



*Cent. Eur. J. Energ. Mater.* 2021, 18(1): 112-123; DOI 10.22211/cejem/135053

Article is available in PDF-format, in colour, at:

[http://www.wydawnictwa.ipo.waw.pl/cejem/Vol-18-Number1-2021/CEJEM\\_01167.pdf](http://www.wydawnictwa.ipo.waw.pl/cejem/Vol-18-Number1-2021/CEJEM_01167.pdf)



Article is available under the Creative Commons Attribution-Noncommercial-NoDerivs 3.0 license CC BY-NC-ND 3.0.

*Research paper*

## Studies on the Properties of a Putty-like Explosive with a Silicone Binder

Karol Zalewski\*, Zbigniew Chylek, Waldemar A. Trzciński

*Military University of Technology, 2 Kaliskiego Street,  
00-908 Warsaw, Poland*

\* *E-mail:* karol.zalewski@wat.edu.pl

**Abstract:** In this work a new putty-like explosive containing 1,3,5-trinitro-1,3,5-triazine (RDX) and polydimethylsiloxane (PDMS) was prepared and its properties were studied. The plasticity and the decomposition temperature of the explosive were determined. The sensitivity to friction, impact, shock wave and internal ignition were tested. The heats of combustion and explosion of the formulation were also measured. The diameter and critical layer as well as the detonation velocity of charges of different diameters were determined. The research results obtained were analyzed.

**Keywords:** polydimethylsiloxanes, silicone, explosive, RDX

### 1 Introduction

Polysiloxanes (silicones) are polymers composed of alternately arranged silicon and oxygen atoms, with side groups, usually organic, attached to the silicon atoms. They show a number of interesting properties [1, 2], thanks to which there is a possibility for their implementation in PBXs (Plastic Bonded Explosives). The polymers used in PBXs must meet a number of requirements that guarantee high chemical and physical stability of the explosive formulations and high detonation properties. The polymers used in PBX formulations should have

the following properties:

- low glass transition temperature,
- the possibility of modifying the viscosity by changing the temperature, plasticizing, curing,
- good mechanical properties,
- thermal resistance,
- chemical stability,
- high bonding affinity to explosive crystals,
- low price and high availability.

Polysiloxanes meet most of the requirements listed. The most important disadvantage, preventing the proper implementation of silicones in explosive formulations, is their poor affinity for the crystals of the explosive. Nevertheless, reports of polysiloxanes being used in PBXs can be found in the literature [3-7]. Formulations containing FOX-7 and HMX mixed with polyNIMMO and silicone grease were investigated in [3]. These formulations, containing the addition of polysiloxane, showed a friction sensitivity greater than 360 N and an impact sensitivity greater than 20 J. One of the explosives tested, with a density of 1.55 g/cm<sup>3</sup> and placed in a PVC tube of diameter 10 mm, detonated at a velocity of 6960 ± 70 m/s. Linear shaped charges with flexible formulations containing room-temperature-vulcanizing (RTV) silicones were investigated in [4]. The densities of the formulations were from 1.28 to 1.40 g/cm<sup>3</sup>, and the content of the RTV silicones was varied from 20 to 30%. The explosives, formed into flat charges (60 by 200 mm), had detonation velocities from 5620 to 7100 m/s. The self-supporting nature of the explosives led to the elimination of a metal cover, which reduced the negative impact of metal fragments on the surroundings. The effect of ageing time and temperature on the detonation velocity of a formulation consisting of 80% PETN and 20% Sylgard silicone rubber were investigated in [5]. The authors proposed an empirical equation to determine the shelf-life of the composition, depending on the storage temperature. The authors of Refs. [6, 7] signal the good phlegmatizing properties of silicones and their neutral influence on the thermal stability of the formulations obtained. The tested formulations were obtained by mixing 88% crystalline nitramine (RDX, HMX, BCHMX or HNIW) and 12% polydimethylsiloxane (PDMS). The detonation velocities and friction and impact sensitivities were compared to those of similar formulations with Viton A fluoropolymer and polybutadiene (HTPB). According to the authors, the use of PDMS may be an optimal solution ensuring high detonation parameters and low sensitivity of a formulation.

