

On The Replacement of Traditional Stabilizers by Guaiacol in Environmentally Safe Nitrocellulose-based Propellants

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Research Article

Keywords: Energetic Material, Stabilizer, Green Propellant, Guaiacol

Posted Date: November 10th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-686720/v1>

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Version of Record: A version of this preprint was published at Clean Technologies and Environmental Policy on March 8th, 2022. See the published version at <https://doi.org/10.1007/s10098-022-02291-4>.

Abstract

In this work we investigated the possibility of substituting diphenylamine (DPA) by the natural product guaiacol, as a stabilizer for nitrocellulose (NC)-based propellants. Stability evaluation, using heat-flux calorimetry (HFC), revealed lower heat flows associated with our guaiacol-stabilized propellant samples when compared to those of propellants stabilized with the traditional stabilizers. Also, pressure-vacuum stability tests (PVST) showed that our propellant exhibited lower evolved gas volumes. Traditional tests, such as the German Test, and the Bergmann-Junk Test, scored a NO volume, after titration, of 0.87 ml (below the limit-value for acceptance, which is 2.0 ml), and the Storage Test, showed that our samples are stable and do not degrade for more than 3 days when submitted to a constant temperature of 100°C. The homogeneity, stability and compatibility of our samples were evaluated through scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and isothermal thermogravimetry (TG). Ballistic parameters were estimated using a closed vessel along with *ad hoc* codes, for comparison purposes. Finally, a high-performance liquid chromatography (HPLC) method developed before allowed inferring the stabilizer consumption after artificial ageing of samples. Such method also showed that the material met the correspondent stability criteria (AOP-48). In short, our results clearly indicate that guaiacol is an effective and efficient substitute for DPA as a propellant stabilizer for single base nitrocellulose-based propellants, making them more environmentally friendly.

Introduction

Nitro esters, such as nitrocellulose (NC), have been extensively used as propellants due to some unique characteristics, such as their high energetic potential. However, over time, several catastrophic accidents resulting from the NC decomposition, have showed that the chemical stability is an important aspect to ensure a safe use and storage of propellants (de Klerk, 2015; Defanti et al., 2020). This NC degradation was identified as being intrinsic to the nitro esters, depending on temperature and time, and happens mainly due to denitration reactions based on the chemical detachment of $-\text{NO}_2$ groups caused by thermal decomposition and hydrolysis reactions involving the residual moisture present in the propellant mass (Bohn, 2007). The products formed during this decomposition are mostly NO_2 , NO , HNO_2 and HNO_3 , which promote, by their turn, consecutive hydrolysis reactions in an auto-catalytic process of degradation. As the decomposition process is exothermic in nature, the rate of degradation of the propellant increases with temperature (Vogelsanger, 2004), and such synergetic processes can even lead to the spontaneous combustion of the material. Therefore, chemical stabilizers are necessary to ensure an adequate shelf-life of NC-based propellants, by capturing the generated radicals or by interrupting, over a period of time, the auto-catalytic process of decomposition. The most commonly used stabilizers are diphenylamine (DPA), ethylcentralite (EC), methylcentralite, akardite-II (AK-II) and 2-nitrodiphenylamine (2-NDPA). However, as these compounds are amines and secondary amides, the degradation process leads to the formation of $\text{R}-\text{N}=\text{N}=\text{O}$ (where R is an alkyl radical), which are suspected of being carcinogenic (Lin, 1990).

DPA is the most used stabilizer for single-base gunpowder and is quite standard for small guns ammunition. It has been cited by the European Union as a recalcitrant pollutant, leading to the

development of standards to evaluate and control the environmental risks associated with its use (Mendonça-Filho et al., 2019). Substances produced within the stabilization process, especially N-nitroso-DPA, which is a major product formed during the degradation of NC-based propellants, have carcinogenic, mutagenic and toxic to reproduction properties, according to toxicological tests (Jain et al. 2020; Rodrigues et al. 2018).

Mestankova et al. (2014) reported that N-alkyl-nitrosamines are known to have a common mutagenic mechanism, triggered by the enzymes of the cytochrome P450, which increase the polarity and water solubility of the substances, through the hydroxylation of the carbon adjacent to the N-nitroso group (Figure 1), which is the case of DPA and 2-NDPA:

Araújo et al. (2000) also reported that N-nitroso-amides, which are the degradation products of EC and AK-II, undergo a hydrolysis process which is similar to the N-nitroso-hydroxylamine decomposition (Figure 2), producing diazo-alkanes that are able to interact with DNA.

The use of natural substances as stabilizers for energetic materials comes up as an excellent alternative to reduce environmental impacts, besides the fact that they are prone to the generation of products that are less harmful to humans. This is particularly important in training facilities, destruction sites and, of course, in manufacturing plants, where ammunition is, respectively, employed, decommissioned and produced for decades. In this context, some studies have suggested the complete replacement of traditional stabilizers by "green" alternatives, especially those that can be found in natural products (Langlet et al., 2007; Dejeaifve et al., 2018).

