

Jess M. Waller,<sup>1</sup> Jon P. Haas,<sup>1</sup> Harold D. Beeson<sup>2</sup>

## **POLYMER-OXYGEN COMPATIBILITY TESTING: EFFECT OF OXYGEN AGING ON IGNITION AND COMBUSTION PROPERTIES**

---

**REFERENCE:** Waller, J. M., Haas, J. P., Beeson, H. D., **Polymer-Oxygen Compatibility Testing: Effect of Oxygen Aging on Ignition and Combustion Properties,** *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Ninth Volume, ASTM STP 1395*, T. A. Steinberg, H. D. Beeson, B. E. Newton, Eds., American Society for Testing and Materials, West Conshohocken, PA, 2000.

**ABSTRACT:** The oxygen compatibility of six polymers used in oxygen service was evaluated after 48 hr exposures at 121 °C (250 °F) to oxygen pressures of 620 and 6200 kPa (90 and 900 psia). Three elastomers were tested: chloroprene rubber (C873-70), fluorocarbon rubber (Viton<sup>TM3</sup> A), and silicone rubber (MVQ type); and three thermoplastics were tested: polyhexamethylene adipamide (Zytel<sup>TM3</sup> 42), polytetrafluoroethylene (PTFE Teflon<sup>TM3</sup> 500A), and polychlorotrifluoroethylene (Neoflon CTFE<sup>TM3</sup> M400H). Post-aged changes in mass, dimensions, tensile strength, elongation at break, durometer hardness, and thermomechanical properties were evaluated. For selected materials, GN<sub>2</sub>-aged controls were used to ascertain the effect of thermal versus oxidative degradation. Finally, the effect of oxygen aging on selected ignition (AIT) and combustion ( $\Delta H_c$ ) properties was determined. As expected, aged polymers were less ignitable and combustible. Special attention was given to Neoflon CTFE; namely, the possible effect of percent crystallinity (quick- versus slow-quenched) on the aging, ignition, and combustion behavior was evaluated.

**KEY WORDS:** oxygen compatibility, oxygen aging, neoprene, Viton, FKM, silicone rubber, MVQ, Zytel, nylon 66, Neoflon, PCTFE, Teflon, PTFE, mechanical properties, TMA, AIT, heat of combustion.

---

<sup>1</sup> Project Leaders, AlliedSignal Technical Services Corp. Team, NASA Johnson Space Center White Sands Test Facility, P. O. Box 20, Las Cruces, NM 88004.

<sup>2</sup> Special Projects Manager, NASA Laboratories Office, NASA Johnson Space Center White Sands Test Facility, P. O. Box 20, Las Cruces, NM 88004.

<sup>3</sup> Teflon<sup>TM</sup>, Viton<sup>TM</sup> and Zytel<sup>TM</sup> are registered trademarks of DuPont Company, Wilmington, DE. Neoflon<sup>TM</sup> is a registered trademark of Daikin America, Inc., Orangeburg, NY.

## Introduction

As part of an effort to evaluate the oxygen compatibility of nonmetals used in manned space flight, the NASA JSC White Sands Test Facility (WSTF) has been involved in the testing of nonmetals used on the Space Shuttle Orbiters, and more recently, nonmetals earmarked for use on the International Space Station. For example, the authors of this study previously reported on the oxygen compatibility of candidate materials to possibly replace EPDM (ethylene propylene diene monomer) elastomer gaskets used in the oxygen/hydrogen auxiliary power unit (APU) fuel cells used on the orbiter [1]. In that study the oxygen compatibility was evaluated for five elastomers, neoprene C873-70. Aflas<sup>1</sup> 7182D, Kalrez 1045, Fluorel 2180, and V884-75 (Fluorel 2174/2181 blend).

In this study, the effect of oxygen aging on ignition and combustion properties was evaluated for three elastomers: neoprene (C873-70), fluorocarbon rubber (Viton A), and silicone rubber (MVQ type); and three thermoplastics: polyhexamethylene adipamide (Zytel 42), polychlorotrifluoroethylene (Neoflon M400H), and polytetrafluoroethylene (Teflon 500A). Since thermoplastics with higher degrees of crystallinity are reputed to exhibit better resistance to oxidative degradation [2], two varieties of Neoflon CTFE M400H were tested: 1) quick-quenched (amorphous) sheet, and 2) air-quenched, (crystalline) sheet. However, the primary goal of the present study was not to develop performance or compatibility rankings as before, but to specifically determine the effect of oxygen aging on the autogenous ignition temperature (AIT), and heat of combustion ( $\Delta H_c$ ).