The aim of the present study was the preparation and characterization of a simple putty-like explosive formulation, containing 73% of highly ground crystalline RDX and 27% of a highly viscous PDMS-based silicone grease. The formulation is hereafter referred to as RDXSil1.

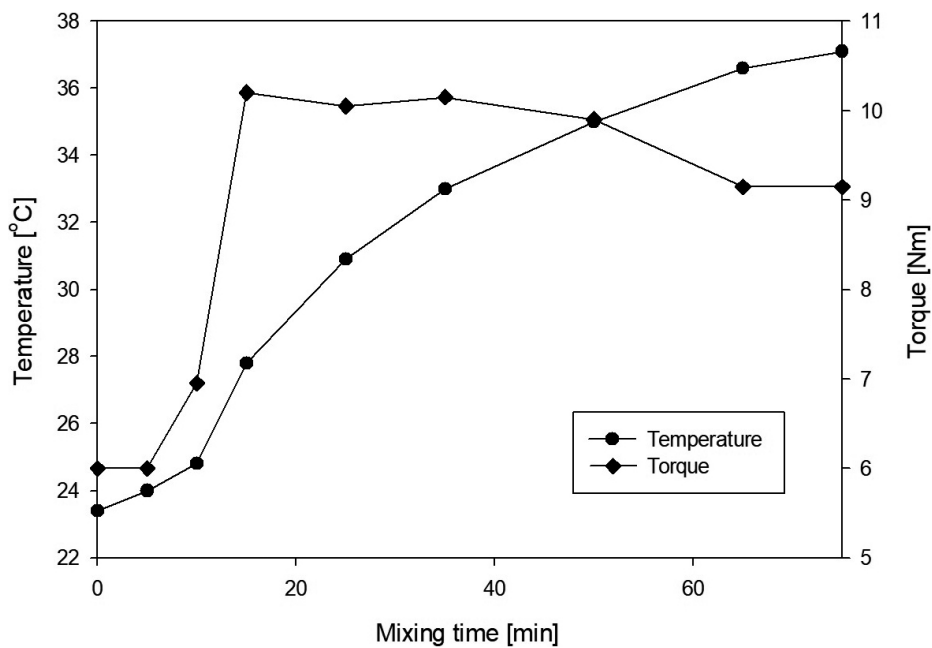
## 2 Preparation of RDXSil1

### 2.1 Ingredients

Coarse crystalline RDX was wet milled in a ball mill. The RDX was then wet sieved through a 75  $\mu\text{m}$  sieve and dried. The fraction below 75  $\mu\text{m}$  was used in the explosive composition. The second ingredient was silicone grease Silpasta A produced by Chemical Plant “Silikony Polskie” Ltd. The density of Silpasta A was from 1.02 to 1.04  $\text{g}/\text{cm}^3$  according to the technical data sheet.

### 2.2 Mixing process

The mixer used in the study was a ZAMAK 947 equipped with two paddle agitators. The volume of the mixing chamber allowed 250 g of the formulation to be prepared in a single batch. All of the required mass of silicone grease (67.5 g – 27%) was loaded into the mixer, and then portions of crystalline RDX were added every 5 min. The mixing speed was 60 rpm. The mass of the first portion of RDX was 62.5 g, the second and third portions were 60 g each, giving a total of 182.5 g (73%). The mixing was continued for 60 min after the last portion had been added. The temperature and the torque on the drive shaft of the mixer were registered (Figure 1). There was an increase in the torque with the addition of RDX, as well as an increase in temperature, related to the resistance of the mixed mass. Figure 2 shows a photograph of the RDXSil1 formulation.



**Figure 1.** Changes in the temperature and torque during the mixing of RDXSil1



**Figure 2.** RDXSil1 formulation

## 3 Experimental

### 3.1 Density

The RDXSil1 formulation was loaded into a plastic tube with known dimensions and mass, and weighed on an analytical balance. The process was repeated five times and the density was calculated as the arithmetic mean. The density was 1.45 g/cm<sup>3</sup>.