Moving on this direction, Krumlinde and coworkers (2017) investigated new stabilizers that were not prone to form by-products containing nitrosamines, concluding that bis(2,6-dimethoxyphenyl)triethyleneglycol was the most promising one. Cherif and co-workers (2020a, 2020b) also studied natural stabilizers, lignin in particular, due to its availability via sustainable processes. The aromatic rings present in this amorphous biomacromolecule, exhibit great potential to sequester NO_x groups during NC degradation, being an attractive option. Chelouche and coworkers (2019) studied a binary eutectic mixture of N-(2-methoxyethyl)-p-nitroaniline (MENA) and DPA, aiming to minimize the number of toxic products resulting from the decomposition of DPA. This molecule was considered compatible and functional as a stabilizer for NC-based propellants. Dejeaifve and co-workers (2020), in addition to their previous works, analyzed potential (natural) substances, such as alpha-tocopherol, alpha-ionone and curcumin for replacing DPA, using Heat Flow Microcalorimetry (HFC) to predict their shelf life when compared to AK-II. In previous works of our research group, we also found promising results for NC-based propellants stabilized with 1.0% of curcumin (Rodrigues et al., 2019, 2021), while very recent research on the use of alpha-ionone as stabilizer (Damseaux et al., 2021), has demonstrated its effectiveness, with the main derivative products identified as: 3-oxo- α -ionone, 4-oxo- β -ionone and 4,5-epoxy- α -ionone.

Meaning to continue contributing to the discover of new green stabilizers, the main goal of the present work was to propose a natural stabilizer as a substituent for synthetic stabilizers that would exhibit equal

or superior stabilizing properties. Guaiacol was chosen due to the fact that this molecule does not exhibit amine or amide groups, which indicates that no carcinogenic, mutagenic or toxic to reproduction derivative will be formed during the stabilization process. Another important aspect is the possibility of improving the propellant shelf life, searching for formulations capable of lasting as long as 10-15 years, which is more elastic than the ones related to conventional ammunition. This can warrant resource savings in several aspects, once it lowers the replacement rates besides demanding lesser testing and destruction operations.

Guaiacol (Figure 3), the common name of 2-methoxyphenol, $C_6H_4(OH)(OCH_3)$, is an organic compound that, in its pure state, is found as an oily and colorless liquid, with molar mass of 124.137 g/mol and a melting point of 28°C. It is water soluble (17 g/L at 15 °C) and can be found in guaco (*Mikania glomerata*) leaves and in wood-tar creosote.

It has been reported that the O-H and O-CH₃ bonds within the guaiacol chemical structure present the weakest bond dissociation energies (BDE), ranging from 87 to 58 kcal mol⁻¹, while the C-H bond in the aromatic ring present the higher BDE, of around 115 kcal mol⁻¹. Thus, the more reactive groups (-OH and -OCH₃) should allow bimolecular H-abstractions by free radicals, acting as potential stabilizers (Nowakowska et al., 2018).

Guaiacol has been cited (Hartman & Morton, 1981) as a potential NC stabilizer along with many other molecules exhibiting at least one aromatic ring substituted with alkoxy groups, such as: 1,3,5-trimethoxybenzene, 2-methoxy-naphthalene (nerolin), catechol, 1,2 dimethoxy benzene (veratrol), and 1,4 dimethoxy benzene (hydroquinone dimethyl ether). No direct investigation has been conducted yet on the products that could be formed during the degradation process of NC stabilized by guaiacol, but Kroflič and co-workers (2015) reported that the guaiacol originated from biomass burning, can interact with nitrite present in the atmosphere, resulting in 4-nitroguaiacol, 6-nitroguaiacol and, after a short interval of time, 4,6-dinitroguaiacol (Kroflič et al., 2015).

In order to investigate the substitution of DPA by guaiacol as a stabilizer we accomplished a set of six performance tests employed for comparison. The stability was first evaluated through HFC, three classical stability tests (Bergmann Junk test, German test and Storage Proof), pressure vacuum stability test (PVST), and ballistic parameter estimation using a closed vessel device along with a regression tool developed by our research group. Finally, the guaiacol concentration depletion after a 10/15-years artificial aging was analyzed using high performance liquid chromatography coupled with ultra-violet detection (HPLC/UV).

Aiming the best analytical scrutinization of the NC propellants under study, the techniques were employed and analyzed in conjunction in order to complement each other, once all present pros and cons. The PVST monitors the evolved gas from a fixed-volume system, being a reliable and accurate test for stability. HPLC/UV was used to determine the remaining amount of the stabilizer after an induced/artificial ageing protocol and a solvent extraction procedure, being crucial for inferring on the

propellant shelf life. However, even though being expedite and effective techniques, there is room for misinterpreting the results, due to the presence of the products of the reaction between the stabilizer and any of the products of the NC degradation. The traditional stability tests, such as the Bergmann-Junk Test, the German Proof and the Storage Test are also based on analysis performed during an artificial ageing of the material that follow different protocols of time and temperature, according to the kind of propellant. These tests exhibit some intrinsic deficiencies such as exhibiting a long measuring period and being too dependent on the experimenter skill and on the quality of the indicator paper employed. Besides, the tests are not able to mimic the conditions in a real ammunition and unstable products and/or impurities can interfere in the results (Trache and Tarchoun, 2019).