In applications involving exposure of nonmetals to high-pressure oxygen-enriched media, the fire hazard will be greater than in air [3, 4]. For example, as the oxygen pressure increases, the catastrophic ignition hazard associated with most nonmetals will also increase [5, 6]. (Neoprene is a notable exception to this rule [7].) This hazard is largely mitigated in applications involving exposure to low to intermediate pressures at temperatures well below the AIT, such as would be encountered in accepted uses of neoprene, Viton, silicone rubber, nylon, PCTFE, and PTFE. However, the long-term, non-catastrophic exposure to oxygen in such cases could lead to cumulative degradation during service. It then becomes important to know whether the ignition hazard is reduced, as expected, or is actually enhanced for certain polymers. Criteria such as  $\Delta H_c$  and AIT are routinely used to evaluate materials for high-pressure oxygen service where ignition and combustion hazards are prominent. In cases where oxygen fires may result from promoted ignition,  $\Delta H_c$  is primarily used to evaluate the ability of a nonmetal to ignite adjacent materials, including metals. For example, materials with heats of combustion less than  $6.3 \text{ MJ kg}^{-1}$  ( $1500 \text{ cal g}^{-1}$ ) generally do not act as ignition promoters at oxygen pressures up to 17.2 MPa (2500 psi) [8]. While the AIT is primarily used to identify the ignition threshold, in the present study, the AIT also allowed identification of the limiting pressure and temperature below which aging tests could be safely conducted.

Finally, since aging, ignition and combustion represent different aspects of the same technological problem, i.e., functional incompatibility with oxygen, possible correlation

---

<sup>1</sup> Aflas<sup>™</sup> and Fluorel<sup>™</sup> are registered trademarks of 3M, Minneapolis, MN. Kalrez<sup>™</sup> is a registered trademark of DuPont Company, Wilmington, DE.

between physico-mechanical property data and available  $\Delta H_c$  and AIT data was sought. Upon first inspection, correlation would appear to be straightforward; namely, nonmetals with low  $\Delta H_c$  and high AIT would be thought to possess superior oxygen-aging resistance as indicated by minimal change in post-aged physico-mechanical properties. However, for reasons pointed out earlier [1], such simplifications can be undermined by potentially overriding effects of polymer formulation and microstructure.

## **Experimental**

### *Materials*

All materials were received in the form of compression-molded sheet with nominal thicknesses of 1.6 mm (0.062 in.). For each O<sub>2</sub>- or N<sub>2</sub>-aging scenario (620 and 6200 kPa), twenty specimens were used. Of these, ten were aged, and the remainder used as unaged controls. All sheet stock was used as-received. Information about each elastomer or thermoplastic formulation is summarized in Table 1.

### *Aging Procedure*

All materials were aged at 620 or 6200 kPa O<sub>2</sub> (or N<sub>2</sub>) at 121 °C for 48 h. All exposures were conducted in a corrosion-resistant Hastelloy C286 stainless steel reaction vessel with a MAWP of 20.7 MPa (3,000 psi). Individual specimens were suspended from a stainless steel wire and separated by 2 mm (0.08 in.) glass spacers. The reaction vessel was sealed, leak checked, and purged several times by pressurizing to the target pressure. The reaction vessel was then pressurized to approximately three-fourths the target pressure, heated to 121 °C, and regulated to the target pressure. All depressurizations were conducted by slow venting to avoid the formation of porosity (especially for elastomers). Vessel temperature and pressure were continuously recorded during each exposure, after which the vessel was vented to ambient pressure and cooled. Aged specimens were allowed to rest not less than 16 h nor more than 96 h before determination of post-aged properties in accordance with guidelines given in ASTM Test Method for Rubber-Deterioration by Heat and Oxygen (D 572). A schematic diagram of the aging apparatus used in this investigation is given in Figure 1.

### *Thermal Analysis*

Thermomechanical properties were determined using a Haake-Fisons (formerly Seiko) Model 120C Thermomechanical Analyzer equipped with liquid nitrogen cooling. Analyses included determination of 1) the room temperature ( $25.0 \pm 0.2$  °C) modulus using a 0.05 Hz,  $15 \pm 10$  g oscillating load, and 2) the dynamic properties  $E'$ ,  $E''$ , and  $\tan \delta$  using a 0.1 Hz  $15 \pm 10$  g oscillating load.

Table 1 — Test Materials

Polymer (Supplier/Molder)	Resin or Gum Composition (Manufacturer)	Cure System or Additives	Comments
Neoprene C873-70 (Parker)	poly(2-chloro-1,3-butadiene), "W"-type (DuPont)	peroxide/MgO/ZnO w/ amine accelerator	N990 carbon black + thermal black
Viton A (West America Rubber)	poly(hexafluoropropylene -co- vinylidene difluoride) (DuPont)	Diak no. 1 (diamine) Curative	unspecified carbon black
Silicone MVQ (Rubberite Corp.)	poly(methylvinyl-co- dimethylsiloxane) (GE Silicones)	dicumyl peroxide/MgO, FeO pigment, heat stabilizer added	20 phr fumed silica, MIL-R-ZZ-765, Class 2, Grade 70
Zytel 42 (A. L. Hyde)	poly(hexamethylene adipamide) (DuPont)	virgin resin, not heat stabilized	high MW general purp. extrusion grade
Teflon 500A (Tex-O-Lon)	polytetrafluoroethylene (DuPont)	non-flowing virgin resin	sintered sheet
Neoflon CTFE M400H (PBY Plastics)	polychlorotrifluoroethylene (Daikin)	virgin resin with heat stabilizer added	high MW sheet, per AMS 3560

