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Effect of plasticiser addition on the properties of solid heterogeneous rocket propellants
Wpływ dodatku plastyfikatora na właściwości stałych heterogenicznych paliw rakietowych

Michał Chmielarek*), Katarzyna Cieślak, Angela Sperelakis

Faculty of Chemistry, Warsaw University of Technology, 3 Noakowskiego Street, 00-064 Warsaw, Poland
** E-mail:* michal.chmielarek@pw.edu.pl

ORCID Information:
Chmielarek M.: 0000-0002-2091-4120
Cieślak K.: 0000-0002-5418-5763

***Abstract**: The effect of plasticiser addition on the properties of solid heterogeneous rocket propellant, was investigated. The main properties which should be affected by a plasticiser in a solid rocket propellant are its mechanical properties and rheology. Hydroxyl-terminated polybutadiene (HTPB) and an oxidiser – ammonium chlorate(VII), NH_4ClO_4 – were used as the basic propellant components. The oxidiser was added as two fractions differing in crystal size. Technological additives such as a stabiliser or crosslinking agent were also used. Dimeryl diisocyanate (DDI) was used as a crosslinking agent. The effect of three different plasticisers (dioctyl adipate, dioctyl terephthalate and dioctyl sebacate) on the properties of solid heterogeneous rocket propellant was investigated. 2.5%, 5% and 7.5% of each plasticiser by weight of the fuel were used. Among others, the life of such mixtures of liquid fuel components and the mechanical properties of the cured propellants were determined. It was shown that the type and amount of plasticiser affects both the life and mechanical properties of the solid heterogeneous rocket propellant.*

***Streszczenie:** Zbadano wpływ dodatku plastyfikatora na właściwości stałego heterogenicznego paliwa rakietowego. Podstawowe właściwości na jakie powinien mieć wpływ plastyfikator w stałym paliwie rakietowym to właściwości mechaniczne oraz reologia paliwa. Jako podstawowe składniki paliwa użyto polibutadien zakończony grupami hydroksylowymi (HTPB) oraz utleniacz – chloranu(VII) amonu, NH_4ClO_4. Utleniacz był dodawany w dwóch frakcjach różniących się wielkością kryształów. Stosowano również dodatki technologiczne takie jak stabilizator czy środek wiążący. Jako środka sieciującego użyto izocyjanianu dimerylu (DDI) w stosunku NCO/OH = 0,9. Zbadano wpływ trzech różnych plastyfikatorów, adypinianu dioktylu, tereftalanu dioktylu i sebacynianu dioktylu, na właściwości stałego heterogenicznego paliwa rakietowego. Zastosowano 2,5%, 5% oraz 7,5% każdego plastyfikatora w masie paliwa. Wyznaczono między innymi czas życia takich mieszanin składników ciekłych paliwa oraz właściwości mechaniczne utwardzonych paliw. Wykazano, że rodzaj i ilość użytego plastyfikatora ma wpływ zarówno na czas życia jak i na właściwości mechaniczne stałego heterogenicznego paliwa rakietowego.*

Keywords: *hydroxyl-terminated polybutadiene, HTPB, plasticizer, dioctyl adipate, ADO, dioctyl terephthalate, TDO, dioctyl sebacate, SDO*
Słowa kluczowe: *α,ω-dihydroksypolibutadien, HTPB, plastyfikator, adypinian dioktylu, ADO, tereftalan dioktylu, TDO, sebacynian dioktylu, SDO*

1. Introduction

Solid heterogeneous rocket propellants (SHRPs) are manufactured in both armament and civilian industries. They are classified as explosives and are used in military rocket technologies and space technology for first stage launchers [1].
The production of SHRP is complex and depends on appropriately selected factors at all technological stages, such as mixture temperature or pressure during mixing, as well as the correct composition or ratio of raw materials used. The process consists of several steps, such as mixing, casting and curing, which are equivalent to each other in terms of complexity [2, 3]. In the mixing stage, liquid and solid chemicals are combined to produce a semi-liquid mass. The resulting mass has the properties of a non-Newtonian and pseudo-plastic fluid and is also known as a highly filled suspension (HSF). This suspension is cast and moulded into a suitable shape of the selected size. After sufficient time, the suspension becomes a solid. Its ignition can be initiated by a firing impulse, even in the absence of oxygen from the air.
Heterogeneous solid propellants are composed of several ingredients, in particular a polymer and an oxidiser. All solid components are evenly distributed in the polymer matrix. This polymer can be HTPB [4]. In addition, various technological additives, such as binder, catalyst or plasticiser, are added to the propellant to make it more elastic. Other additives can be energetic additives, burning rate modifiers and others [3, 5, 6].
The mechanical properties of HTPB-based propellants continue to be an important part of ongoing research work in solid rocket propellant technology. Tests are carried out to determine the maximum tensile strength of a sample containing HTPB as a binder [7, 8]. The most important aspect of a propellant is its structure, while the related properties determine how efficient the propellant will be in use. Propellants are inherently elastic and resilient, which means that the main asset of their mechanical properties is their tensile strength. It is important to know the parameters for a given propellant at low temperatures and at high stress. Experimental results indicated that HTPB has large deformation limit capabilities, even at low temperatures as well as at high stress values. Elasticity increases with decreasing temperature and increasing stress. However, at room temperature, damage can occur to the propellant structure and even more so to its matrix, rendering the propellant unusable. The difference between room temperature and low temperature is that, at low temperature, the propellant may be in a vitreous state. Propellants containing HTPB take several days to crosslink and cure, but when the crosslinking temperature is raised above 80 ºC, the density of the propellant increases and it becomes stiffer. Maximum strength during stretching also increases. An oxidation reaction can also occur in the propellant matrix, leading to chain decomposition, which causes the propellant to soften. As a result, the strength of the propellant decreases but it becomes more extensible. However, cross-linking under oxidation causes the propellant to become hard and less flexible [9, 10].
A plasticiser is a liquid organic, non-volatile, non-reactive compound with low viscosity. It is added to the propellant mixture in small quantities. Thanks to its presence, the viscosity of the suspension is reduced, which facilitates mixing, casting and moulding. The presence of a plasticiser also extends the technological useful life and improves the mechanical properties of the propellant. A plasticiser is added to the propellant to improve processability, elasticity and mechanical properties. This effect occurs by reducing the cohesion effect between the polymer chains, which increases the mobility of such a segment, thereby reducing the vitrification temperature. In summary, a plasticiser assists the movement of the polymer chain, without the occurrence of a chemical reaction. The desired plasticiser amount is around 20 to 45% (relative to the polymer), otherwise problems may arise during storage (e.g. plasticiser evaporation).
The requirements for plasticisers used for SHRP are: low molecular weight, high boiling point, low volatility and compatibility with the other propellant components, and a high heat of combustion. When choosing

