Kalrez 1045 composition is believed to be 67 mol% TFE, 33 mol% PMVE, 0.5 mol% perfluoro-(2-phenoxypropyl vinyl ether) (PPVE) as cure site monomer, bisphenol AF as the crosslinking agent, and titanium dioxide (TiO<sub>2</sub>) as filler. *Figure 1* shows the chemical structures of the monomers, crosslink agents and polymer.

Samples of Kalrez 1045 were supplied by DuPont in the form of pellets and O-rings. Two pellets from lot 711 and two from lot 712 were obtained for use in the weight gain and hardness tests. As received, the pellets measured approximately 1.9 cm (0.75 in) in diameter and 1.3 cm (0.5 in) in height. The pellets were quartered through the centreline to provide the number of samples required for this study. The original height of 1.3 cm was not altered on any sample. The O-rings from lot 2194 were 2.54 cm (1 in) in diameter and 0.23 cm (0.09 in) thick. They were sectioned into samples 1 cm long and used for the mass spectrometric analysis.

#### Nitrogen tetroxide

Nitrogen dioxide from Matheson Gas Products of 99.5% minimum purity was employed for this study. Below 20°C and at 101 kPa (1 atm) pressure, the commercial product is a brown liquid consisting of an equilibrium mixture of nitrogen dioxide, NO<sub>2</sub> (16%), and its dimer nitrogen tetroxide, N<sub>2</sub>O<sub>4</sub> (84%). Since the major constituent of the liquid under both sets of exposure conditions used here was the dimer, we refer to the mixture exclusively as N<sub>2</sub>O<sub>4</sub>. The cylinder was equipped with an eductor tube to deliver the liquid instead of a mixture of the vapours. The liquid N<sub>2</sub>O<sub>4</sub> was used without further purification.

#### Instruments

A Pacific Transducer Corp. model 306L type A durometer (Shore A hardness) was used for all hardness measurements. This durometer is designed for testing rubber and soft plastic and conforms to ASTM 2240-75. Ten individual hardness measurements were taken and averaged to obtain each reported value.

A Mettler AE160 laboratory analytical balance with 0.1 mg sensitivity was used for all weight measurements. Weight measurements are subject to variability at early times after N<sub>2</sub>O<sub>4</sub> exposure due to clinging drops of N<sub>2</sub>O<sub>4</sub> liquid, which may or may not have oozed from the material. This source of variability is absent in later recovery tests since enough N<sub>2</sub>O<sub>4</sub> had evaporated to prevent drop formation.

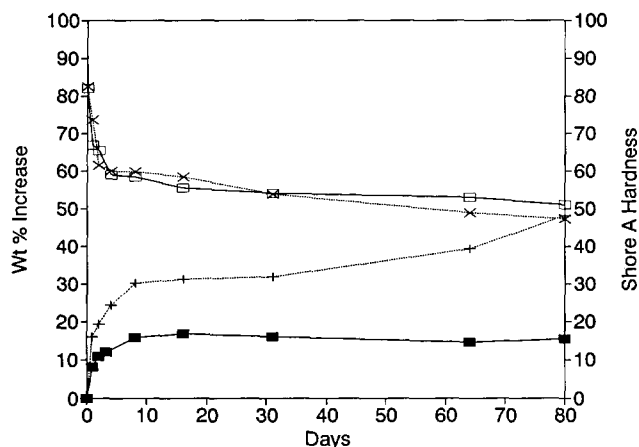
The solid probe-mass spectrometric (s.p.-m.s.) analysis was performed using a Kratos MS-25 RF magnetic mass spectrometer. The Kratos data system DS-90 was used for data acquisition and processing.