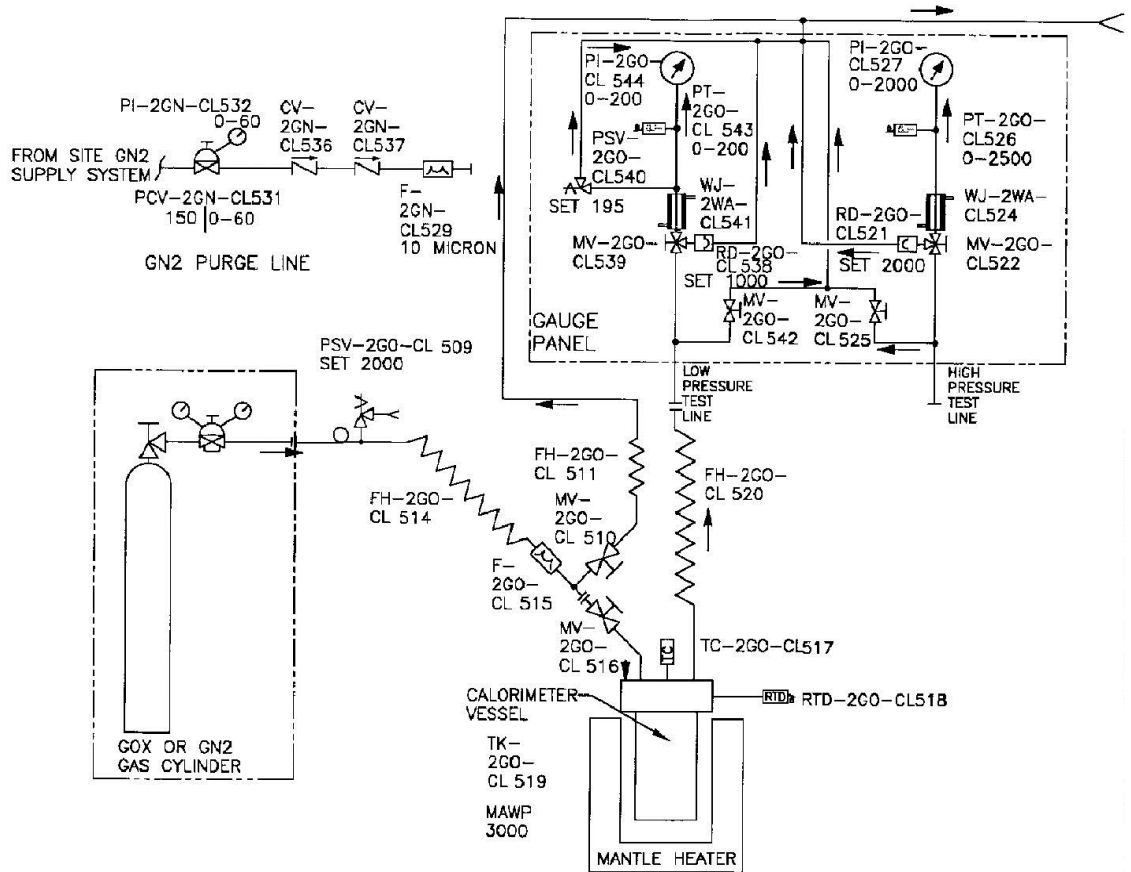


Figure 1 – Schematic diagram of the aging apparatus used at White Sands Test Facility.

## *Ignition, Combustion, and Impact Tests*

Autogenous Ignition Temperature determinations were made according to ASTM Test Method for Autogenous Ignition Temperature of Liquids and Solids in a High-Pressure Oxygen-Enriched Environment (G 72). Samples of each material were evaluated three times in 100 percent oxygen at an initial pressure of approximately 10.3 MPa (1500 psia). The average sample weight for each test was  $0.20 \pm 0.02$  g. The heating rate in the reaction vessel was  $5 \pm 1$  °C ( $9 \pm 2$  °F) per minute for the entire heating range. The maximum temperature of the reaction vessel was set at 450 °C (842 °F). The AIT was identified by a sudden increase in the temperature and/or pressure in the reaction vessel.

Gross heat of combustion determinations were carried out in accordance with ASTM Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (D 240) using a Parr© Model 1261 isoperibol bomb calorimeter operating in its dynamic mode. Three samples of each material were tested. The focus was not to correct gross heats for combustion product formation, but rather to compare the overall effects of oxygen aging on various materials.

## *Physico-Mechanical Property Evaluations*

Mass changes were determined by measuring five specimens measured to the nearest  $\pm 0.0001$  g before and after aging. A hand-held micrometer and a Mitutoyo dial indicator were used to determine cross-sectional gage region  $w$  and  $t$ , respectively, to the nearest  $\pm 0.01$  mm. Shore A and D Durometer hardnesses were determined using a Shore Model 902 Hardness Tester and 1 s indentation times per ASTM Test Method for Rubber Property – Durometer Hardness (D 2240). For elastomers, Shore M (micro-) Durometer hardnesses were also measured. Ultimate tensile strength (UTS) and percent elongation at break ( $\epsilon_{\max}$ ) were determined per ASTM Test Methods for Vulcanized Rubber and Thermoplastic Elastomers – Tension." (D 412) (Type C die, rubbers), or ASTM Standard Test Method for Tensile Properties of Plastics (D 638) (Type V die, plastics) using an Instron® Model TTC Universal Tester.

