Compatibility of an elastomeric material with hydrazine propellant

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Abstract. In aerospace industry, different kinds of elastomeric materials have been used in low-cost, light weight diaphragms and bladders in hydrazine propellant tanks. The compatibility of a new kind of vulcanized rubber compound 1803-1 with hydrazine propellant is studied experimentally, including immersion test, catalytic decomposition test and penetration test. The experiment process and test data are given about the permeation rate, mass change rate, volume change rate and other mechanical properties. The results show that most of the properties of material 1803-1 after compatibility test comply with the requirements of Chinese national standard. Rubber compound 1803-1 provides a reference when selecting the material for diaphragm tank bladders.

1. Introduction
As an important fuel storage equipment of an astrovehicle, diaphragm tanks can provide realiable storages of propellant during on-orbit mission, and provide sustaining propellant supply for the thrusters with stable flow rate during re-entry. In a diaphragm tank, liquid phase and gas phase are segregated by the diaphragm, so that the tank can adopt in any acceleration or any flow rate operation conditions. Thus, the performance of the diaphragm is significant for the propellant tanks. Diaphragm tanks can be easily folded and provide reusable storages of more than 50 cycles. However, one of the disadvantages is the low compatibility with liquid propellant. For N₂O₄ propellant, few kinds of rubber material are long-term compatible.

Researchers and engineers are searching for different materials for diaphragm tank bladders. Some kinds of rubber material compatible with anhydrous hydrazine were developed in past decades. Normane Beach [1] gave a rearrangement of the published compatibility data from the standpoint of the plastic (or elastomeric) material by grading their behaviours in different oxidizers and propellants. Among the listed materiales, ethylene propylene diene–modified (EPDM) elastomeric materials have been widely used in hydrazine propellant tanks [2]. Ethylene-propylene elastomer AF-E-332 is capable of ten-year 100-mission operation lifetimes with minimum refurbishment. Coulbert [3, 4] carried out long-time tests to compare compatibilities of two kinds of ethylene-propylene elastomers EPT-10 and AF-E-332 with hydrazine. In swelling test, a weight increase of over 30% for EPT-10 was recorded, compared to 3% for the AF-E-332. However, due to obsolescence issues with the EPDM rubbers used in the AF-E-332, a new formulation named SIFA has recently been developed using alternative EPDM rubbers [5]. Ping Li, et al. [6] studied the compability of EPDM AF-E-332 by histogram analyses of atomic force microscopy (AFM) phase images.
Aiming at an application on a return vehicle equipped with 15L diaphragm tanks, a new kind of elastomeric material, nominated with rubber compound 1803-1, is developed by Xi’an Aerospace Propulsion Institute. Its main component is vulcanized rubber, shown as khaki elastomer in Figure 1. The mechanical properties under normal conditions are listed in Table 1. In this paper, compatibility of this vulcanized rubber compound with anhydrous hydrazine is studied experimentally. To guarantee the long term stable storage of anhydrous hydrazine, compatibility tests including immersion, calalytic de-composition and penetration are carried out during a period of half year. Performances changes after tests are summarized. The compatibility of the rubber compound 1803-1 with anhydrous hydrazine is concluded.

**Figure 1.** Rubber compound 1803-1 material pecie.

**Table 1.** Mechanical properties of rubber compound 1803-1 under normal conditions.

| index | term                                      | value       |
|-------|-------------------------------------------|-------------|
| 1     | Hardness (Shore)                          | 70±5        |
| 2     | Tensile strength (MPa)                    | ≥14.5       |
| 3     | Stretching strength of 100 % (MPa)        | ≥2.0        |
| 4     | Elongation at rupture (%)                 | 400~630     |
| 5     | Tearing strength (N/mm)                   | ≥30         |
| 6     | Compression set (70℃×72h compression in hot air 20%) (%) | ≤35        |
| 7     | 120℃×72h hot air aging stretching strength (MPa) | ≥12.0       |
|       | 120℃×72h hot air aging elongation at rupture (%) | ≥200       |

2. Experimental

2.1. Experimental conditions

Temperature: Operating temperatures are (23±2)℃ for immersion test, 50℃ calalytic decomposition test and 43℃ penetration test.

Periods: Calalytic decomposition test: 15 days; Immersion test: 14days; Penetration test: 180 days.

Test medium: The test medium anhydrous hydrazine is achromatous transparent liquid. The anhydrous hydrazine should be up to standard of propellant-level according to national standard [7], as shown in Table 2.