a plasticiser, attention should be paid to its solubility in the polymer. It does not have to be high, just sufficient. This means that a plasticiser must dissolve better in it than in the inert phase which surrounds the propellant. Otherwise, this could lead to the propellant's reduced adhesion to the engine casing or the thermal insulation. If the plasticiser has a high vapour pressure, then the composition of the propellant can change over time, which also alters its properties. This means that the choice of plasticiser affects the properties of the SHRP and allows it to be modified to achieve the desired results [3, 11].

An SHRP is a multicomponent mixture consisting mainly of two or three solid components, one of which must be an inorganic oxidant. Thus, in the first stage of the process, there is a HFS, which is characterised by a high concentration of solid phase particles. Its apparent viscosity depends on, among other things, the viscosity of the liquid phase, the shape and size of the solid particles and the content of each of the solid phase fractions, temperature and time. It is also referred to as its life, i.e. the time during which the HFS is sufficiently fluid for casting and moulding. The minimum life, i.e. the processability of the propellant is approximately 6 h. The viscosity of such an HFS after this time should be less than or equal to 1.5 kPa. Plasticisers are added to the propellant to extend life or reduce viscosity, making them one of the most important ingredients. [3, 10, 12-14].

The lack of availability of SHRP components on the domestic market is a common problem in solid rocket propellant production technology. This article presents tests on the effect of a plasticiser on the properties of solid rocket propellants. Three different plasticisers were used: the most popular and widely used in SHRP technology, dioctyl adipate (DOA), as well as domestically available dioctyl sebacate (DOS) and dioctyl terephthalate (DOT), which meet the requirements for these compounds as SHRP components. The percentage of plasticiser in the propellants made was altered and, on this basis, changes in the properties of a given sample, such as viscosity or tensile strength, were studied.

2. Experimental part

2.1. Raw materials used in the production of SHRP

The raw materials listed in Table 1 were used for the experimental tests. All the raw materials were commercial products and did not undergo additional purification or drying. The plasticisers – DOA, DOS and DOT – are manufactured domestically and there is no problem with their market availability. Table 2 shows their properties, while Figures 1-3 show their structure. These plasticisers differ in their physico-chemical properties (different setting points and viscosity values) and molecular structure (differences in alkyl chain length or presence of an aromatic ring).

Table 1. Properties of individual raw materials

Raw material	Manufacturer	Properties
HTPB R45 HTLO	Cray Valley	M_n = 4000 g/mol, L_{OH} = 48 mg KOH/g
Dimeryl diisocyanate (DDI)	CRS Chemicals	NCO content = 14%
NH_4ClO_4	no data	meets the requirements of MIL-A-192B
DOA	Boryszew ERG	purity ≥95%
DOS	Boryszew ERG	purity ≥95%
DOT	Boryszew ERG	purity ≥95%
HX-752*)	Yingkou Tanyun CRIC	purity ≥99.0%
AO 2246**)	Sigma-Aldrich	purity 100%

*) 1,1'(1,3-phenylenedicarbonyl)bis[2-methylaziridine]

**) 2,2′-methylenebis(6-tert-butyl-4-methylphenol)

Table 2. Properties of individual plasticisers

Plasticiser	Density [g/cm^3]	Setting point [°C]	Viscosity [mPa·s] / Temperature [°C]
DOA	0.98	–70	14 / 20
DOS	0.91-0.92	–48	59 / 20
DOT	0.99	–67	66 / 25

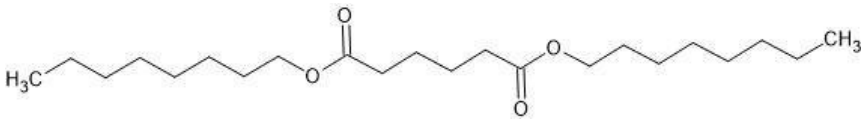

Figure 1. DOA structure

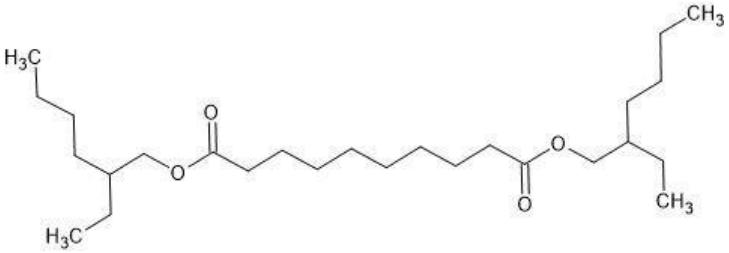

Figure 2. DOT structure

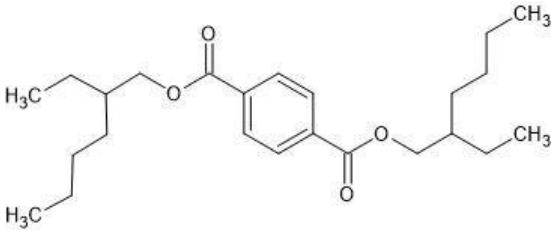

Figure 3. DOS structure

2.2. Testing methods

2.2.1. Viscosity measurement

The viscosity of the prepared samples was measured using a Brookfield DV2T Viscometer. An attachment was used to measure small-volume samples using the SC4-21 spindle. The tests were carried out at 65 °C (propellant cross-linking temperature). Each sample stayed in the viscometer for about 5.5 h in order to examine the liquid phase life of the propellant as accurately as possible. The amounts of individual components in the viscosity test samples were added in proportion to the amounts used in the given propellant type.