#### N<sub>2</sub>O<sub>4</sub> exposure and measurements

Samples for the pressure test were trimmed slightly to ensure an easy fit in the pressure vessel and to allow for any swelling of the sample material during the exposure. Samples were placed loosely in the vessel, and the vessel was filled with N<sub>2</sub>O<sub>4</sub> liquid. The vessel was then attached to the manifold and pressurized with nitrogen to 7320 kPa (72.5 atm). During the 80 day exposure, the samples were depressurized seven times. At each depressurization, and at the end of the 80 day exposure, the weight and Shore A hardness were measured. Measurements were taken after 1, 2, 4, 8, 16, 31, 64 and 80 days of exposure. For comparison, another set of examples was soaked in N<sub>2</sub>O<sub>4</sub> liquid at a pressure of 101 kPa (1 atm) and measured at the same intervals.

Five samples from each lot number were exposed to N<sub>2</sub>O<sub>4</sub> at ambient pressure. Each sample was exposed for a different length of time. After the designated time, exposure was ended, and the samples were measured for weight and hardness. N<sub>2</sub>O<sub>4</sub> exposure times were 1, 8, 32, 60 and 80 days. After the initial measurement, the samples were stored in a closed container under nitrogen. Measurements to track the recovery of the samples following exposure were made after 1 and 4 h, and after 1, 3, 7, 14 and 21 days. Recovery tests were conducted by storing the samples in a closed container under nitrogen to limit the amount of oxidizer that could evaporate from the surface of the sample to the final equilibrium partial pressure inside the vessel. The various conditions and sequences were chosen to approximate the potential exposure environment experienced within a Titan IV thrust vector control (TVC) unit after it is initially charged with N<sub>2</sub>O<sub>4</sub> but before it is launched.

The samples analysed by s.p.-m.s. were sections of O-rings that had been immersed in liquid N<sub>2</sub>O<sub>4</sub> for 0, 16, 24, 96 and 150 h, and 30, 60 and 90 days. After removal from the N<sub>2</sub>O<sub>4</sub>, the samples were exposed to flowing air for 80 h. The air was held at 32°C and 100% relative humidity. The mass spectrometer magnet was scanned from mass 13 to 600. The 8 mg samples were introduced into the mass spectrometer by means of a solid probe that was temperature programmed linearly from 25 to 350°C at a rate of 15°C min<sup>-1</sup>.



**Figure 2** Hardness and weight gain of Kalrez 1045 specimens from lot 711 plotted against  $N_2O_4$  exposure time. Two different exposure pressures were employed: 7320 kPa (■, weight; □, hardness) and 101 kPa (+, weight; ×, hardness)

## RESULTS AND DISCUSSION

### Exposure tests

Samples appeared greyish-white prior to exposure to  $N_2O_4$ . Appearance of the samples following exposure to  $N_2O_4$  showed no obvious changes except for a slight yellowing due to the absorbed oxidizer. Samples exposed to  $N_2O_4$  at high pressure for 60 days or more exhibited some surface roughness.

The measured weights of each exposed sample were divided by the initial pre-exposure weights to determine a fractional weight gain. *Figures 2 and 3* display the weight gained during exposure to  $N_2O_4$  as a percentage of the initial weight for lot numbers 711 and 712, respectively. Each point represents the average of a number of measurements made on a single specimen after the indicated time of exposure. These figures clearly show several interesting results. Most of the weight gain occurred during the first 8 days of exposure. The specimen from lot 711 that was exposed at 101 kPa (1 atm) gained the most (30%) during this period. Both specimens exposed at 101 kPa (1 atm) continued to show gradual weight gain with continued exposure ending up to 35–50% heavier after the full 80 days. The specimens from both lots exposed at 7320 kPa pressure showed less gain in the initial 8 days (15–20%) and gained very little in the last 72 days. Thus, the samples exposed at 101 kPa (1 atm) ultimately showed 35–50% gain while the specimens exposed at 7320 kPa gained less than 20% of their original weight. This is attributed to the fact that the higher pressure physically restrained the samples from swelling and absorbing additional  $N_2O_4$ .

Butyl rubber samples gained weight much more rapidly than Kalrez on exposure to  $N_2O_4$ . At 101 kPa, samples of B591-80 butyl rubber gained 10–20% in the first 15 min and 40–50% of their initial weight after only 16 h. Samples exposed for as long as 3 days doubled their initial weight.