Experimental Methods

Sample preparation

The inputs used in the sample preparation were: a 2:1 mixture of a NC with low nitrogen content (ranging from 10.8–12.3%) and a NC with high nitrogen content (ranging from 12.5–13.4%), supplied by Nitrochemie Wimmis (Switzerland); traditional stabilizers DPA and EC, used in the reference samples and guaiacol, all supplied by Sigma-Aldrich (USA); Acetone analytical grade (CAS N° 67-64-1, analytical grade > 99.5 %), supplied by Isofar (Brazil), which was used for the NC gelatinization, and a vehicle for incorporating the stabilizers in the propellant mass.

Samples were produced according to the procedures depicted in Figure 4. Both NCs (with high and low nitrogen content) were mechanically mixed with a spatula and the mixture was air dried (25 ° C) for 72 hours to reduce the moisture content. The equivalent of 1.0% of the mass of both DPA and guaiacol were weighted in beakers, solubilized in 30 ml of acetone and added to the mass, along with enough acetone to gelatinize the NC. As 1.0% is the percentage of DPA found in commercial products available in Brazilian ordnance, we decided to apply it for comparison purposes. Besides, this concentration is considered economically feasible for the new commercial products that might be developed based on this study.

After, the mixture was macerated for 1 h and the acetone excess was evaporated by letting the mixture rest, until a consistency that allowed lamination and cutting was observed. The lamination was conducted by passing the mass through unheated stainless-steel cylinders, resulting, at each pass, in sheets that were repeatedly grouped and reprocessed, to ensure good dispersion and sample homogeneity. Finally, the sheets were sliced, and the slices had their edges cut, for the standardization of samples. After cutting, the average grain size of the samples was 1.40 x 0.73 x 15.00 mm in a spaghetti-like shape.

Stability tests

Heat Flow Microcalorimetry

The heat-flux calorimeter employed was a TNO-HFC Mod. P0810, which measures the total heat generated during the artificial ageing process of 5.00 g samples of each propellant and detects the heat flux in a microwatt scale (μW). Well-established protocols (NATO Standardization Agency 2007) on chemical stability states that single-based (SB) propellants with a heat flux of less than $201 \mu\text{W/g}$, at 85°C , are considered, by safety standards, to have a minimum 10-year shelf life, when stored at 25°C .

Old School Chemical Stability Tests (German test, Storage proof, and Bergmann-Junk test)

The old school chemical stability tests consist of heating propellant samples at different temperatures and time periods to simulate its natural ageing and infer whether the stabilizer is able to ensure the stability of the propellant during its actual storage time. A brief description of each old school method used in this work is made below.

a. German chemical stability test (Methyl Violet Test)

The German chemical stability test consists in heating a 5.00 g sample up to 120°C , when analyzing a SB propellant and up to 134.5°C , when analyzing a double-based (DB) propellant. The test is conducted in sealed test tubes, placed inside a metallic thermostatic block, in which a litmus indicator paper is inserted. After the desired temperature is reached, a time count is started and, when the indicator paper turns salmon-red, the time is recorded as the "turning point". In the second stage of the test, a diluted solution of iodine (0.01 N) is added to each test tube and another time count is started. When the solution becomes reddish-brown, due to the evolution of nitrous vapors, the time is recorded as the "vapor point". In the last step, the time required for the ignition or detonation of the sample is recorded as "explosion point", which is noted as $\text{EXP} > 360 \text{ min}$ if that doesn't take place within 6 h. For analysis of the result, these three times noted will allow scoring the propellant. These points are converted to scores that take into account other stability tests (presented in the following sections), according to specific standards (Exército Brasileiro, 2007), and the NC-based propellants are classified as having "good", "fair" or "poor" stability.

b. The Storage proof

The storage test consists in heating 10.00 g samples up to 100°C in test tubes also placed in a thermostatic block. The tubes remain open for the first 8 hours to eliminate the moisture and, after being closed, they are re-opened for 10 minutes every 24 hours for the oxidation of the nitrous vapors eventually generated. The vapors must have their color compared to a 0.03 N iodine solution and, when the same reddish-brown color is achieved, the test is considered concluded. The number of days is then recorded for the composition of the already mentioned score and a maximum of 6 days is allowed.

c. Bergmann-Junk Stability Test

The Bergmann-Junk stability test consists in heating, for 5 h, a 5.00 g sample up to 120° C, when analyzing a SB propellant and up to 132° C, when analyzing a DB propellant. The samples are placed in special tubes equipped with bulbs that receive a 4.5% (in weight) potassium iodide (KI) solution and are further placed in a thermostatic block. The nitrous vapors that evolve from the samples oxidize the iodide to iodine (I₂) which is then titrated with a 0.01 N solution of sodium thiosulfate (Na₂S₂O₃) using starch as indicator. When the blue solution turns colorless, the volume of Na₂S₂O₃ consumed (V_{Na₂S₂O₃} in mL) is used to calculate the volume of nitrous vapors evolved (V_{NO} in mL/g of sample) according to the formula in Equation (1), where NO is considered as an ideal gas, and f_{Na₂S₂O₃} is the correction factor of the 0.01 N sodium thiosulfate solution.