Table 3. Sample compositions of liquid components for viscosity measurements

Raw material	Mass [g] in propellant for plasticiser content			
	2.5% / 5% / 7.5%	2.5%	5%	7.5%
HTPB	35	10	10	10
Plasticiser	10/20/30	2.86	5.71	8.57
DDI	7.84	2.24	2.24	2.24

At first, 10 g of HTPB was added to vessel, followed by the appropriate amount of plasticiser. The sample was left in a dryer for 10 min to reduce the viscosity of the system and facilitate mixing of the components. Then, DDI was added as the last ingredient and the sample life was measured from this point onwards. This is defined as the change in viscosity of the propellent mass during the crosslinking process. The propellant viscosity must not exceed 1.5 kPa·s over a period of no more than 6 h. The whole mixture was mixed and then transferred to a 10-cm^3 measuring vessel and the measurement was started. The change in viscosity values over time was observed. Data was obtained every 15 min.

2.2.2. Measurement of mechanical properties

Tensile strength was measured on an Instron 3366 testing machine. Samples were prepared as follows: a cuboid was cut from a cuboid sample of cast propellant, from which a propellant shape for mechanical testing was subsequently cut using a press and cutter. The dimension and shape of the samples were in accordance with the JANNAF requirement [15].

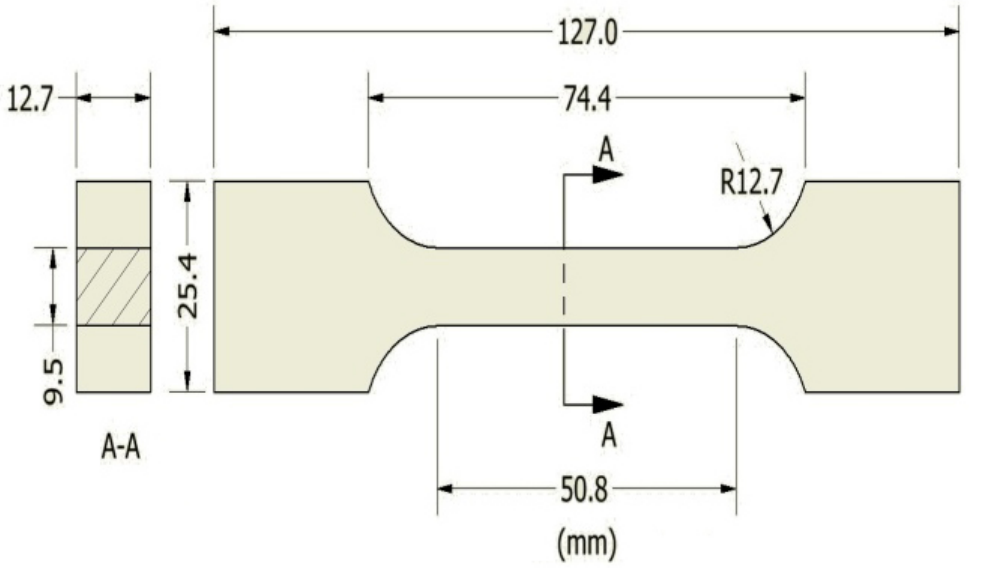

Figure 4. Dimensions of rocket propellant shapes for mechanical testing according to JANNAF

The tensile strength of the resulting propellants was then measured using the apparatus indicated earlier. The testing machine beam speed was 50 mm/min. Using the cutter shown, shapes were cut from a block of hardened propellant for mechanical property testing. Subsequently, the samples thus prepared were cured for 24 h at room temperature. This was followed by mechanical testing.

2.2.3. DSC analysis

DSC analysis was used to determine the effect of changing the plasticiser content on the propellant vitrification temperature. The analysis was performed using a DSC Q2000 apparatus. An airtight aluminium vessel was used. The test was performed for the three samples with the highest plasticiser content of DOA, DOT and DOS (7.5%). The tests were performed at a nitrogen flow rate of 50 cm^3/min.

2.3 Manufacturing process for solid heterogeneous rocket propellant

The production of solid heterogeneous rocket propellant samples consists of three main parts – mixing, casting and crosslinking. The first step involves weighing the appropriate quantities of ingredients and then placing them in a planetary laboratory mixer. The next process is casting into a mould, using a heated hopper and vacuum chamber. The final step is to place the samples in a heating chamber, where the propellant hardens.

The station for measuring the components for mixing the propellant was a Radwag PS200/2000.R2 laboratory scale. A Netsch planetary laboratory mixer, model PML1, was used for mixing. The capacity of the mixing vessel is 1.2 litres, while its working capacity is 0.7 litres. The mixer was equipped to allow mixing under reduced pressure. A sabre-type planetary mixer system was used to mix the HTPB-based propellant. In addition, a Teflon® scraper was also employed to scrape the material from the walls of the mixer vessel. Propellant samples were cast under reduced pressure into cuboid moulds made of stainless steel. Surfaces in contact with the propellant were first coated with a Teflon® layer. The 20-litre pouring chamber used for propellant casting was made of aluminium. The lid of the chamber, on the other hand, was made of thick transparent polycarbonate, which made it easier to control the process of casting the propellant into the moulds. The chamber also contained two ball valves to control the pressure during propellant pouring. The chamber was also equipped with a vacuometer, used to indicate the vacuum in the chamber. Cross-linking took place in a POLEKO laboratory dryer, model SL. The curing process was carried out at 65 °C.