### 3.2 Plasticity

The plasticity of the composition was tested as described in [8]. An RDXSil1 sample with diameter 30 mm and height 45-50 mm ( $h_0$ ) was pressed for 10 s with a weight of 3.6 kg, which corresponded to a pressure of 0.05 MPa. After removing the loading, the height of the sample ( $h_1$ ) was measured, and then its plasticity ( $P$ ) was calculated according to the Equation 1. The test was performed at 20 °C. The plasticity of RDXSil1 was equal to 13%. For comparison, the plasticity of Semtex 1H, determined by this method and at the same temperature, was 29%. The RDXSil1 formulation is therefore less plastic than Semtex 1H.

$$P = \frac{h_0 - h_1}{h_0} \times 100 \% \quad (1)$$

### 3.3 Decomposition temperature

A thermal mineralizer with Wood's alloy was used to determine the decomposition temperature. A 0.40 g sample of the formulation was placed in an aluminum tube and then placed in the mineralizer at 170 °C. The temperature was then increased to 240 °C at a rate of 5 °C/min. The temperature at which signs of decomposition of the sample (smoke, flame, hiss) were observed was taken as the decomposition temperature. The determined decomposition temperature of RDXSil1 was 218 °C.

To check for any negative interactions between RDX and the silicone, additional DTA/TG analysis was performed using a Labsys SETRAM thermal analyzer. The sample mass was 6.5 mg, the heating rate was 5 °C/min and the argon gas flow was 50 cm<sup>3</sup>/min. The onset point of the exothermic peak associated with decomposition of the sample was 210.9 °C. The difference between the decomposition temperatures determined in the mineralizer and the DTA/TG apparatus is small and results from a large difference in the masses of the tested samples.

### 3.4 Impact and friction sensitivity

The impact sensitivity was tested using a fall hammer according to the standard [9]. The lowest impact energy value at which the signs of sample decomposition (flame, crackle, smoke, smell) were noticeable in at least one of six trials was considered the impact sensitivity. Samples weighing 0.06 g were tested (volume 40 mm<sup>3</sup> [9]). The impact sensitivity of RDXSi11 was equal to 28 J.

The friction sensitivity was tested using a friction apparatus according to the standard [10]. The lowest normal force value at which the signs of sample decomposition (flame, crackle, smoke, smell) were noticeable in at least one of six trials was considered the friction sensitivity. The friction sensitivity of RDXSi11 was equal to 330 N.

### 3.5 Shock sensitivity

The gap test described in [11] was performed to determine the shock sensitivity of the composition. The test setup consisted of a donor with a diameter of 50 mm (RDX phlegmatized by wax, 80 g, 1.67 g/cm<sup>3</sup>), a block made of polyamide, a copper tube with an internal diameter of 25 mm loaded with 70 g of RDXSi11, a steel plate (witness) and a steel sleeve. The shock sensitivity was defined as the greatest thickness of the inert barrier at which witness plate puncture occurred. The shock sensitivity was 43 mm. For comparison, the shock sensitivity of TNT in this test was also 43 mm [11].

### 3.6 Internal ignition sensitivity

The internal ignition test was carried out in a seamless steel tube closed on both sides with two steel caps. The steel tube had an inner diameter of 31.4 mm, a wall thickness of 6 mm, and a length of 253.5 mm. The formulation (276 g) was loaded into the tube, along with the ignition primer black powder (1.5 g) placed under one of the caps. The electric cables led outside through a small hole in the cap. There was no change in the tube integrity after initiation of the primer. Burning had stopped quickly after initiation and most of the formulation was intact. The mass of the system after the test had decreased by 2 g. The result of the test can be classified as a “0/1” category [12], as the tube was not damaged and the change in mass was negligible.