The Shore A hardness measured on exposed specimens from lots 711 and 712 is also plotted against total time exposed to  $N_2O_4$  in *Figures 2 and 3*. Several generalizations can be immediately made about these results. Most obvious is that the hardness drops dramatically during the first 4 days from more than 80 to about 60. Following this rapid decline, the reduction in hardness is limited to less than 15 additional units

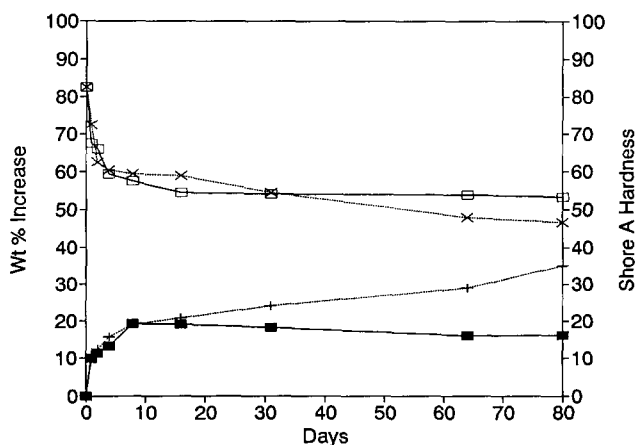
over the next 76 days. Note also that there are only slight differences between lots 711 and 712. There are also no dramatic differences between the hardness of samples exposed to  $N_2O_4$  under high pressure and the hardness of samples exposed to  $N_2O_4$  at atmospheric pressure. This is true even though ultimately the samples exposed at atmospheric pressure absorbed more  $N_2O_4$ . Although most of the softening is attributed to the plasticization by the absorbed  $N_2O_4$  and not to chemical degradation, i.e. crosslink and chain scission of the Kalrez, the hardness measurements do not quantitatively reflect the amount of absorbed  $N_2O_4$ .

In comparison to Kalrez, the hardness of butyl rubber B591-80 samples changed very rapidly when exposed to  $N_2O_4$  under the same conditions as the Kalrez samples. The hardness increased from 80 to 100 on the Shore A scale during the first 2 h of exposure at 101 kPa. Following this initial increase, the hardness dropped rapidly so that after a total of 5 h the material had softened to the extent that the measurement was meaningless.

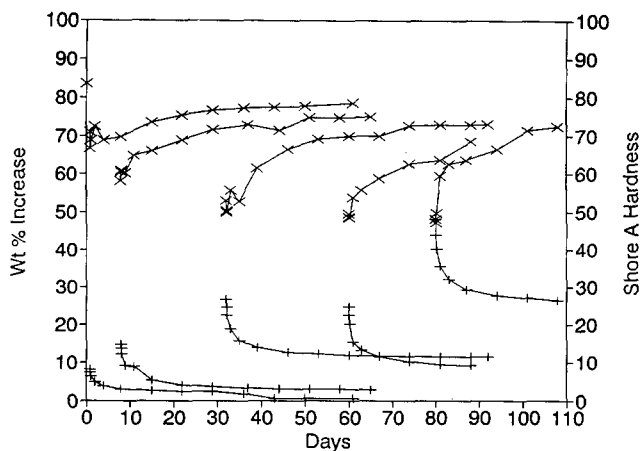
### Post-exposure recovery tests

The yellowish appearance of the samples following exposure to oxidizer slowly faded during the recovery period. After 30 days, the samples that had been exposed to  $N_2O_4$  were somewhat whiter than samples that had not been exposed. The surface roughness evidenced by the samples exposed to elevated pressures disappeared completely after 30 days.