All propellants were prepared in the same way. Initially, the mixer thermostat was set at 65 °C. Once the set temperature was established, first the binder, which in this case was HTPB, then the plasticiser – DOA, DOS or DOT in the appropriate amount – and the antioxidant, AO 2246, were added to the mixer. The mixer was closed and the components were mixed for 5 min at 175 rpm. After this time, the pressure in the mixer was reduced until a vacuum of 5 mbar was obtained. The components were mixed under these conditions for 15 min at 320 rpm. The oxidant, NH_4ClO_4, was then added; first, the lower fragment fraction. The mass was stirred for 15 min at 175 rpm, then at a pressure of 5 mbar for the same period of time. In the same way, the mass was dosed and mixed after the addition of the larger fragment fraction of NH_4ClO_4. The addition of the oxidiser to the mixture in two different crystal sizes, was to facilitate mixing and ensure that the binder is better filled with solid components. After the addition of both oxidant fractions, the mass was stirred for 45 min at 5 mbar at 175 rpm. In the next step, an appropriate amount of binder (HX-752) was added and the entire mass was mixed first for 10 min at 175 rpm and then for another 10 min at 5 mbar with the same mixing speed. The last component to be added was the crosslinking agent DDI. After the addition of DDI, the mass was stirred for 5 min at 175 rpm and then 10 min at 5 mbar.

When the propellants were mixed with different amounts and types of plasticiser, the rheology of the mixed mass changed. When 2.5% DOS and DOT were used, problems with mixing the mass were observed once all solid components were added. The mass was dry which made it difficult to mix all the ingredients. The problem was solved by reducing the pressure inside the mixer (10 mbar). Once the pressure was reduced, propellant mixing could continue. No such problem was observed with the DOA plasticiser. When 5% and 7.5% plasticiser were added, the problem did not occur. Figures 5-7 show the consistencies of the mixed propellant mass with different amounts of plasticiser.

Figure 5. Consistency of propellant mass with 2.5% DOA

Figure 6. Consistency of propellant mass with 2.5% DOS and DOT

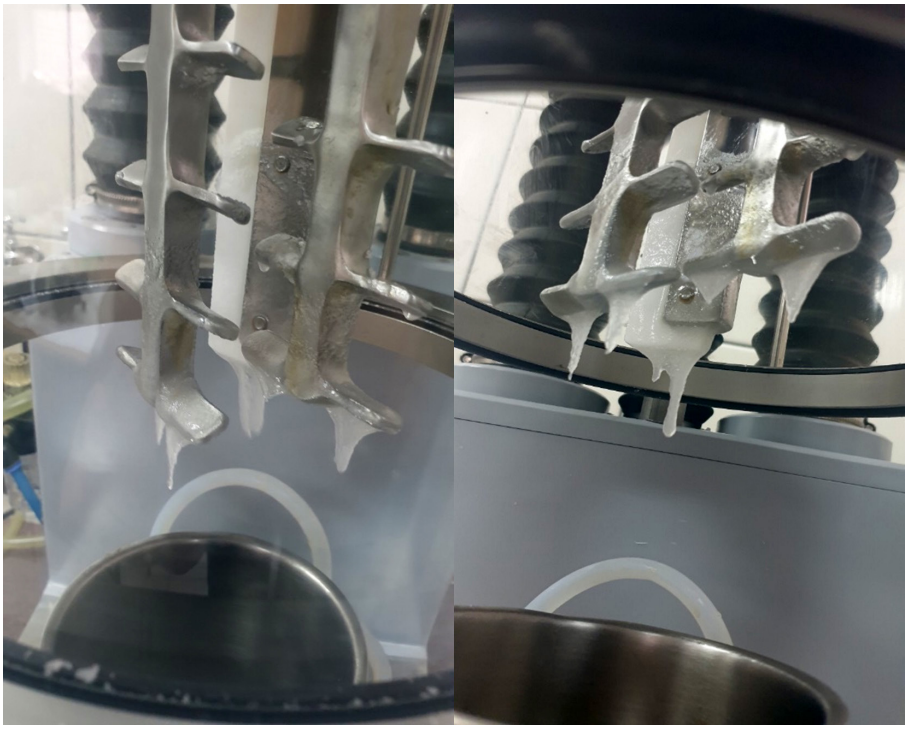

Figure 7. Consistency of propellant mass with 7.5% DOS and DOT

The propellant was placed in a heated pouring hopper. The mould was initially heated for 4 h in an oven at 65 °C before being placed in a vacuum chamber. The chamber was connected to the mixer's vacuum system. Once the set vacuum was achieved, pouring into the mould started. The propellant was then left in the chamber and conditioned for several minutes. The vacuum was released and the mould with the propellant was transferred to a dryer.

The propellant poured into the mould was placed in a laboratory dryer. The cross-linking process was conducted at 65 °C for five days. After curing, the mould was removed from the dryer and the propellant, once cool, was removed from the mould. The resulting propellant was subjected to testing.

To investigate the effect of plasticiser content on the mechanical properties of the resulting propellant, it was decided to increase the plasticiser amount in the propellant composition without changing the amount of the other liquid and solid components thereby changing the ratio of solid to liquid components in the propellant composition. At the same time, the percentage of plasticiser relative to the polymer increased from 22.2% to 53.8%. If a constant solid/liquid ratio were chosen, then with a change in the plasticiser amount, the amount of polymer and crosslinking agent would have to be reduced, which would also have a significant impact on the mechanical properties of the propellant. For a plasticiser content of 7.5% by weight of propellant, HTPB would be practically eliminated from the propellant composition. Table 4 shows the compositions of the prepared heterogeneous rocket propellants.

Table 4. Tested compositions

Raw material	Plasticiser content [%]		
	2.5	5	7.5
	Raw material content [g]		
DOA / DOT / DOS	10	20	30
HTPB	35		
AO 2246	0.64		
NH_4ClO_4 (200 µm)	252.8		
NH_4ClO_4 (20 µm)	84.2		
HX-752	1.8		
DDI	7.84		

3. Results and discussion of the results

3.1. Life and viscosity of liquid component samples

Measurements of the viscosity of the liquid components were carried out for each sample with the particular plasticiser – DOA, DOT and DOS. Viscosity measurements were taken with the plasticiser content corresponding to the amount used in the mass of the propellant in question – 2.5%, 5% and 7.5%. Each viscosity test was conducted for 5.5 h. The start of the test (time zero) was taken as the moment of isocyanate addition to the HTPB/plasticiser system. The results of the 5.5-h measurements are shown in Figures 8-10 below as graphs for each plasticiser and its percentage content in the mixture with HTPB.