## **Results and Discussion**

### *Visual, Mass and Dimensional Changes*

The visual appearance of all test specimens was essentially unchanged with the exception of O<sub>2</sub>-aged C873-70 and Zytel 42. While the Zytel 42 became discolored (unaged – beige, 620 kPa aged – light yellow; 6200 kMPa-aged – dark yellow), the 6200 kPa-aged C873-70 appeared melted and embrittled, and was hardly recognizable as tensile specimens after aging. The comparable effect of 6200 kPa O<sub>2</sub>-aging on C873-70 *O-rings* under similar conditions is shown in Figure 1 in reference [1].

The poorer resistance to oxygen aging exhibited by C873-70 compared to the other materials tested in this study was attributed to the oxidation of unsaturated monomer repeat units, coupled with dehydrochlorination reactions. As was described earlier [1], the presence of unsaturation is a distinct disadvantage when comparing the age resistance

of C873-70 to mostly or wholly saturated materials such as Viton<sup>1</sup> and silicone elastomers, fluoroplastics (PCTFE and PTFE), or nylon (Zytel).

Percent mass changes as measured 16 to 24 hr after aging were small (< 1 percent) for all materials tested with the exception of 620 and 6200 kPa O<sub>2</sub>-aged C873-70, which gave mass changes of +1.8 and -12.4 percent, respectively. In the former case, the observed mass increase is consistent with oxygen uptake involving reaction of oxygen with carbon-centered radicals to form peroxy radicals [9], thereby leading to increases in density and mass. In the later case, mass loss due to dehydrochlorination and volatilization of process oils and chain scissioning products, etc., appears to have predominated. During dismantling of the aging apparatus after the 6200 kPa O<sub>2</sub>-aging run, there was condensed liquid with the vessel, which was acidic as revealed by pH paper.

The next largest mass change was observed for Zytel 42, which gained 0.7 percent mass after aging in 6200 oxygen. This observation was not surprising, given the aliphatic character of Zytel 42 (more susceptible to oxygen uptake).

In the absence of oxygen, C873-70 specimens are expected to lose mass due to predominant dehydrochlorination [1]. Aging of C873-70 in 6200 kPa N<sub>2</sub> at 121 °C for 48 h verified this expectation. More specifically, 6200 kPa N<sub>2</sub>-aged C873-70 exhibited a 0.3 percent mass loss, consistent with earlier observations.

The dimensional data also revealed small to moderate changes. Most prominent were the +5.8 and +3.1 percent increases in the thickness and width, respectively, observed for 6200 kPa O<sub>2</sub>-aged Viton A. This observation was consistent with the previous work of Irani, et al., who observed significant swelling followed by a rapid decrease in the thickness of Viton A O-rings after removal from 10 to 20 MPa (1500 to 3000 psi) oxygen [10]. The plastics (Zytel, PCTFE, and PTFE) also exhibited significant dimensional changes; however, these changes could arise from annealing effects, rather than from the effect of oxygen pressure. For example, annealing effects in PCTFEs leading to dimensional instability are discussed in greater detail in another paper in this publication [11].

### *Mechanical Properties*

Values of tensile properties show that only C873-70 and Zytel 42 exhibited large drops in the ultimate tensile strength (UTS), while C873-70, Zytel 42, and PCTFE exhibited large drops in the percent elongation at break ( $\epsilon_{\max}$ ) (Table 2). Changes in the tensile properties were considered negligible if the change compared to the original, unaged value was less than 5 percent. Drops in the UTS are generally attributed to scissioning reactions which lead to a net reduction in the number of load-bearing bonds over the material cross section. All other materials showed excellent UTS retention. The UTS of the 620 kPa-O<sub>2</sub>-aged PCTFEs tested actually appear to increase as a result of annealing leading to higher percent crystallinity. It is interesting to note that the UTS of Viton A was essentially unaffected by oxygen aging in this study, yet in a previous

---

<sup>1</sup> In the case of Viton, only residual unsaturation created during vulcanization is expected. Such unsaturation is expected to be strongly deactivated to attack by oxygen by adjacent —CF<sub>3</sub> and —CF<sub>2</sub>— groups.

Table 2 — *Effect of Aging on Tensile Properties*<sup>a</sup>

	as-received UTS	O <sub>2</sub> -aged UTS		N <sub>2</sub> -aged UTS <sup>b</sup>
	MPa	620 kPa-aged MPa (%)	6200 kPa-aged MPa (%)	6200 kPa-aged MPa (%)
<i>Elastomers:</i>				
Neoprene C873-70	16.1	8.7 (-46)	degraded <sup>c</sup>	16.4 ( <i>negl.</i> )
Viton A	8.4	8.1 ( <i>negl.</i> )	7.6 (-9)	8.2 ( <i>negl.</i> )
Silicone MVQ	4.3	4.5 ( <i>negl.</i> )	4.4 ( <i>negl.</i> )	...
<i>Thermoplastics:</i>				
Zytel 42	66.3	32.9 (-50)	12.5(-81)	74.9 (+8)
Neoflon M400H- <i>amorph.</i>	34.1	40.4 (+18)	36.2 ( <i>negl.</i> )	...
Neoflon M400H- <i>cryst.</i>	41.7	43.9 (+5)	40.9 ( <i>negl.</i> )	...
Teflon 500A	26.7	26.5 ( <i>negl.</i> )	27.1 ( <i>negl.</i> )	...