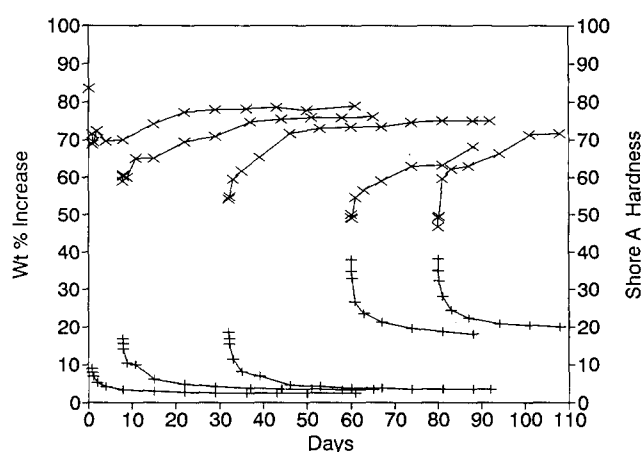
*Figures 4 and 5* show the change in weight and hardness as a function of time throughout the recovery period for individual samples of Kalrez. Data in these figures are plotted against actual test time. Each curve is therefore displaced away from the starting time by an amount that represents the period of exposure to liquid  $N_2O_4$  at 101 kPa (1 atm) pressure. The earliest point of each curve represents the increase in weight or the decrease in hardness of a sample measured immediately after being removed from  $N_2O_4$ . The locus of these earliest points can be directly compared with the exposure data of *Figures 2 and 3*, which follow the cumulative changes in single samples. This comparison shows very close agreement among the hardness measurements, regardless of the lot, the exposure pressure or the individual specimen. A wider variation is observed in the comparison of weight gains, although the same general



**Figure 3** Hardness and weight gain of Kalrez 1045 specimens from lot 712 plotted against  $N_2O_4$  exposure time. Two different exposure pressures were employed: 7320 kPa (■, weight; □, hardness) and 101 kPa (+, weight; ×, hardness)



**Figure 4** Recovery of hardness ( $\times$ ) and weight (+) of Kalrez 1045 specimens from lot 711. Each curve begins at the time the  $N_2O_4$  exposure ended for that specimen



**Figure 5** Recovery of hardness ( $\times$ ) and weight (+) of Kalrez 1045 specimens from lot 712. Each curve begins at the time the  $N_2O_4$  exposure ended for that specimen

trends are observed. This variation is probably due to the variable amounts of  $N_2O_4$  lost when a sample is taken fresh from its oxidizer bath and weighed.

Regardless of the initial weight increase, all weight recovery curves are similar in appearance. In every case, more than half of the weight gained during exposure is lost after only 10 days of recovery. With the exception of a single sample (lot 711 exposed to  $N_2O_4$  for 1 day), none of these samples recovered to its original weight following exposure to  $N_2O_4$ . The permanent increase in weight experienced by the samples correlates with total exposure time, with the longest exposures resulting in a permanent weight gain of more than 20%.

Figures 4 and 5 also display the hardness of the samples as a function of time following exposure to  $N_2O_4$ . Results for both lots 711 and 712 are remarkably similar in shape and absolute values. We readily see the similarities between all hardness curves. The hardness begins to increase immediately after a sample is extracted from the liquid  $N_2O_4$ , reaching a small peak. This relaxes over the next several days, followed by a smooth increase to a new, higher level by the end of the tests. In all cases, the final hardness of the samples never fully recovers to its original value before exposure. This final hardness is lower for samples that were exposed to the oxidizer for longer times.