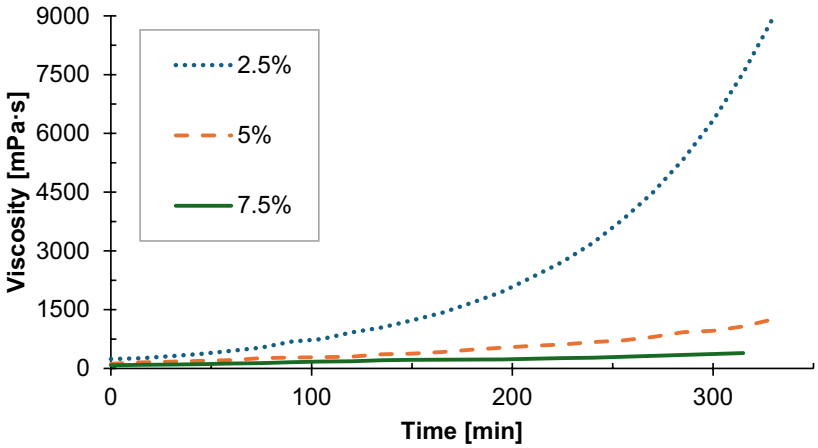

Figure 8. Relationship between viscosity and time for 2.5%, 5% and 7.5% DOA

When DOA is used as a rocket propellant plasticiser, along with the DOA content, the life of the liquid component mixture is extended. Increasing the DOA content from 2.5% to 5% or 7.5% in the rocket propellant mass results in a tenfold reduction in system viscosity after more than 300 min from time zero.

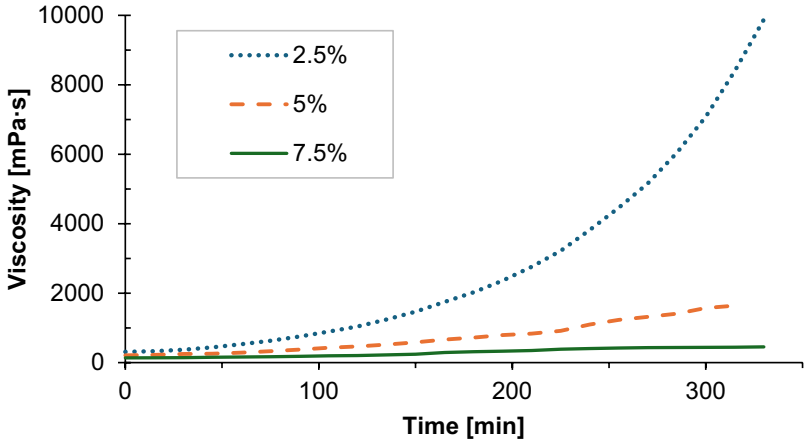

Figure 9. Relationship between viscosity and time for 2.5%, 5% and 7.5% DOT

When DOT is used as a plasticiser, the system shows a similar relationship during crosslinking as the system with DOA. As the plasticiser content in the propellant mass increases, its life increases and, after 5.5 h from time zero, the viscosity reaches a value of approximately 2000 mPa·s. This value is more than five times lower than when 2.5% DOT by weight of the propellant is used.

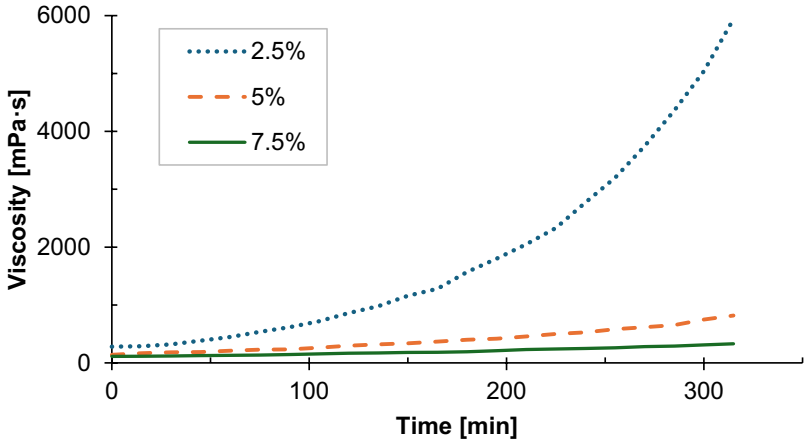

Figure 10. Relationship between viscosity and time for 2.5%, 5% and 7.5% DOS

The use of DOS as a plasticiser leads to a reduction in the viscosity of the system and, after 5.5 h from time zero, a maximum viscosity of 6,000 mPa·s was obtained for 2.5% DOS by weight of propellant.
By comparing the viscosities of the tested systems for different plasticiser content values, differences can be found in the lifes and viscosity values of the tested mixture. Figures 11-13 show summary graphs of the plasticisers used for the different percentages by weight of propellant.

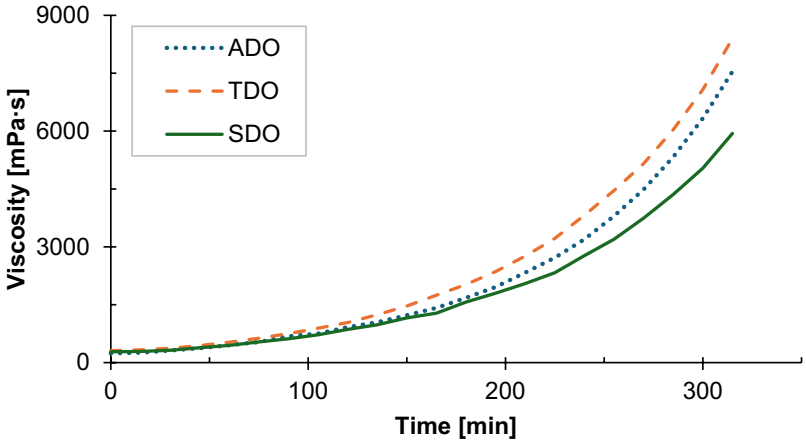

Figure 11. Relationship between viscosity and time for 2.5% DOA, DOT and DOS

For a content of 2.5% plasticiser by weight of propellant (Figure 11), the viscosity values and lifes tested indicate that crosslinking runs fastest and the viscosity value increases fastest when DOT is used. The slowest increase in system viscosity values was observed for the system when DOS was used as a plasticiser.