$$V_{NO} = 0.224 \times f_{Na_2S_2O_3} \times V_{Na_2S_2O_3} \quad (1)$$

Pressure Vacuum Stability Test (PVST)

The PVST was performed in duplicate with samples of both propellants: the reference one - stabilized by DPA (1.00%) - and the one stabilized by guaiacol (1.00%). This test consists in heating the samples inside tubes that are subject to vacuum and measuring the volume of evolved. Initially, the samples were submitted to a pressure smaller than 670 Pa, according to the prevailing standards STANAG 4556 (NORTH ATLANTIC TREATY ORGANIZATION - NATO, 1999). After, in the preset experimental runs, all tests were initiated at 26°C and ended at 27°C (after cooling).

The volume of gas evolved is reported as "cold-cold" when it refers to the entire experiment, from initial heating until cooling to room temperature. On the other hand, the volume of gas calculated as "hot-hot" is the amount of gas evolved during the 100°C step. The STANAG-4556 uses the "cold-cold" gas volume for approval criteria and the standard MIL-STD-1751A (USDoD, 2001) establishes, as an approval criterion, that samples of 5.00 ± 0.01 grams of propellants under heating at 100°C for 40 hours, should produce less than 2mL/g of gas evolved. The equipment used was a Deltima Delti Vac Mil and the test followed well-established standards.

Stabilizer Concentration Depletion Test

Once again, an artificial ageing was conducted, operating the Deltima Delti Vac Mil heating block at a constant temperature of 90°C. The protocol establishes that, in order to simulate a 10-year ageing, the temperature must be kept for 3.43 days, while for a 15-year simulation, 5.145 days are necessary. Two 5.00 g samples of the propellant stabilized by DPA were weighed, one for the 10-year simulated ageing and one for the 15-year simulated ageing; the same was carried out for the propellant stabilized by guaiacol. All samples were admitted to glass tubes in a loading density of 0.25 g/cm³ and closed with glass stoppers containing silicone grease without applying any force/pressure.

The aged samples were then compared to fresh ones using HPLC-UV analysis. For that, 0.8000 grams of all propellants (unaged, 10-year aged and 15-year aged) were weighed and treated with 200 ml of methanol analytical grade in a Becher to extract the NC degradation products along with the remaining

unreacted propellants. To ensure in depth extraction, ultrasonic vibration was employed (using an Unique Ultrasonic Cleaner) for 4 h at 25°C, avoiding exposure to sunlight. After extraction, the solution was diluted to 250 ml with Methanol analytical grade and the supernatant liquid from each sample was percolated through a 0.45 µm polypropylene filter with PVDF membrane (Agilent). Aliquots of 10 µL were injected into an ACE5-C18-HL (Octadecyl) 150 x 4.6mm reverse phase column with 5 µm diameter particles.

The HPLC analysis was performed on a Prominence LC (Shimadzu, Kyoto, Japan) Ultra Fast Liquid Chromatography (UFLC) system equipped with a SIL-20AC self-injector, two LC-20AD solvent pumping units and a DGU-20A. Data were acquired using Labsolution software (Shimadzu, Kyoto, Japan). The mobile phase was composed of HPLC grade methanol and distilled water (75:25, v/v) for isocratic elution at a flow rate of 0.8ml/min; the column temperature was kept at 20°C and the UV detector was set at a wavelength of 272 nm.

According to AOP-48 (NATO, 2018), a maximum reduction (after ageing) of 80% of the stabilizer concentration with respect to the initial concentration and a remaining minimum of 0.2% of the initial stabilizer amount were established as the stability criterion.

For quantitative purposes, calibration curves for each stabilizer were constructed, using the same chromatographic method and conditions. For this, solutions with 0.003, 0.01, 0.0305 and 0.0609 mg/mL, were produced from successive dilutions of a stock solution of 0.6092 mg/ml.

Ballistic Parameters Estimation

Pressure *versus* time data of a confined burn of the propellants under evaluation were acquired in a 200 cm³ HPI Closed Vessel B-180.2 at a loading density of 0.1 g/cm³. This was used to calculate propellants vivacity (roughly the first derivative of the pressure with respect to time), as well as to estimate the parameters of Vielle-Saint Robert burning (rate) law along with the co-volume of the Nobel-Abel equation of state and the specific force; this set will be, henceforth, referred as the “ballistic parameters” of the propellant.

The fitting algorithm was based on a Maximum Likelihood criterion and was implemented in SciLab (a free, open-source software available in <https://www.scilab.org>), producing coherent and unbiased estimates, along with their variances (Rodrigues et al., 2006).