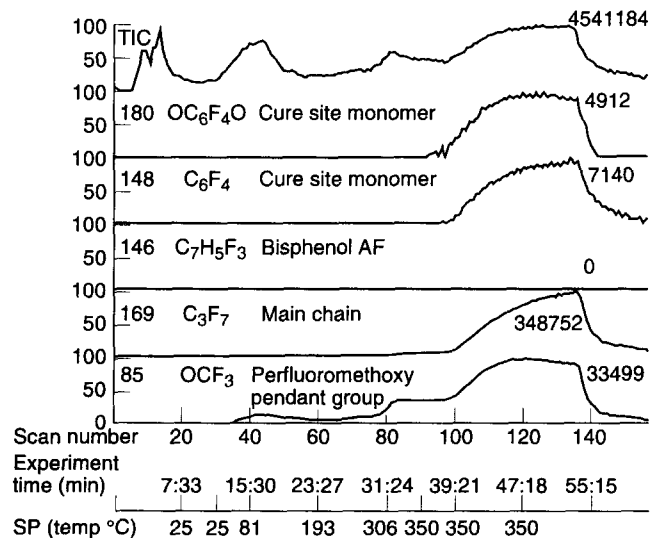
The incomplete recovery to the original values for both weight and hardness during the recovery period indicates that a chemical change has occurred in the polymeric structure of the Kalrez material. Mass spectrometry was used to detect these changes.

#### Solid probe-mass spectrometric analysis

The chemical stability of the Kalrez material as a function of time exposed to  $N_2O_4$  was monitored with solid probe mass spectrometry. Below  $350^\circ C$ , the major outgassing product for the unexposed Kalrez was water, and for the exposed samples it was the adsorbed  $N_2O_4$ . The adsorbed  $N_2O_4$  was not removed by the flowing air or by vacuum; heating was necessary to remove the  $N_2O_4$ . This was determined after the same amount of  $N_2O_4$  was detected from two pieces of the same O-ring in which one piece was outgassed for 3 days at a pressure of  $10^{-6}$  torr.

Comparisons between the unexposed and the exposed samples were used to determine the chemical changes. Figures 6 to 9 show the total ion currents (TIC) and the selected ion plots for the masses 85, 146, 148, 169 and 180 of representative samples analysed. In Figures 6 to 9 the x-axis gives the scan number, the analysis time and the temperature of the solid probe. The y-axis displays relative intensity. The full-scale, 100% intensity is indicated by the number to the right of each plot.

These specific ions were chosen because they are characteristic of a particular fragment of the polymer structure (see Figure 1), and were interpreted as representing a certain type of chemical degradation. Mass 85 corresponds to the  $(-OCF_3)$  group found in the pendant group from the main chain and was interpreted as resulting from a reaction that causes the loss of this pendant group. Mass 146 is the main ion observed from the mass spectrum of bisphenol AF and was interpreted as resulting from the loss of the crosslink. Mass 148, corresponding to the  $(-C_6F_4-)$  group, and 180, corresponding to the  $(-OC_6F_4O-)$  group, are found in the cure site monomer. Their detection was interpreted as resulting from the degradation of the PPPVE. Mass 169 corresponds to the  $(-C_3F_7-)$  group found in the main chain and was interpreted as resulting from scission of the main chain.



**Figure 6** Plot of the solid probe-mass spectrometric analysis of unexposed Kalrez 1045

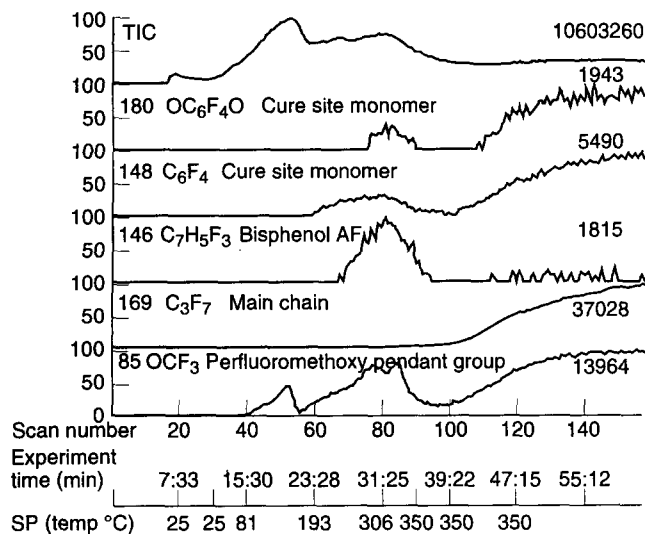


Figure 7 Plot of the solid probe-mass spectrometric analysis of Kalrez 1045 exposed to  $N_2O_4$  for 6 days