### 3.7 Heat of combustion and heat of detonation

Approx. 0.3 g of RDXSi11 was placed in a calorimetric bomb (volume 350 cm<sup>3</sup>), which was then filled with either oxygen or argon to a pressure of 2 MPa. The bomb was placed in a calorimeter filled with water for 30 min before the test. A resistance wire was used to ignite the sample. The heat of combustion

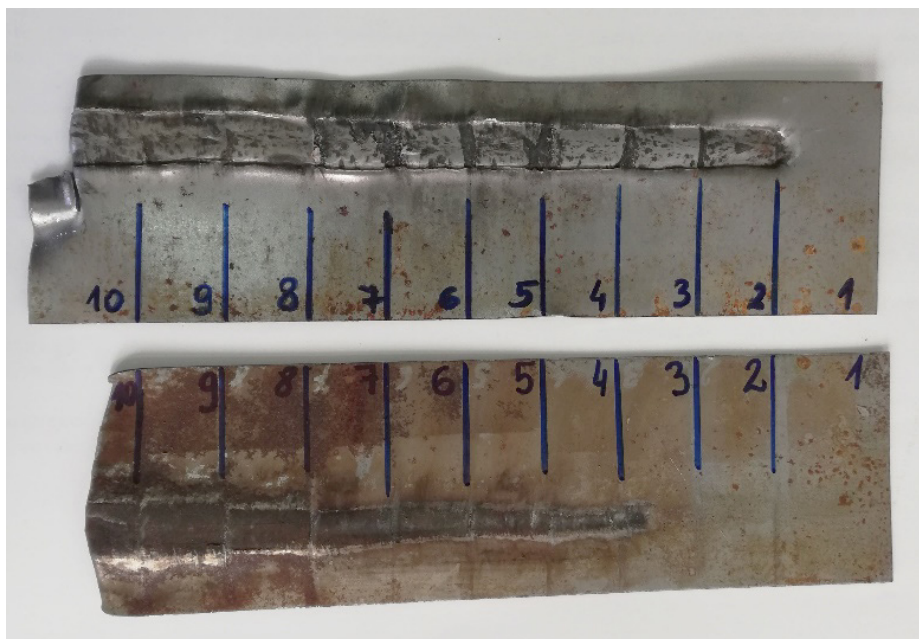
of RDXSi11 in oxygen, determined on the basis of three trials, was  $13480 \pm 69$  J/g. A ball of porous silica was found in the bomb after the test. The heat of combustion in argon was determined on the basis of one successful trial and was 3507 J/g. Combustion in argon generated a large amount of white foam, which was likely to be silica fibers.

A 5600 cm<sup>3</sup> calorimetric bomb was used to determine the heat of detonation. A sample of mass approx. 20 g was placed in the bomb, which was then filled with argon to a pressure of 2 MPa. The bomb was placed in a calorimeter filled with water for 30 min before the test. An electric detonator with a blasting cap was used to initiate the detonation. The heat of the detonator was taken into account in the calculations [13]. The heat of detonation of RDXSi11, determined on the basis of three trials, was  $4010 \pm 14$  J/g.

### 3.8 Critical diameter and layer

A telescopic charge was prepared with diameters from 10 to 1 mm every 1 mm. The formulation was loaded into 20 mm long paper tubes. The charge was placed on a steel plate and detonated with an electric detonator. The smallest diameter at which detonation occurred was considered as the critical diameter.

The critical layer was determined using stepped charges. The charges, 10 mm wide and 20 mm long, had a thickness of 10 to 1 mm, in steps of 1 mm. The RDXSi11 charge composed of the stepped charges was placed on a steel plate and detonated in a similar manner to the critical diameter test. The smallest thickness at which detonation occurred was considered the critical layer. Figure 3 shows the steel plates after the critical diameter and critical layer tests.



**Figure 3.** The steel plates after the critical layer test (layer above) and critical diameter test (layer below)

In the critical layer test a clear boundary was observed between charges with 2 and 1 mm thickness. Thus, the critical layer was equal to 2 mm. In the critical diameter test, the detonation process entered the charge with 3 mm diameter, but ceased before the end of the charge. The critical diameter of RDXSil1 was equal to 4 mm.