Differential Scanning Calorimetry and Thermogravimetry

Samples of NC stabilized with 1% of either DPA or guaiacol were analyzed through Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG). The chemical compatibility between components in energetic materials can be evaluated by thermal studies (DSC and TG) as a complement to VST. Thermal analysis gives fast results and requires lower amounts of sample, although may not be representative of the whole propellant grain. Nevertheless, DSC and TG provide good hints about the compatibility when

new molecules are being tested to be used as stabilizers, and it was already reported in the literature (Chelouche et al., 2020; Krabbendam-La Haye et al., 2003; Li et al., 2020; Trache et al., 2019).

These studies were performed in Shimadzu Thermal Analysis systems, models DSC-60 and DTG-60 H, under a 50 mL/min nitrogen gas purge. For the DSC it was used a heating rate of 2°C/min from ambient temperature up to 280°C, with a sample mass around 1 mg in a closed aluminum crucible. For the TG experiment, a heating rate of 5°C/min was used to heat an amount of 3 mg of each sample in a platinum open crucible, up to an isotherm of 145°C for 150 minutes.

Results And Discussion

Stability tests

Heat-Flow Microcalorimetry

Results depicted in Figure 5 indicate that all formulations of SB propellants would pass the approval criteria established by the standard STANAG 4582 (NATO Standardization Agency, 2007). It must be noticed that the formulation stabilized by guaiacol exhibits a smaller area below the heating isotherm, when compared to the ones of the traditional formulation with DPA and EC, which is associated with a longer shelf life, according to the prevailing literature (Bohn, 2009). The proposed deduction of the useful life from the amount of heat released during the ageing of the energy material compares the area predicted by the procedure described in STANAG – 4582 for 10 years of artificial ageing with the area of the propellant investigated.

Old School Chemical Stability

According to Table 1, all SB propellant samples would be approved by the traditional chemical stability.

Table 1
Traditional stability test results.

Stabilizer	Bergmann-Junk/ V _{NO}	Storage test	German Test
DPA (1.0%)	Stable/ 0.52mL	Stable	Stable
EC (1.5%)	Stable/ 0.94mL	Stable	Stable
Guaiacol (1.0%)	Stable/ 0.87mL	Stable	Stable

Pressure Vacuum Stability

Vacuum stability tests (PVST) were ran in duplicate with the DPA and guaiacol propellant samples and results in Table 2 show the average between the values found for the volume of gas released per propellant sample.

It must be said that all propellants were considered to exhibit a 1.20 g/cm³ density, since all contained 99.00% of NC in its formulation and only 1.00% of stabilizer.

All NC propellant samples were approved according to the related standards MIL STD 1751A, once they all presented results under the 2mL/g limit.

Table 2
Results of pressure vacuum stability test

Stabilizer	Gas Volume (cold-cold)	Gas Volume (hot-hot)
DPA (1.0 %)	1.083 mL/g	0.8561 mL/g
Guaiacol (1.0 %)	0.90 mL/g	0.53 mL/g

Stabilizer concentration depletion

The procedure of HPLC-UV used for the determination of DPA and guaiacol in propellants was successfully established before (Rodrigues, 2021) and within this work showed again to be pertinent, fast, simple and specific for DPA and guaiacol analysis, which standard peaks can be found in Figures 8 and 9.

Table 3 shows the result of the maximum peak area decrease of each stabilizer for the unaged and aged (10 years and 15 years) propellant samples, where concentrations were calculated using the calibration curves determined in Fig. 3 and 4.

Table 3
Maximum peak decrease and final fraction of stabilizer (with respect to the initial concentration).

Stabilizer	Aging (years)	Maximum Decrease (%)	Concentration (%)
DPA	10	26.95 %	75.82 %
	15	75.09 %	32.62 %
Guaicol	10	11.91 %	85.26 %
	15	20.67 %	74.41 %

Following the AOP-48 (NATO Standardization Agency, 2008) criterion, the final stabilizer concentration (after artificial ageing) should be not less than 80% of the initial concentration. A second stability criterion

states that at least 0.2% of the initial stabilizer concentration should remain in the material for a propellant to be approved.

The last column in Table 3 shows the remaining amount of stabilizer in relation to the initial concentration after artificial ageing. Both samples were approved, but the propellant stabilized by guaiacol exhibited lower levels of stabilizer depletion, indicating that this propellant can be stored for longer times (or can be more safely stored) than the reference propellant with DPA. Such difference was especially acute when comparing the results associated with 15 years of (artificial) ageing.

One must be aware of the possibility of the decomposition of guaiacol (Nguyen et al., 2018). The products of the reaction of the products of this decomposition with NC derivatives are still a subject to be studied. However, they are expected to be less toxic than the nitrosamines formed by DPA stabilizers, despite this assumption has still to be confirmed through toxicity studies.

Ballistic Parameters Estimation

As described previously (Rodrigues et al., 2006) three tests must be conducted with different loading densities for the estimation of the force (F) and co-volume (η) of each propellant. Therefore, 6 shots were fired, three with the reference propellant and three with the proposed propellant.