	as-received $\epsilon_{\max}$	O <sub>2</sub> -aged $\epsilon_{\max}$		N <sub>2</sub> -aged $\epsilon_{\max}$ <sup>b</sup>
	%	620 kPa-aged % (%%)	6200 kPa-aged % (%%)	6200 kPa-aged % (%%)
<i>Elastomers:</i>				
Neoprene C873-70	580	63 (-89)	degraded <sup>c</sup>	512 (-11)
Viton A	335	328 ( <i>negl.</i> )	331 ( <i>negl.</i> )	315 (-6.)
Silicone MVQ	382	376 ( <i>negl.</i> )	365 ( <i>negl.</i> )	...
<i>Thermoplastics:</i>				
Zytel 42	444	10 (-98)	3 (-99)	430 ( <i>negl.</i> )
Neoflon M400H- <i>amorph.</i>	314	259 (-18)	267 (-15)	...
Neoflon M400H- <i>cryst.</i>	174	130 (-25)	73 (-58)	...
Teflon 500A	1257	1245 ( <i>negl.</i> )	1350 (+7.)	...

<sup>a</sup> Abbreviation used: UTS, ultimate tensile strength;  $\epsilon_{\max}$ , percent elongation; ; *negl.*, negligible change (< 5 percent change).

<sup>b</sup> ... Denotes not tested.

<sup>c</sup> Severely degraded - no mechanical properties left.

study [1], the UTSs of Fluorel 2180 and V884-75, which are close relatives of Viton A, dropped ~20-50 percent after an equivalent aging. Changes in the design of the aging apparatus or formulation differences could explain the apparent discrepancy.

The percent elongation data (Table 2, bottom) paralleled trends in the UTS data, except that significant reductions in the percent elongation were also noted for crystalline and amorphous PCTFE. Note that the percent elongations given are *ultimate* elongations. Perhaps a more revealing measure of the stress/strain characteristics of the thermoplastics (nylon, PCTFE, and PTFE) tested in this study would be a comparison of the *yield* stress and strain.

This notwithstanding, the large drops in the percent elongation noted for crystalline PCTFE, and to a lesser extent, amorphous PCTFE, were surprising, especially in light of the fact that both PCTFEs showed excellent retention of all other properties (mass, dimensions, UTS, hardness (Table 3), AIT (Table 4), and  $\Delta H_c$ (Table 4)). An interesting control would be to age the two PCTFEs in nitrogen to determine whether heat or oxygen was responsible for observed reductions in the percent elongation. At this juncture, temperature appears to be the culprit. PCTFEs are noted for their tendency to degrade at during processing (230-290 °C), and are known to become brittle as a consequence of becoming more crystalline after exposure to annealing temperatures (150-175 °C) [12]. The two PCTFEs tested in the study were found by DSC [11] to have percent crystallinities ranging from 26 (amorphous quick-quenched sheet) to 32 percent (crystalline air-quenched sheet). Both values are much lower than values approaching 60 to 70 percent normally expected for isotactic linear homopolymers [13].

In thermooxidative aging environments, most polymers harden, i.e., their modulus increases. While the durometer hardness data (Table 3) did show substantial changes in the Shore A or M hardness of C873-70, the remainder of the data was essentially invariant with respect to aging condition. For the thermoplastics tested, especially Zytel and PCTFE, Shore D hardness data does not appear to be sensitive the underlying factors responsible for the observed tensile property reductions. Investigations are underway to determine if Knoop hardness, for example, is more sensitive to hardness changes accompanying oxidative degradation of rigid thermoplastics.

It should be noted that the Shore A and M results for 6200 kPa O<sub>2</sub>-aged C873-70 are in apparent contradiction. Both softening (Shore A) and hardening (Shore M) were indicated. The origin of this apparent contradiction may be artifactual (sensitive to method and indenter), or may result from specimen-to-specimen differences within the given sample (property gradient).

In order to determine whether thermal or oxidative degradation was responsible for the observed mechanical property changes, 6200 kPa GN<sub>2</sub>-aged controls were used (right column in Tables 2 and 3). As can be seen, tensile properties and Durometer hardnesses were essentially unchanged after GN<sub>2</sub>-aging. This is a direct indication that the tensile property reductions, for example, observed for C873-70 and Zytel 42 were a direct consequence of exposure to oxygen. Although GN<sub>2</sub>-aged control data is not presently available for the two Neoflon PCTFEs (in progress at the time of this report); the observed drops in the percent elongation could well result from temperature (which would cause annealing and/or thermal degradation), rather than exposure to oxygen.