### 3.9 Detonation velocity

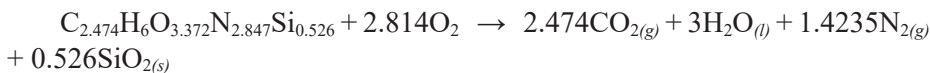
The detonation velocity was measured in charges with four different diameters: 10, 15, 20 and 30 mm. In the cases of the first three charges, the formulation was loaded into 200 mm long paper tubes. In the fourth case, a plastic tube with a wall thickness of 1 mm, made of poly(lactic acid), was used. Short-circuit sensors connected to an electronic timer were used. There were three 30 mm long measuring bases in each charge. The detonation was initiated with an electric detonator. Signal registration for some sensors ended with failure. The measured detonation velocities were equal to 6600, 7000, 6900 and 7100 m/s for the diameters of 10, 15, 20 and 30 mm, respectively.



## 4 Theoretical Calculations

The CHEETAH thermochemical code [14] and the BKWS constants [15] for the BKW equation of state for gaseous detonation products were used to calculate the detonation velocity, pressure, temperature and energy. The detonation energy was defined as the maximum work performed by the detonation products during expansion from the volume at the Chapman-Jouguet point to infinite volume, which was reduced by the shock energy at the front of the detonation wave [16]. The detonation energy is approximately equal to the calorimetric heat of detonation [17].

In order to calculate the detonation parameters of RDXSi1, the enthalpy of formation was determined using the calorimetric heat of combustion in oxygen. For the specified composition of RDXSi1, the following equation for the combustion in oxygen was used:



Using Hess's law, the enthalpy of formation was calculated to be  $-363.37$  kJ/mol. The detonation parameters calculated using CHEETAH are presented in Table 1.

**Table 1.** The theoretical detonation parameters of RDXSi1

Parameter	Value
Detonation velocity [m/s]	6949
Detonation pressure [GPa]	15.4
Detonation temperature [K]	3191
Detonation energy [J/g]	4447

## 5 Summary of Results and Discussion

The experimental parameters of the RDXSil1 formulation are summarized in Table 2.

**Table 2.** The experimental parameters of RDXSil1

Parameter	Value
Density [g/cm <sup>3</sup> ]	1.45
Plasticity [%]	13
Heat of combustion (oxygen) [J/g]	13480 ±69
Heat of combustion (argon) [J/g]	3507
Temperature of decomposition [°C]	218
Impact sensitivity [J]	28
Friction sensitivity [N]	330
Shock sensitivity [mm]	43
Critical diameter [mm]	4
Critical layer [mm]	2
Heat of detonation [J/g]	4010 ±14
Detonation velocity (Φ10 mm) [m/s]	6600
Detonation velocity (Φ15 mm) [m/s]	7000
Detonation velocity (Φ20 mm) [m/s]	6900
Detonation velocity (Φ30 mm) [m/s]	7100

The high content of the silicone binder lowered the density of the RDXSil1 formulation. The determined decomposition temperature suggested that there were no negative interactions between the binder and the crystalline nitramine. The decomposition of the formulation was a direct result of the RDX decomposition. The presence of polydimethylsiloxane provided a much lower friction sensitivity compared to pure ground RDX (172 N). The impact sensitivity was also low (28 J); for pure ground RDX it was 3 J. The shock sensitivity was equal to that of cast TNT with a density of 1.6 g/cm<sup>3</sup> [11].

The heat of detonation of RDXSil1 is similar to that of TNT (4050 J/g [13]). A comparison of the theoretical detonation velocity (Table 1) with the results of the detonation velocity measurements (Table 2) suggests that the ideal detonation regime was not achieved with the 10 mm diameter charge. The detonation velocity of the RDXSil1 formulation is slightly higher than that of TNT. For example, cast TNT detonates at a velocity of 6730 m/s at a density of 1.6 g/cm<sup>3</sup>, and at a velocity of 6820 m/s at a density of 1.61 g/cm<sup>3</sup> [11].

However, the theoretical detonation pressure of RDXSi11 (15.4 GPa) is lower than the detonation pressure of TNT (18.12 GPa from CHEETAH; 20.1 GPa from the plate dent test for TNT of density 1.61 g/cm<sup>3</sup> [11]).