**Table 2.** Anhydrous hydrazine composition.

| parameter             | Propellant-level | Normal-level |
|-----------------------|------------------|--------------|
| hydrazine %           | 98.5             | 98.5         |
| H₂O %                 | 1.0              | 1.0          |
| particulate matter mg/L | ≤1              | 1            |
| non-volatile residue % | ≤0.003           | 0.005        |
| Fe %                  | 0.0005           | 0.002        |
| chloride %            | 0.0005           | 0.0005       |
| CO₂ %                 | 0.02             | 0.02         |
2.2. **Experiment process**

2.2.1. **Immersion test.** The process of the immersion test is given below.

a) Every five sample pieces are grouped and suspended in a numbered immersion container with immersion time and operating temperature marked. The hanging height and the volume of anhydrous hydrazine are controlled to ensure the sample piece immersed in liquid phase. The sample should not contact the container wall.

b) The sample groups with different immersion time are placed in different test containers. Square sample pieces and dumbbell sample pieces with same test conditions are placed in the same closed container. Propellant is filled only after the air tightness test is acceptable.

c) Anhydrous hydrazine should be filled into the containers until the volume area ratio is 44.2 mm.

d) Perform the immersion test at room temperature, check the tightness of the containers during the test, and take appropriate measures in case of any leakage;

e) Open the container after 180 days, make the following examine.
   - Take out the sample and record the appearance of the test;
   - Clean the test pieces with distilled water and absolute ethanol, and wiped off the liquid on the piece surface with filter paper. Sample pieces are weighed after keeping the test pieces in the air for 30 minutes at room temperature. The mass change rates after the immersion are calculated. The volume of the sample is calculated by the drainage method, then volume change rates after the immersion are calculated;
   - The tensile strength test is performed to get the mechanical property of the sample piece, and mechanical properties such as tensile strength and elongation at break are obtained;
   - The composition of the propellant is analyzed based on Chinese national standard [8], and the amount of non-volatile residue and chemical composition change after the immersion test were measured.

f) After the tests above, the mass change rate, volume change rate, mechanical properties and propellant composition of the test piece under different time conditions can be obtained.

2.3. **Catalytic decomposition test.** The process of the immersion test is given below.

a) Refer to Chinese national standard [9] for catalytic decomposition test about the test pieces in anhydrous hydrazine;

b) The test lasts for 15 days, and the test temperature is 50°C;

c) Each kind of sample piece is tested for three times in parallel. The median value is taken as test results.

d) The volume of generated gas in the propellant decomposition is $V = V_f - V_0$, where $V_f$ is the final volume of gas, and $V_0$ is the initial volume of gas.

e) The gas generation rate $S_s$ in the standard state is converted by the following formula:

$$S_s = 2.694 \frac{V \cdot P}{F \cdot t_1 \cdot T}$$

(1)

where

- $S_s$: The gas generation rate in the standard state (mL/cm$^2$·d);
- $P$: Test environment atmospheric pressure (kPa);
- $F$: Surface area (cm$^2$);
- $t_1$: Test time (d);
- $T$: Test temperature (K).
2.3.1. **Penetration test.** The process of the penetration test is given below.

a) Refer to national standard [10] for the penetration test of material test pieces and anhydrous hydrazine;

b) The test lasts for 14 days, and the test temperature is 43°C;

c) Each kind of test piece was tested in parallel for three times, and the median value was taken as the test result, accurate to three decimal places.

d) The propellant penetration rate of the test piece is calculated by the following formula:

\[
V = \frac{W_0 - W_t}{S \cdot t}
\]

where

- \(V\) - Permeation rate, \((g/(m^2 \cdot h))\);
- \(W_0\) - Initial mass of the penetration cup, \((g)\);
- \(W_t\) - Final mass of the penetration cup, \((g)\);
- \(S\) - Active area, \((m^2)\);
- \(t\) - Penetration time, \((h)\).

3. **Results**

3.1. **Immersion test**

Based on national standard [8], a 180-day immersion test of the rubber compound 1803-1 in anhydrous hydrazine was performed, and change rate of mass and volume for the test piece were examined. Part of mechanical properties are measured based on the national standard [9]. The mechanical properties and propellant composition were analyzed. The test results are shown in Table 3, Table 4, Table 5, and Table 6, respectively.

| Test label | Period (day) | Initial mass (g) | Final mass (g) | Change ratio (%) | average |
|------------|--------------|------------------|----------------|------------------|---------|
| 1          | 180          | 1.4710           | 1.5488         | 5.2889           |         |
| 2          | 180          | 1.4295           | 1.5068         | 5.4075           |         |
| 3          | 180          | 1.4015           | 1.4770         | 5.3871           |         |
| 4          | 180          | 1.3272           | 1.4022         | 5.6510           |         |
| 5          | 180          | 1.3599           | 1.4338         | 5.4342           |         |

| Test label | Period (d) | Initial volume (mL) | Final volume (mL) | Change ratio (%) | average |
|------------|------------|---------------------|-------------------|------------------|---------|
| 1          | 180        | 1.2902              | 1.3484            | 4.5109           |         |
| 2          | 180        | 1.2545              | 1.3187            | 5.1176           |         |
| 3          | 180        | 1.2268              | 1.2937            | 5.4532           | 5.2320  |
| 4          | 180        | 1.1635              | 1.2265            | 5.4147           |         |
| 5          | 180        | 1.1830              | 1.2500            | 5.6636           |         |
### Table 5. Mechanical properties after immersion test.