Each set of such pressure *versus* time data (which examples can be found in Figure 10) was then used as input to a nonlinear fitting algorithm based on a Maximum Likelihood criterion used in the regression of a semi-empirical model comprised of material balances and Vieille-Saint Robert's burning law ($v = \beta \cdot P^a$). When convergence was achieved, model parameters were estimated, along with the model variance (S^2) and the values can be found on Table 4.

Table 4
Fitted ballistic parameters for propellants stabilized by DPA and guaiacol.

Sample	α (m/s)	β (Pa) ^a	η (m ³ /kg)	F (J/kg)	S ²
DPA (1.0%)	1.0001±10 ⁻⁴	(2.7±0.1)10 ⁻⁹	0.0010±10 ⁻⁴	806377±2.10 ⁵	2.554.10 ¹³
Guaiacol (1.0%)	1.0140±10 ⁻⁴	(2.6±0.1)10 ⁻⁹	0.0010±10 ⁻⁴	751225±2.10 ⁵	1.482.10 ¹³

It can be noticed that the sets of ballistic parameters of the propellants do not differ in a great extent from each other, indicating that slight adjustments in grain dimensions can compensate for differences.

Figure 11 depicts the vivacity and Table 5 reports some relative vivacity of both propellants, which are both related to the derivative of the pressure and characterize the burning of a propellant, confirming the slight increase in pressure of the guaiacol sample and its quickness compared to DPA.

Table 5
Relative vivacity of the propellant's samples stabilized with DPA and guaiacol.

Pressure (MPa)	DPA	Guaicol
	dP/dt (MPa/ms)	dP/dt (MPa/ms)
7	4.88	6.63
14	7.42	10.28
21	9.11	12.05
28	10.48	13.05
35	11.78	14.29
35 – 70	12.78	15.04
70 – 100	2.65	5.38

These results indicate that the use of guaiacol can motivate a change in the grain ballistic length (in this case, the thickness), in order to correct its relative quickness when compared to the reference propellant. This adjustment can also be carried out by changing the shape of the grain, modifying the formulation or even the load density.

Differential Scanning. Calorimetry (DSC) and Thermogravimetry (TG)

Regarding the DSC, the test followed STANAG 4147 (NATO Standardization Agency, 2001) to give a preliminary analysis on compatibility. If the peak related to the exothermic decomposition of the samples with stabilizer deviates by 4°C or more from the decomposition temperature of the pure NC, that is an indication that the stabilizer is not compatible with NC. In addition to that, any change in the curve profile is considered as an indication of incompatibility. On the other hand, the isothermal TG is a method to indicate if a stabilizer is efficient to delay the mass loss at a temperature close to the main decomposition of the energetic material. This method has consistently been applied in the literature to assess stabilizer performance (Trache et al. 2019; Chelouche et al. 2020; Rodrigues et al. 2021; Krabbendam et al. 2003; Li et al. 2020). In addition to that, the TG is also helpful to evaluate comparatively the chemical compatibility of different formulations once the lack of compatibility may induce an increase in the rate of decomposition at high temperatures.

Figure 12 shows that the exothermic decomposition measured in DSC is similar for all samples (pure NC and with stabilizers), with only one main decomposition event occurring at a very narrow temperature range (less than 4°C). Table 6 depicts the results of the thermal analysis, and the mass loss curves of the samples analyzed for 150 minutes at 145°C are shown in Figure 13. Both stabilized nitrocellulose presented a continuous decomposition with no thermal runaway or any unexpected spontaneous decomposition. The NC stabilized with guaiacol presents slightly better performance, i.e., less mass loss

after 150 min at 145°C and lower decomposition rate, although the comparison with DPA-stabilized NC is still statistically similar.

Studies reported that the decomposition of pure guaiacol starts around 375°C (Nguyen et al., 2018; Nowakowska et al., 2018). This indicates that the stabilizer decomposition during the TG experiment is negligible. In general, the results indicated that this stabilizer delays the decomposition rate and provides a good thermal stability to NC.

Table 6
Results of the thermal analysis of the NC and NC-stabilizers samples.

Sample	DSC exothermic peak (°C)	Mass loss after 150min isothermally at 145°C (% wt.)	Decomposition rate (average linear fit- $\%.min^{-1}$) $\times 10^{-2}$
Pure NC	194.44 ± 0.10	-	-
NC + 1 % DPA	193.86 ± 0.27	5.04 ± 0.72	2.98 ± 0.58
NC + 1 % guaiacol	193.91 ± 0.06	3.11 ± 1.22	1.47 ± 0.93

Conclusion

The development of green propellants is a modern initiative in the field of energetic materials aimed to extinguish the use of substances used in propellants suspected of being harmful to humans and the environment. This research has highlighted this worrying issue with stabilizers traditionally employed in SB propellants and their degradation products with NC, prioritizing formulations with longer shelf life due to better chemical stability.