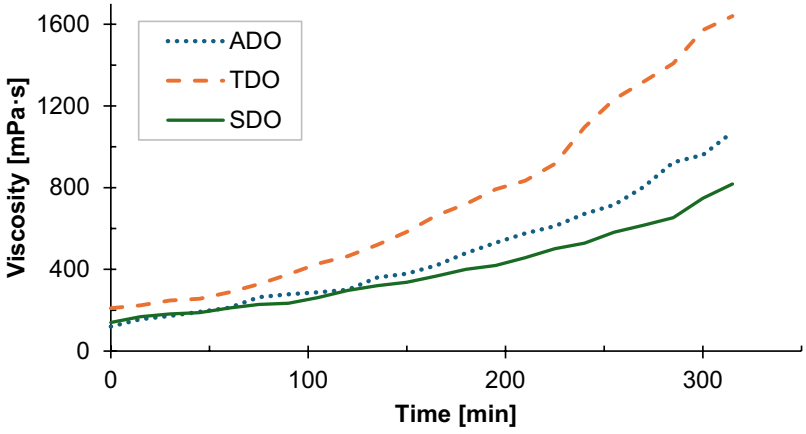

Figure 12. Relationship between viscosity and time for 5% DOA, DOT and DOS

With 5% plasticiser by weight of propellant (Figure 12), the rate of viscosity increase is the highest in the system containing DOT. In this case, the difference between the system containing DOT and that containing DOA is more than 40%. The viscosity value of the system with DOT compared to the system with DOS is approximately 100% higher.

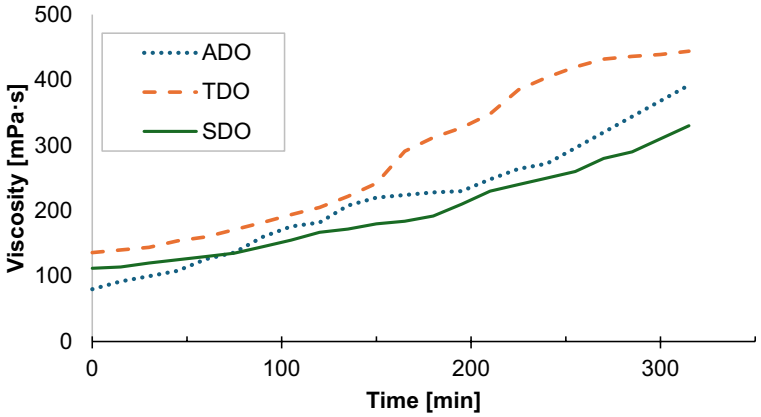

Figure 13. Relationship between viscosity and time for 7.5% DOA, DOT and DOS

Using 7.5% plasticiser by weight of propellant (Figure 13), results in a drastic decrease in the viscosity of the systems. Regardless of the plasticiser type, a maximum of 450 mPa·s was reached after 5.5 h from time zero, the effect of the crosslinking reaction on the system viscosity. The order of the viscosity increase rate was identical to the previous cases. The highest viscosity increase was observed for the system where DOT was used as a plasticiser and the slowest when DOS was used.

Propellant life is the time during which the mixture is liquid and suitable for pouring into a mould or engine compartment without an increased risk of spatial defects. From a processing point of view, extended life is a positive and desirable feature, e.g. when obtaining large propellant grains. The nine samples that were tested showed that the plasticiser used, as well as its percentage in the mixture, has a bearing on the viscosity and therefore the life of the propellant.

3.2. Testing of mechanical properties

Nine propellant samples were subjected to tensile strength measurements. One of the plasticisers – DOA, DOT or DOS – was added to each sample. For each plasticiser, measurements were taken with the content of the given plasticiser corresponding to the amount used by weight of the given propellant – 2.5%, 5% and 7.5%. Each test was conducted until the sample ruptured. The measurement results are shown in Figures 14-16 as graphs for each plasticiser and its percentage in the propellant mixture.

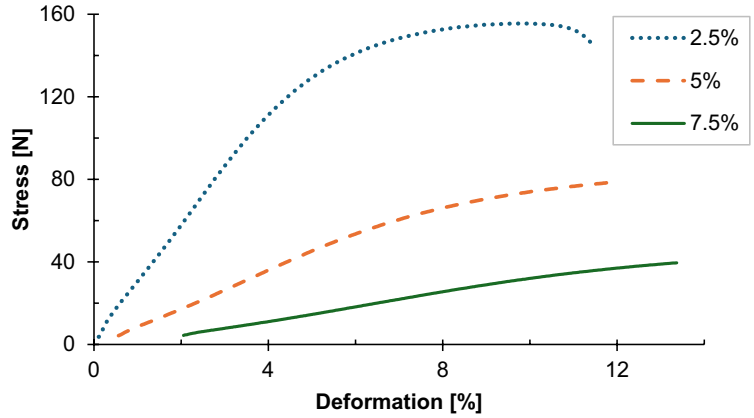

Figure 14. Stress to deformation relationship for 2.5%, 5% and 7.5% DOA

When DOA is used as a propellant plasticiser (Figure 14), the stress which must be applied to the sample to make it rupture, decreases with the DOA content. Increasing the DOA from 2.5% to 5% or 7.5% in the composition of the rocket propellant mass, results in an increase in tensile strength.