Table 3 — Effect of Aging on Shore A, D, and M Durometer Hardness<sup>a</sup>

	as-received H <sub>A</sub>	O <sub>2</sub> -aged H <sub>A</sub>		N <sub>2</sub> -aged H <sub>A</sub> <sup>b</sup>
	Shore A units	620 kPa-aged Shore A units (%)	6200 kPa-aged Shore A units (%)	6200 kPa-aged Shore A units (%)
<i>Elastomers:</i>				
Neoprene C873-70	67	88 (+31)	61 (-9) <sup>c</sup>	69 ( <i>negl.</i> )
Viton A	74	74 ( <i>negl.</i> )	71 ( <i>negl.</i> )	75 ( <i>negl.</i> )
Silicone MVQ	74	75 ( <i>negl.</i> )	74 ( <i>negl.</i> )	...
	as-received H <sub>M</sub>	O <sub>2</sub> -aged H <sub>M</sub>		N <sub>2</sub> -aged H <sub>M</sub> <sup>b</sup>
	Shore M units	620 kPa-aged Shore M units (%)	6200 kPa-aged Shore M units (%)	6200 kPa-aged Shore M units (%)
<i>Elastomers:</i>				
Neoprene C873-70	69	86 (+25)	87 (+26) <sup>c</sup>	71 ( <i>negl.</i> )
Viton A	78	77 ( <i>negl.</i> )	75 ( <i>negl.</i> )	77 ( <i>negl.</i> )
Silicone MVQ	75	75 ( <i>negl.</i> )	74 ( <i>negl.</i> )	...
	as-received H <sub>D</sub>	O <sub>2</sub> -aged H <sub>D</sub>		N <sub>2</sub> -aged H <sub>D</sub> <sup>b</sup>
	Shore D units	620 kPa-aged Shore D units (%)	6200 kPa-aged Shore D units (%)	6200 kPa-aged Shore D units (%)
<i>Thermoplastics:</i>				
Zytel 42	83	84 ( <i>negl.</i> )	82 ( <i>negl.</i> )	84 ( <i>negl.</i> )
Neoflon M400H- <i>amorphous</i>	76	77 ( <i>negl.</i> )	75 ( <i>negl.</i> )	...
Neoflon M400H- <i>crystalline</i>	76	78 ( <i>negl.</i> )	78 ( <i>negl.</i> )	...
Teflon 500A	53	53 ( <i>negl.</i> )	54 ( <i>negl.</i> )	...

<sup>a</sup> Abbreviation used: H<sub>A</sub>, H<sub>M</sub>, and H<sub>D</sub> refer to the Shore A, M (micro-), and D Durometer hardnesses, respectively; *negl.*, negligible change.  
<sup>b</sup> ... Denotes not tested.  
<sup>c</sup> Severely degraded - no mechanical properties left.

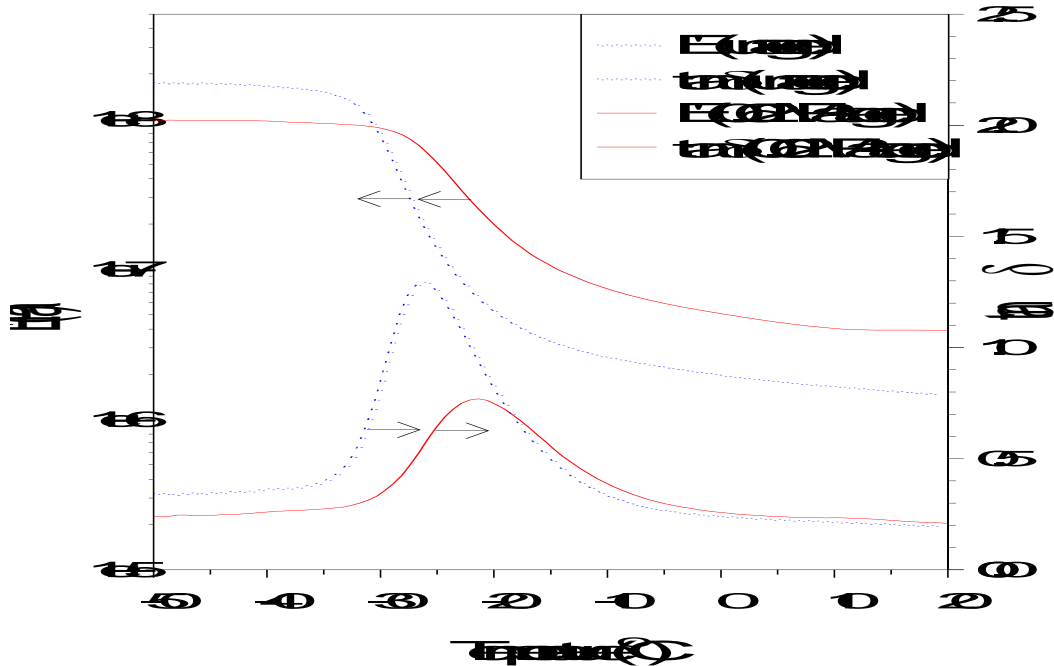


Figure 2 – Effect of 620 kPa oxygen aging at 121 °C on the  $\tan \delta$  (resiliency) and  $E'$  (storage modulus) of neoprene C873-70, as determined by TMA at 0.1 Hz.

### *Thermomechanical Properties*

The data presented thus far indicate significant mechanical property changes for C783-70 and Zytel 42 (due to oxygen exposure), and Neoflon M400H (due to oxygen exposure and/or temperature). To further characterize the property changes occurring in C873-70, for example, dynamic TMA using a 0.1 Hz oscillating load profile was conducted (Figure 2). Inspection of Figure 2 shows that 620 kPa- $O_2$  aging led to 1) a shift in the  $\tan \delta$  peak<sup>1</sup> towards higher temperature, accompanied by 2) simultaneous broadening. Both features are indicative of hardening and loss of resiliency in the 620 kPa  $O_2$ -aged material. Hardening is further evidenced by the higher value of the ambient (20 °C)  $E'$  (storage modulus) of aged versus unaged material. The peak  $\tan \delta$  of 6200 kPa  $O_2$ -aged material (data not shown) was dampened to point where the anelastic spectrum ( $\tan \delta$  versus temperature curve) became almost featureless.