| Test label | Period (d) | Tensile strength (Mpa) | Longation at rupture (%) | Permanent compression ratio (%) | Hardness (ShoreA) |
|------------|------------|------------------------|--------------------------|--------------------------------|------------------|
| 1          | 180        | 20.23                  | 672.95                   | 19.1                           | 61.0             |
| 2          | 180        | 18.62                  | 610.25                   | 13.1                           | 60.9             |
| 3          | 180        | 21.7                   | 661.52                   | 16.38                          | 60.5             |
| 4          | 180        | 22.58                  | 680.54                   | 18.3                           | 61.0             |
| 5          | 180        | 20.97                  | 657.99                   | 16.6                           | 61.0             |
| Mid-value  |            | 20.97                  | 661.52                   | 16.6                           | 60.9             |

### Table 6. Chemical constituents changes of anhydrous hydrazine after immersing 180 days.

| label | items                      | Initial value | Final value | Requirements in national standard[7] |
|-------|----------------------------|---------------|-------------|-------------------------------------|
| 1     | hydrazine %                | 99.76         | 99.80       | ≥98.5                               |
| 2     | H₂O %                      | 0.07          | 0.05        | ≤1.0                                |
| 3     | particulate matter mg/L    | 0.15          | 0.66        | ≤1                                  |
| 4     | non-volatile residue %     | 0.00048       | 0.00059     | ≤0.003                              |
| 5     | Fe %                       | 0.000027      | 0.000027    | ≤0.0005                             |
| 6     | chloride %                 | 0.000072      | 0.000030    | ≤0.0005                             |
| 7     | CO₂ %                      | 0.00093       | 0.00067     | ≤0.002                              |
| 8     | appearance                 | Colorless transparent uniform liquid | Colorless transparent uniform liquid | Colorless transparent uniform liquid |

#### 3.2. Catalytic decomposition test

Based on national standard [10], the decomposition rate of the test piece in anhydrous hydrazine during 15 days was measured. The test results are listed in Table 7.

### Table 7. Catalytic decomposition test results of rubber compound 1803-1.

| Pieces label | Period (d) | Volume of decomposition (mL) | Superficial area (cm²) | decomposition rate (mL/cm²d) | decomposition rate (mid-value) (mL/cm²d) | Requirements in national standard[11] (mL/cm²d) |
|--------------|------------|------------------------------|------------------------|------------------------------|------------------------------------------|-----------------------------------------------|
| 1            | 15         | 0.015                        | 5.5064                 | 0.0002                       |                                          |                                               |
| 2            | 15         | 0.185                        | 5.3270                 | 0.0020                       | 0.0002                     | <0.002                                        |
| 3            | 15         | 0.015                        | 5.0469                 | 0.0002                       |                                          |                                               |

#### 3.3. Penetration test

Based on national standard [12], the permeation rate of the test piece in the anhydrous hydrazine after test was measured for 336 hours duration. The test results are listed in Table 8, respectively.

### Table 8. Penetration test results of rubber compound 1803-1.

| Mass of penetration cup after 72 hours (g) | Final mass of penetration cup(g) | Effective penetration area(m²) | Penetration time (h) | Penetration rate (g/m²h) | Penetration rate (mid-value) (g/m²h) | Requirements in national standard[11] (g/m²h) |
|-------------------------------------------|---------------------------------|-------------------------------|----------------------|--------------------------|---------------------------------------|-----------------------------------------------|
| 78.323                                    | 78.3083                         | 0.000491                      | 336                  | 0.0891                   | 0.0891                               | <0.25                                         |
| 75.1259                                   | 75.0987                         | 0.000491                      | 336                  | 0.165                    | 0.0891                               | <0.25                                         |
| 74.9003                                   | 74.887                          | 0.000491                      | 336                  | 0.0806                   | 0.0891                               | <0.25                                         |
4. Conclusions
The catalytic decomposition test, permeation rate test and immersion test of the rubber compound 1803-1 were carried out in the anhydrous hydrazine medium. The results show that the catalytic decomposition rate of rubber compound 1803-1 is 0.0002 mL/cm²•d; The rate test results show that the permeation rate of 1803-1 rubber to anhydrous hydrazine is 0.0891 g/m²•h. These performances of elastomeric material are complied with national standard [11], usable under the compatibility restrict for hydrazine propellants.

The 180-day normal temperature immersion test showed that the mass change rate of the test piece was 5.4%, and the volume change rate was 5.2%. The analysis results show that the quality of anhydrous strontium does not change significantly before and after immersion. Although the particulate matter and non-volatile residue increase after immersion, it still meets the technical specifications of Chinese national standard [7], and the non-volatile residue increment is less than 50 ppm. It is indicated that the rubber compound 1803-1 does not have a concernful effect on the anhydrous hydrazine.

After immersion test, the mechanical properties of 1803-1 still shows good tensile strength and elongation. However, the shore hardness is only 60.9, decreased about 11.7%~14.2%, which does not meet the requirement for Grade B anhydrous hydrazine resistant in standard [11]. It should be cautious when being selected as the material for diaphragm tank bladders.

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