From the results obtained here, it can be concluded that the green propellant stabilized with guaiacol is viable to replace the DPA stabilized propellant without producing toxic products. All samples passed the stability tests, with better quantitative results than the DPA stabilized sample. Regarding the estimation of ballistic parameters, the propellant stabilized with guaiacol was the fastest. However, this can be corrected through simple alterations in the propellant grain size, especially thickness, which should adjust its combustion speed proportionally to the DPA stabilized propellant.

Future works can be devoted to analytically elucidate the chemical composition of the degradation products from this new propellant, aiming a deeper knowledge of the guaiacol stabilization mechanism. At this point, a pilot batch will be scheduled to take place in an industrial facility, which will be of assistance for additional tests, including the shooting of real rifle rounds, in which the muzzle velocity, ash content and residues will be measured/evaluated.

Abbreviations

2-NDPA: 2- Nitrodiphenylamine; AK-II: Akardite-II; BDE: Bond dissociation energies; DPA: Diphenylamine; DSC: Differential scanning calorimetry; EC: Ethycentralite; F: Force; HFC: High flux calorimetry; HPLC: High performance liquid chromatography; MENA: N-(2-methoxyethyl)-P-nitroaniline; NC: Nitrocellulose; N-NO: N-Nitrous group; PVST: Pressure vacuum stability test; SEM: S²: Variance; Scanning electron microscopy; TG: Isothermal thermogravimetry; UFLC: Ultra-fast liquid chromatography; UV: Ultra-violet; η : Co-volume.

Declarations

Acknowledgments

The authors thank the financial support of the Brazilian agencies Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), grant numbers 308225/2018-0, and Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ), grant number E-02/202.961/2017. The authors also wish to thank the Military Institute of Engineering and Instituto de Pesquisa da Marinha for the research infrastructure. The University of Hradec Králové also supported this work.

Funding

Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), grant numbers 308225/2018-0, and Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ), grant number E-02/202.961/2017.

Conflicts of interest/Competing interests

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Availability of data and material

Not applicable.

Code availability

Not applicable.

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Figures

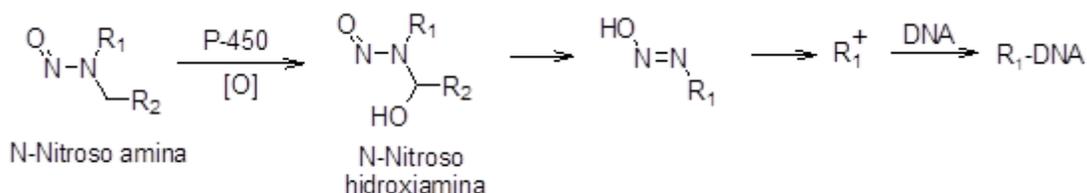


Figure 1

N-nitroso-amine metabolization (Mestankova et al., 2014).

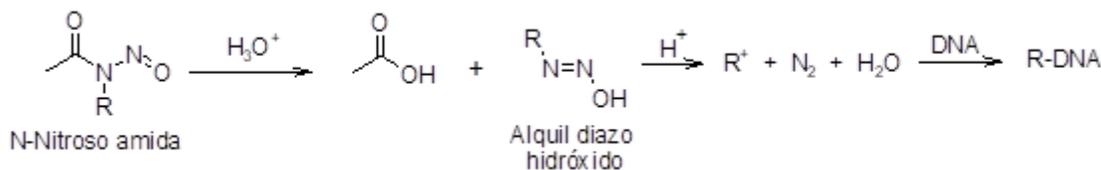


Figure 2

N-nitroso-amide hydrolysis (Araujo et al., 2000).

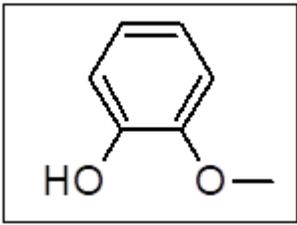


Figure 3

Chemical structure of guaiacol.