## 6 Summary

The new RDXSi11 formulation is a putty-like explosive with good detonation performance, comparable to TNT, and low friction and impact sensitivity. RDXSi11 achieved a very good result in an internal ignition sensitivity test. The results of these studies show that it is possible to use polysiloxanes in putty-like explosives.

## Acknowledgements

This work was financed by Military University of Technology under research project UGB 761.

## References

- [1] Mazurek, M. Organosilicon Polymers. (in Polish) In: *Chemia polimerów*. Vol. 2 (Florjańczyk, Z.; Penczek, S., Eds.), Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa, **2002**; ISBN 83-7207-368-6.
- [2] Chandrasekhar, V. *Inorganic and Organometallic Polymers*. Springer, Berlin, **2005**; ISBN 978-3-540-26215-2.
- [3] Chyłek, Z.; Jurkiewicz, R. Investigation of the Properties of Polymer Bonded Explosives Based on 1,1-Diamino-2,2-dinitroethene (FOX-7) and 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX). *Cent. Eur. J. Energ. Mater.* **2016**, 13(4): 859-870.
- [4] Nikolczuk, K.; Hadzik, J.; Wilk Z. New Shaped Charges with Elastic Properties as an Example of the Use of Silicone Polymers in the Technology of Explosives. (in Polish) *CHEMIK* **2013**, 67(1), 33-40.
- [5] Golopol, H. Hetherington, N.; North, K. Aging Effects on The Detonation Velocity of XTX-8003. *J. Hazard. Mater.* **1980**, 4: 45-55.
- [6] Elbeih, A.; Zeman, S.; Jungova, M.; Vavra, P.; Akstein, Z. Effect of Different Polymeric Matrices on Some Properties of Plastic Bonded Explosives. *Propellants Explos. Pyrotech.* **2012**, 37: 676-684.
- [7] Elbeih, A.; Zeman, S.; Jungova, M.; Akstein, Z. Effect of Different Polymeric Matrices on the Sensitivity and Performance of Interesting Cyclic Nitramines. *Cent. Eur. J. Energ. Mater.* **2012**, 9(2): 131-138.

- [8] Zeman, S.; Jungova, M. *Technology of Explosives, A Textbook*. University of Pardubice, Pardubice, **2019**.
- [9] Polish European Standard PN-EN 13631-4 *Explosives for Civil Use – High Explosives – Determination of Sensitiveness to Impact of Explosives*. (in Polish) **2004**.
- [10] Polish European Standard PN-EN 13631-3 *Explosives for Civil Use – High Explosives – Determination of Sensitiveness to Friction of Explosives*. (in Polish) **2006**.
- [11] Trzciński, W.A.; Lasota, J.; Chyłek, Z.; Szala, M.; Paszula, J. NTO-based Melt-cast Insensitive Compositions. *Cent. Eur. J. Energ. Mater.* **2016**, *13*(3): 592-611.
- [12] *Energetic Materials Testing and Assessment Policy Committee, Manual of Tests*. Defence Ordnance Safety Group, Great Britain, **2005**.
- [13] Cudziło, S.; Trębiński, R.; Trzciński, W.A.; Wolański, P. Comparison of Heat Effects of Combustion and Detonation of Explosives in a Calorimetric Bomb. *Proc. 29<sup>th</sup> Int. Annu. Conf. ICT*, Karlsruhe, Germany, **1998**.
- [14] Fried, L.E. *CHEETAH 1.39 User's Manual*. Lawrence Livermore National Laboratory, Livermore, UCRL-MA-11754 Rev.3, CA, USA, **1996**.
- [15] Hobbs, M.L.; Baer, M.R. Non-ideal Thermoequilibrium Calculations Using a Large Product Species Data Base. *Shock Waves* **1992**, *2*(3): 177-187.
- [16] Fickett, W.; Davis, W.C. *Detonation*. University of California Press, Berkeley, **1979**.
- [17] Trzciński, W.A.; Szymańczyk, L.; Kramarczyk, B. Determination of the Equation of State for the Detonation Products of Emulsion Explosives. *Cent. Eur. J. Energ. Mater.* **2019**, *16*(1), 49-64.

Received: September 17, 2020

Revised: March 26, 2021

First published online: March 30, 2021