### *Autogenous Ignition Temperature and Heat of Combustion*

Inspection of AIT and  $\Delta H_c$  data on unaged and aged materials (Table 4) showed that in cases where the AIT increased, the  $\Delta H_c$  decreased with increasing oxygen pressure. This is in agreement with the expectation that pre-oxidized or aged polymers should have

<sup>1</sup>  $\tan \delta$  is generally equated with the resiliency of a material and is equal to  $E'/E''$ , where  $E'$  and  $E''$  are the storage and loss components of the complex modulus.

Table 4 — *Effect of Aging on Ignition and Combustion*<sup>a</sup>

	as-received AIT	O <sub>2</sub> -aged AIT		N <sub>2</sub> -aged AIT <sup>b</sup>
	°C	620 kPa-aged °C (%)	6200 kPa-aged °C (%)	6200 kPa-aged °C (%)
<i>Elastomers:</i>				
Neoprene C873-70	262	328 (+25)	317 (+21) <sup>c</sup>	255 (-3)
Viton A	257	282 (+10)	396 (+54)	278 (-6)
Silicone MVQ	281	283 ( <i>negl.</i> )	281 ( <i>negl.</i> )	...
<i>Thermoplastics:</i>				
Zytel 42	188	191 ( <i>negl.</i> )	203 (+8)	185 ( <i>negl.</i> )
Neoflon M400H- <i>amorphous</i>	382	380 ( <i>negl.</i> )	381 ( <i>negl.</i> )	...
Neoflon M400H- <i>crystalline</i>	377	384 ( <i>negl.</i> )	380 ( <i>negl.</i> )	...
Teflon 500A	431	>450 ( <i>negl.</i> )	423 ( <i>negl.</i> )	...
	as-received ΔH <sub>c</sub>	O <sub>2</sub> -aged ΔH <sub>c</sub>		N <sub>2</sub> -aged ΔH <sub>c</sub> <sup>b</sup>
	cal g <sup>-1</sup>	620 kPa-aged cal g <sup>-1</sup> (%)	6200 kPa-aged cal g <sup>-1</sup> (%)	6200 kPa-aged cal g <sup>-1</sup> (%)
<i>Elastomers:</i>				
Neoprene C873-70	6720	6300 (-6)	5900 (-12) <sup>c</sup>	6680 ( <i>negl.</i> )
Viton A	3020	2990 ( <i>negl.</i> )	3010 ( <i>negl.</i> )	3030 ( <i>negl.</i> )
Silicone MVQ	2310	2290 ( <i>negl.</i> )	2310 ( <i>negl.</i> )	...
<i>Thermoplastics:</i>				
Zytel 42	8830	7480 (-15)	7380 (-16)	7550 (-14)
Neoflon M400H- <i>amorphous</i>	1220	1210 ( <i>negl.</i> )	1220 ( <i>negl.</i> )	...
Neoflon M400H- <i>crystalline</i>	1230	1220 ( <i>negl.</i> )	1230 ( <i>negl.</i> )	...
Teflon 500A	1350	1320 ( <i>negl.</i> )	1360 ( <i>negl.</i> )	...

<sup>a</sup> Abbreviation used: AIT, autogenous ignition temperature; ΔH<sub>c</sub>, gross heat of combustion; *negl.*, negligible change.

<sup>b</sup> ... Denotes not tested.

<sup>c</sup> Severely degraded - no mechanical properties left.

less combustible or ignitable material remaining. Also, the decreases observed in the  $\Delta H_c$  of both O<sub>2</sub>- and N<sub>2</sub>-aged Zytel 42 specimens were virtually the same, and therefore essentially independent of the oxygen aging pressure. Restated, differences in the level of oxidation in aged materials can result in drastic property reductions; yet these same difference can have little or no effect on subsequent ignition or combustion. Furthermore, the decrease (-14 percent) in the  $\Delta H_c$  of N<sub>2</sub>-aged Zytel was virtually the same as the decrease (-15 to -15 percent) in the  $\Delta H_c$  of O<sub>2</sub>-aged Zytel. This indicates that the decrease in the  $\Delta H_c$  observed for Zytel 42 was attributable to prior heating, not oxygen exposure. In contrast, the  $\Delta H_c$  of O<sub>2</sub>-aged C873-70 specimens decreased (-6 to -12 percent), while that of N<sub>2</sub>-aged C873-70 specimens was virtually the same compared to unaged C873-70. This indicates that the decrease in the  $\Delta H_c$  observed for C873-70 was attributable to oxygen exposure. The tendency of MVQ, Neoflon M400H (both crystalline and amorphous grades), and Teflon 500A to ignite or combust was not appreciably influenced by prior aging.