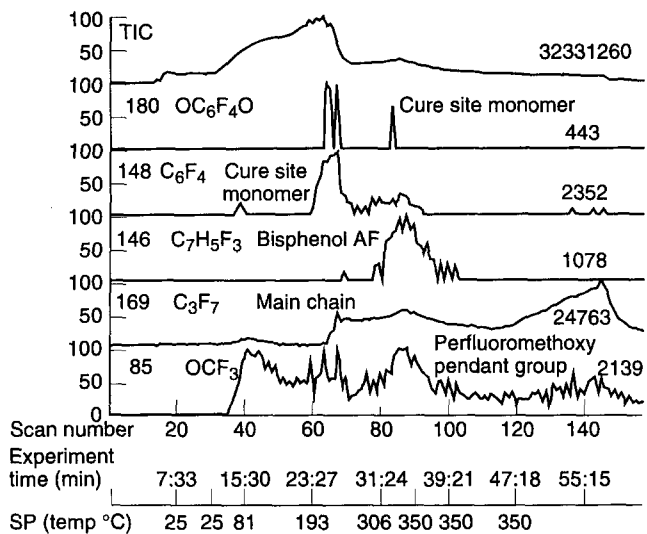


Figure 9 Plot of the solid probe-mass spectrometric analysis of Kalrez 1045 exposed to  $N_2O_4$  for 90 days

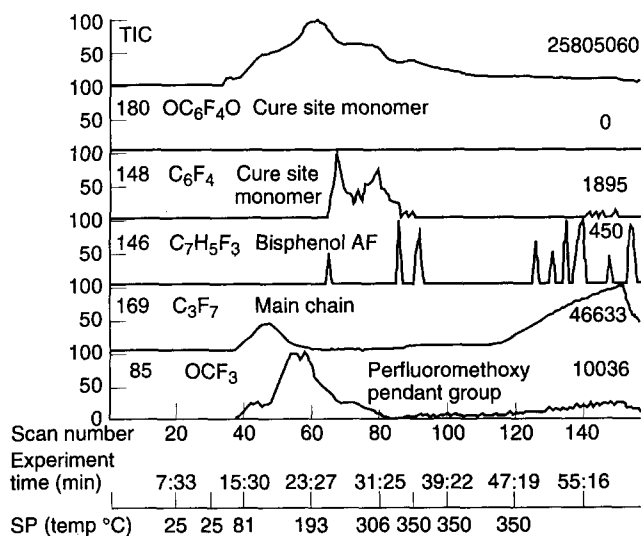


Figure 8 Plot of the solid probe-mass spectrometric analysis of Kalrez 1045 exposed to  $N_2O_4$  for 60 days

#### Chemical effects of $N_2O_4$

From the structure of Kalrez shown in Figure 1, the sites most vulnerable to chemical attack by  $N_2O_4$  are the various ether ( $-C-O-C-$ ) linkages and the phenyl rings of the bisphenol AF (crosslinking agent). Changes in the polymeric structure of Kalrez were assigned when the s.p.-m.s. analysis of the Kalrez exposed to  $N_2O_4$  detected ions characteristic of Kalrez's chemical structure at analysis temperatures below  $350^\circ C$ , the beginning of thermal decomposition (i.e. peaks were observed in the limited mass plots at scans below 100).

Scission of the main chain pendant group, perfluoromethoxy, was assumed when the analysis of the exposed samples detected the masses of 85, the ( $-OCF_3$ ) group, and of 66, the ( $-OCF_2-$ ) group, at lower scan number, or a lower temperature than in the unexposed sample (see Figure 6). These ions were detected after only 16 h of  $N_2O_4$  exposure. The fact that scission of the pendant group was detected after a short exposure time does not mean that these changes should be expected to correlate with significant changes in the physical properties of the material. M.s. analysis is a very sensitive technique, and

only a very small fraction of the pendant groups need be removed before detection is possible.