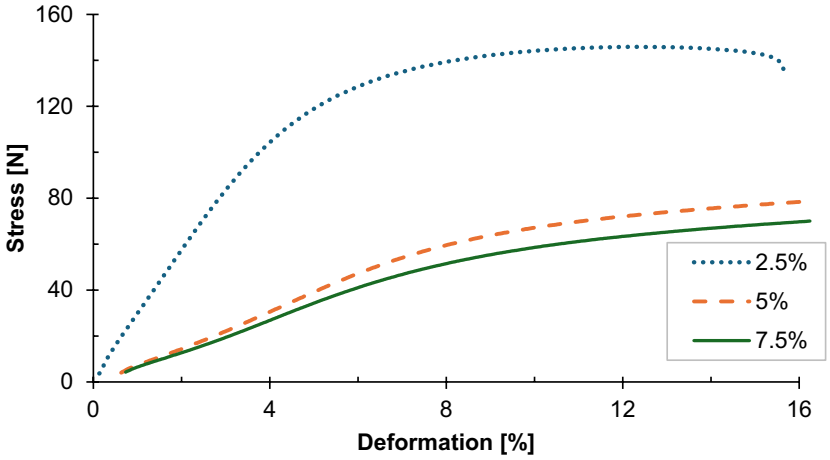

Figure 15. Stress to deformation relationship for 2.5%, 5% and 7.5% DOT

When DOT is used as a plasticiser (Figure 15), the system shows a similar relationship during the test as the system with DOA. However, the stress and deformation values for 5% and 7.5% are higher than for the samples with the DOA plasticiser. As the DOT content increases, the maximum stress value for the sample decreases.

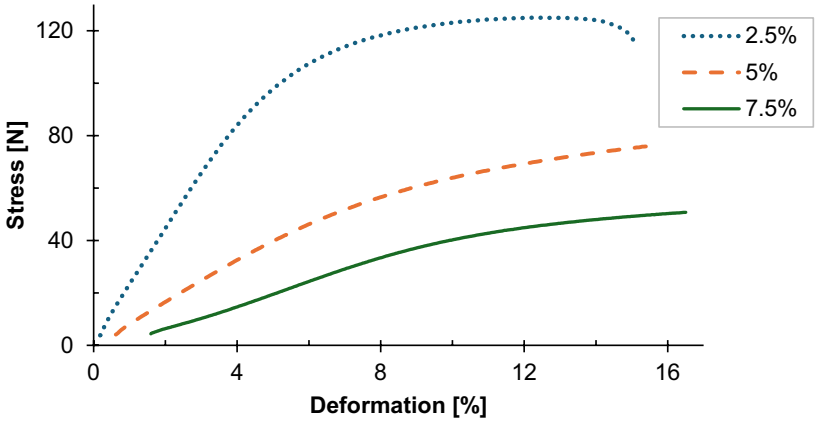

Figure 16. Stress to deformation relationship for 2.5%, 5% and 7.5% DOS

Using DOS as a plasticiser (Figure 15) leads to similar results to those obtained for DOA and DOT. With decreasing plasticiser content, the maximum stress value drops.

By comparing the tensile strength of the tested systems at different plasticiser contents, differences can be found in the values of maximum stress and stress to deformation ratio for the different plasticiser percentages in the propellant. Figures 17-19 show summary graphs of the plasticisers used for the different percentages by weight of propellant.

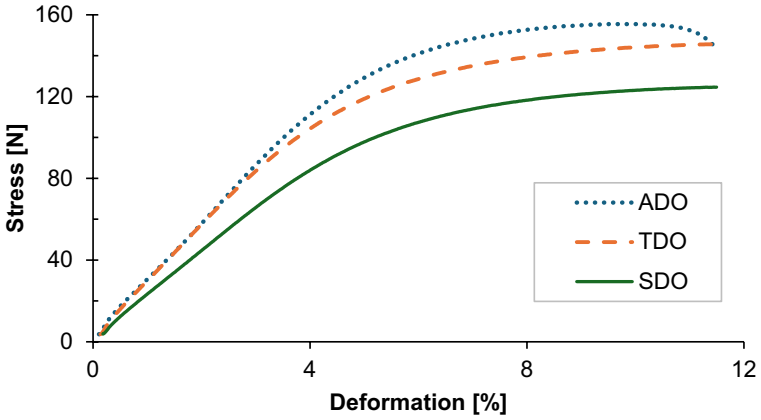

Figure 17. Stress to deformation relationship for 2.5% DOA, DOT and DOS

For a plasticiser content of 2.5% by weight of propellant, the stress and deformation values obtained indicate that the highest value of maximum stress is possible when DOA is added. The mass containing DOS has the lowest maximum load value, but the sample reaches the highest deformation value.

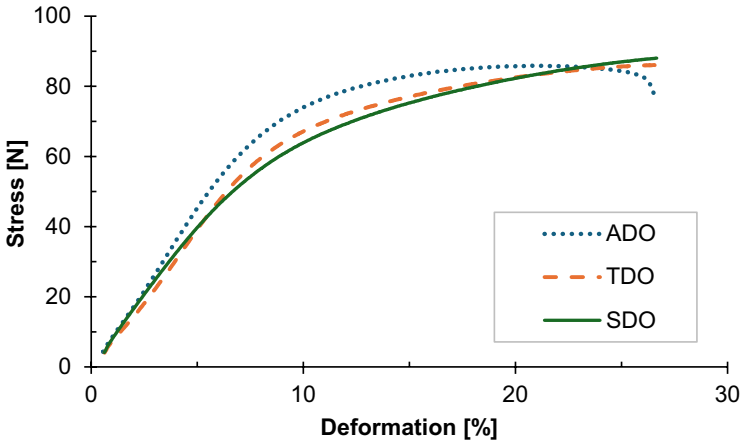

Figure 18. Stress to deformation relationship for 5% DOA, DOT and DOS

When 5% plasticiser by weight of propellant is used, the systems with DOT and DOS reach the highest maximum stress value. The sample containing DOA reaches high stress values the fastest, but ruptures at a lower value than samples with DOT and DOS.