## Conclusions

Evaluation of changes in the properties of O<sub>2</sub>-aged elastomers and plastics allowed several conclusions to be drawn regarding the effect of aging on ignition and combustion:

- Mechanical property reductions observed for C873-70 and Zytel 42 were a direct consequence of oxygen exposure. Similar mechanical property reductions observed for Neoflon M400H were due either to oxygen exposure and/or temperature.
- The poorer resistance to oxygen aging exhibited by C873-70 compared to the other materials tested in this study was attributed to the oxidation of unsaturated monomer repeat units, coupled with dehydrochlorination reactions
- Mechanical property reductions observed for Neoflon M400H probably resulted from temperature (annealing) effects, rather than exposure to oxygen.
- Inspection of AIT and  $\Delta H_c$  values measured for unaged and aged C873-70 and Viton A, revealed that as the AIT increased, and the  $\Delta H_c$  decreased with increasing level of prior aging.
- The tendency of MVQ, Neoflon M400H (both crystalline and amorphous grades), and Teflon 500A to ignite or combust was not affected by prior aging.
- Differences in the level of oxidation in aged materials can result in drastic property reductions; yet these same difference can have little or no effect on subsequent ignition or combustion (Zytel).

## Acknowledgments

Helpful discussions with D. D. Davis are gratefully acknowledged. The authors are also indebted to R. Massey for aging apparatus development, P. R. Spencer, S. Rojas, and B. Wolle for mechanical property testing, and J. Taylor, S. Bailey, and S. Motto for AIT and  $\Delta H_c$  determinations.

## References

- 
- [1] Waller, J. M., Hornung, S. D., and Beeson, H. D., "Fuel Cell Elastomeric Materials Oxygen Compatibility Testing: Effect of 450 and 6200 kPa Oxygen," *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Eighth Volume, ASTM STP 1319*, W. T. Royals, T. C. Chou, and T. A. Steinberg, Eds., American Society for Testing and Materials, 1997.
  - [2] Mucha, M., Kryszewski, "The Effect of Morphology on Thermal Stability of Isotactic Polypropylene in Air," *Colloid and Polymer Science*, Vol. 258, 743-752 (1980).
  - [3] Hirsch, D. B., Bunker, R. L., and Janoff, D. D., "Effects of Oxygen Concentration, Diluents, and Pressure on Ignition and Flame Spread Rates of Nonmetals: A Review Paper," *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Fifth Volume, ASTM STP 1111*, J. M. Stoltzfus and K. McIlroy, Eds., American Society for Testing and Materials, Philadelphia, 1991, pp. 179-190.
  - [4] Hirsch, D. B., and Bunker, R. L., "Effects of Diluents on Flammability of Nonmetals in High Pressure Oxygen Mixtures," *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Sixth Volume, ASTM STP 1197*, D. D. Janoff and J. M. Stoltzfus, Eds., American Society for Testing and Materials, Philadelphia, 1993, pp. 74-80.
  - [5] Wharton, R. K., Nolan, P. F., and Swindells, I., "Further Studies of Factors That Affect the Spontaneous Ignition Temperatures of Nonmetallic Materials in Gaseous Oxygen," *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Fourth Volume, ASTM STP 1040*, J. M. Stoltzfus, F. J. Benz, and J. S. Stradling, Editors., American Society for Testing and Materials, Philadelphia, 1989, pp. 106-124.
  - [6] Swindells, I., Nolan, P. E., and Wharton, R. K., "Spontaneous Ignition Temperatures of Nonmetals in Gaseous Oxygen," *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Third Volume, ASTM STP 986*, D. W. Schroll, Ed., American Society for Testing and Materials, Philadelphia, 1988, pp. 206-217.

- 
- [7] Schmidt, H. W., Forney, D. E., ASRDI Oxygen Technological Survey, Vol XI: Oxygen Systems Engineering Review, NASA, Washington, D.C., 1975.
- [8] Lowrie, R., "Heat of Combustion and Oxygen Compatibility," *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, ASTM STP 812, B. L. Werley, Ed., American Society for Testing and Materials, Philadelphia, 1983, pp. 84-96.
- [9] Carlsson, D. J. and Wiles, D. M., "Degradation," *Encyclopaedia of Polymer Science and Engineering*, Volume 4, 631-696 (1989)
- [10] Irani, R. S., Currie, J. L., Wilson, N. J., and Sanders, J., "Dimensional Changes in Elastomers Under High-Pressure Oxygen," *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Third Volume*, ASTM STP 986, D. W. Schroll, Ed., American Society for Testing and Materials, Philadelphia, 1988, pp. 346-358.
- [11] Waller, J. M., Newton, B. E., Haas, J. P., Beeson, H. D., "Comparison of the Dimensional Stability of Kel-F 81 and Neoflon CTFE M400H Polychlorotrifluoroethylenes used in Valve Seat Applications," *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Eighth Volume*, ASTM STP 1395, T. A. Steinberg, H. Barthelemy, Beeson, H. D., Newton, B. E., Eds., American Society for Testing and Materials, West Conshohocken, PA, 2000.
- 12 Sheirs, J., "Structure/Property Considerations for Fluoropolymers and Fluoroelastomers to Avoid In-Service Failure," in *Modern Fluoropolymers, High Performance Polymers for Diverse Applications*, Sheirs, Ed., J. Wiley & Sons, Chichester, Chapter 1, 1997
- 13 Wunderlich, B., *Macromolecular Physics*, Academic Press, Volume 1, Chapter 4, pp. 382-387, 1976.