The other ether linkages that could be affected are those of the cure site monomer PPPVE. Ions of mass 180 ( $-OC_6F_4O-$ ), mass 164 ( $-OC_6F_4-$ ), mass 148 ( $-C_6F_4-$ ), mass 183 ( $-OC_6F_5-$ ), mass 167 ( $-C_6F_5-$ ), mass 166 ( $-OC_3F_6-$ ) and mass 182 ( $-OC_3F_6O-$ ) that could be produced from the cure site monomer were detected at scan numbers below 100 (i.e. below the decomposition temperature). For simplicity, only masses 148 and 180 were chosen to represent scission of the cure site monomer in Figures 6 to 9. Although the exposure times at which the ions were initially detected varied, all the other ions from PPPVE behave similarly. Scission of the cure site monomer will affect the polymer crosslink. Mass 146 is the main ion observed in the mass spectrum of bisphenol AF. Scission of the crosslinking agent was not observed in samples exposed for less than 6 days, indicating that scission of the cure site monomer and the crosslink agent do not occur at the same time. Loss of the crosslink results in a softer material. The s.p.-m.s. analysis was unable to determine if nitration of the phenyl groups from the bisphenol AF had occurred.

Evidence of the main chain scission, detected by the presence of mass 169 ( $-C_3F_7-$ ), was observed in samples after 60 days of exposure. Mass 169 ( $-C_3F_7-$ ) ions can only be produced from the polymer main chain.

In summary, the solid probe-mass spectrometric analysis has provided evidence of structural degradation of Kalrez from exposure to  $N_2O_4$ . The loss of ether pendant groups, the crosslink, and crosslink site monomer in Kalrez was detected after a few hours of exposure to  $N_2O_4$ , and main chain scission was detected after 60 days of exposure. When similar experiments were conducted on butyl B591-80 O-rings, the s.p.-m.s. results showed a loss of phthalates, used as plasticizers, and main chain scission after only 16 h of exposure to  $N_2O_4$ .

#### CONCLUSIONS

It is conclusive from these tests that Kalrez offers superior resistance to  $N_2O_4$  relative to the butyl rubber seals presently employed in launch vehicles. This is evident from the measurements, which show that Kalrez retains

a significant fraction of its initial hardness even after 80 days' exposure to N<sub>2</sub>O<sub>4</sub>. In addition, the material shows no blistering or deformation after exposure. The only change in appearance is a slight yellowing. Even under the repeated exposures at high pressure, which were designed to simulate worst-case launch delays, the Kalrez specimens retained 60% of their initial hardness. Since hardness is a key measure of the material's resistance to extruding through a gap in a seal, its persistence under N<sub>2</sub>O<sub>4</sub> exposure is excellent evidence that the seal will continue to function under these circumstances.

However, the present measurements show that the material does not recover to its original hardness or density as reported in the Aerojet manuscript<sup>4</sup>. This is clear evidence of an irreversible chemical change in the material. In fact the detection of specific ions by solid

probe-mass spectrometry confirms that the N<sub>2</sub>O<sub>4</sub> affects the loss of the ether pendant groups, the crosslink, and crosslink site monomer within a few hours of exposure. Main chain scission is not evidenced until samples are exposed for 60 days. These results indicate that Kalrez cannot withstand indefinite exposure to N<sub>2</sub>O<sub>4</sub>.

## REFERENCES

- 1 Azbielski, M. F. and Blaszyk, P. R. *J. Vacuum Sci. Technol.* 1976, **13**, 644
- 2 de Chernatony, L. *Vacuum* 1977, **27**, 605
- 3 Peacock, R. N. *J. Vacuum Sci. Technol.* 1980, **17**, 330
- 4 Schnell, R., DuPont Corporation, personal communication, 1991
- 5 Barney, A. L., Keller, W. J. and Van Gullick, N. M. *J. Polym. Sci., A-1* 1970, **8**, 1091