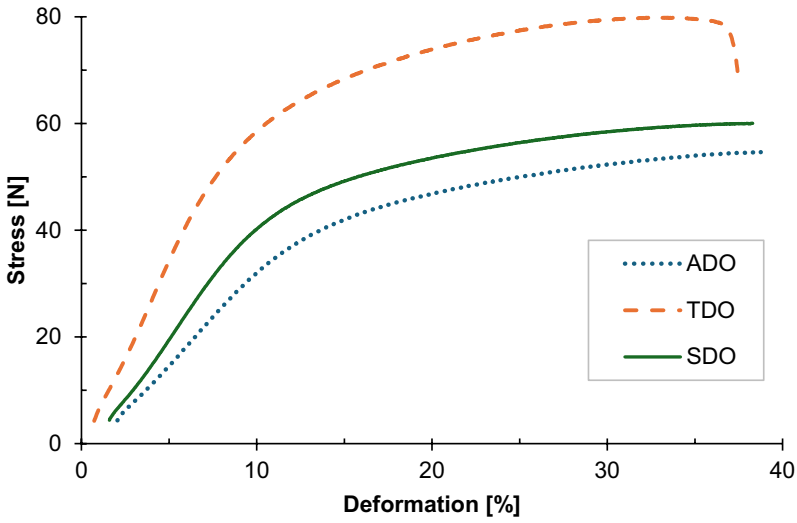

Figure 19. Stress to deformation relationship for 7,5% DOA, DOT and DOS

Using 7.5% plasticiser by weight of propellant, results in a decrease in the maximum stress value of the systems. By far the highest value is obtained with the DOT plasticiser. At a plasticiser content of 7.5%, the deformation of the sample increases. The highest increase in the stress to deformation ratio was observed for the system where DOT was used and the lowest for DOA.

3.3. DSC analysis

DSC analysis was performed to check the effect of the type and amount of plasticiser on the vitrification temperature of the propellant (polyurethane). Tests on the vitrification temperature of propellants with 2.5% and 5% plasticiser content showed no effect on its value. Due to HTPB having a low vitrification temperature, propellants based on this binder have very good mechanical properties at low temperatures. The analysis of propellants at such low temperatures has reached the limit of what the used apparatus can do. Therefore, further testing of propellants was carried out with 7.5% plasticiser content. If the plasticisers used affect the thermal properties of the propellant, then such a large plasticiser addition should affect the vitrification temperature value. Figure 20 shows the DSC curves for propellants with 7.5% plasticiser content by weight of propellant. The test showed no increase in the vitrification temperature of the propellants tested. Even the 7.5% DOS addition at its freezing point of –48 °C did not increase the vitrification temperature of the system and it is above –75 °C.

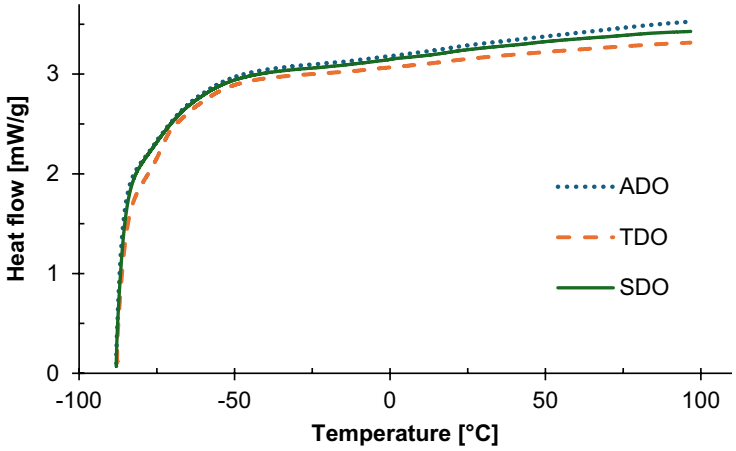

Figure 20. DSC curves for propellants with 7.5% DOA, DOT and DOS content

4. Summary and conclusions

- The effects of the plasticiser amount and type on the mechanical properties of the propellant and on the life and viscosity of the liquid component system of the propellants tested were investigated. The life of the binder/plasticiser/isocyanate system was investigated.
- Each of the samples achieved viscosity values within the range of requirements for rocket propellants. According to literature, the propellant viscosity must not exceed 1.5 kPa·s over a period of no more than 6 h. None of the samples showed such a high viscosity value after 5.5 h. All three plasticisers used in the tests – DOA, DOT and DOS – met the requirements set in rocket propellant standards. With an increase in the plasticiser percentage in the propellant, there is an increase in the life of the propellant. After 300 min, at 2.5% plasticiser content in the propellant, viscosities ranged from 6,000 to 8,000 mPa·s (the highest value being achieved with DOA plasticiser, the lowest with DOS). For the 7.5% content, the values are much lower, within the range of 330 to 450 mPa·s, with the higher value being obtained with DOA and the lowest with DOS.
- The next test conducted was tensile strength. Satisfactory results were reported for all nine samples. The results showed slight differences in the mechanical properties of propellants with different content of plasticiser tested – the maximum stress for systems with DOA was the highest and for systems with DOS the lowest with reference to a given percentage content. For a plasticiser content of 2.5%, the stress values were the highest, with a value of 90 N, and the deformation was the lowest, at around 12%. In contrast, when 7.5% plasticiser in the system was used, the maximum stress was lower, around 60 N, but the deformation was higher, just below 40%. The greater the amount of plasticiser used, the more flexible the propellant was, allowing the propellant to be stretched more with less force.
- Vitrification temperature tests were also carried out for three samples – with 7.5% plasticiser DOA, DOT and DOS. For systems with a plasticiser content of 2.5% and 5%, no effect of the plasticiser amount or type on the vitrification temperature was indicated. One of the important properties of HTPB is its low vitrification temperature, so, as expected, the study showed that even a plasticiser content as high as 7.5% did not adversely affect the vitrification temperature. All three systems with plasticisers DOA, DOT and DOS achieved the expected results with the vitrification temperature of the propellant not rising above –75 °C.
- In summary, changing the plasticiser and its quantity in a solid heterogeneous rocket propellant, affects the propellant's properties. Each of the systems, regardless of the plasticiser used, met the required targets for solid rocket propellants. Propellants with DOA, DOT and DOS at all three percentages –

2.5%, 5% and 7.5% – show equally good mechanical properties at low temperatures as indicated by the low vitrification temperatures measured. The viscosity of the tested systems does not increase above the limit of 1.5 kPa·s within 6 h of cross-linking, which means that their life meets the requirements for SHRPs.

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