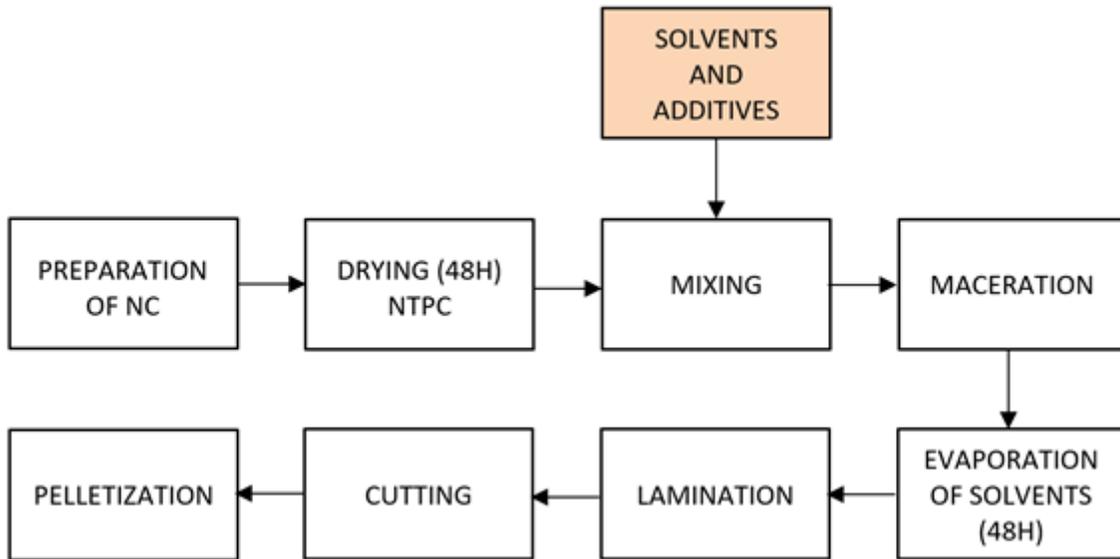


Figure 4

Sample preparation protocol.

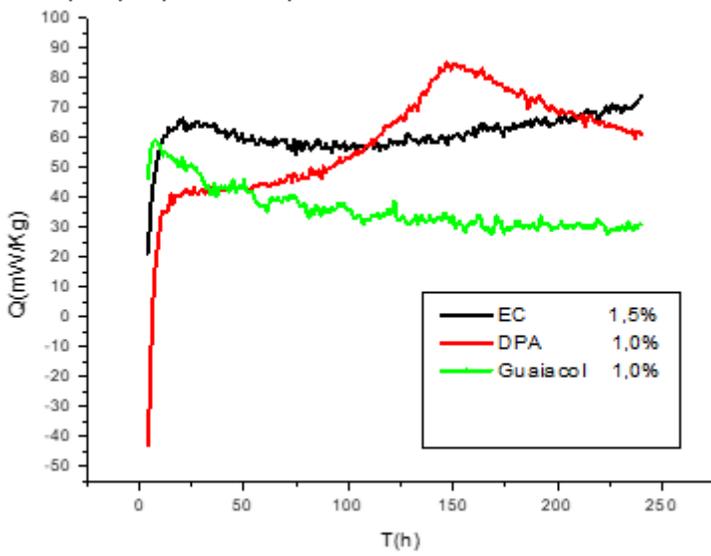


Figure 5

Heat-Flow Microcalorimetry results.

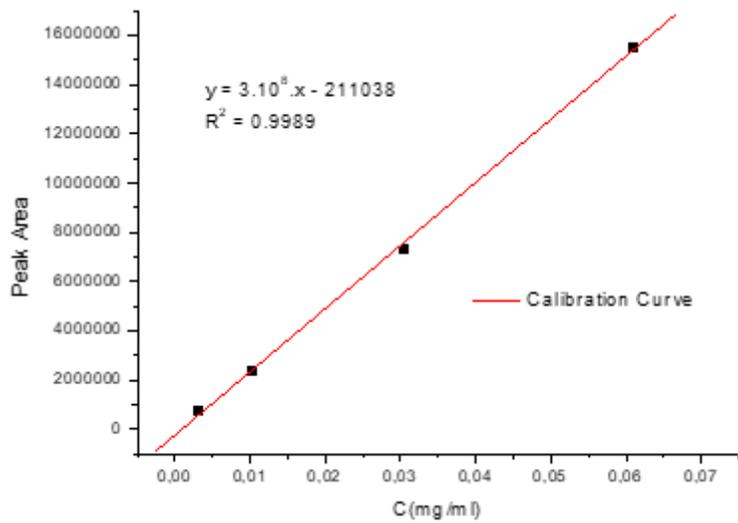


Figure 6

HPLC-UV calibration curve of DPA.

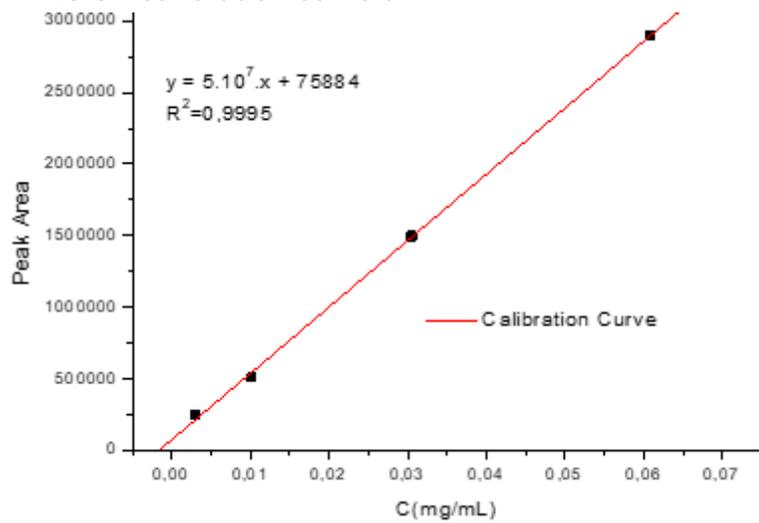


Figure 7

HPLC-UV calibration curve of guaiacol.

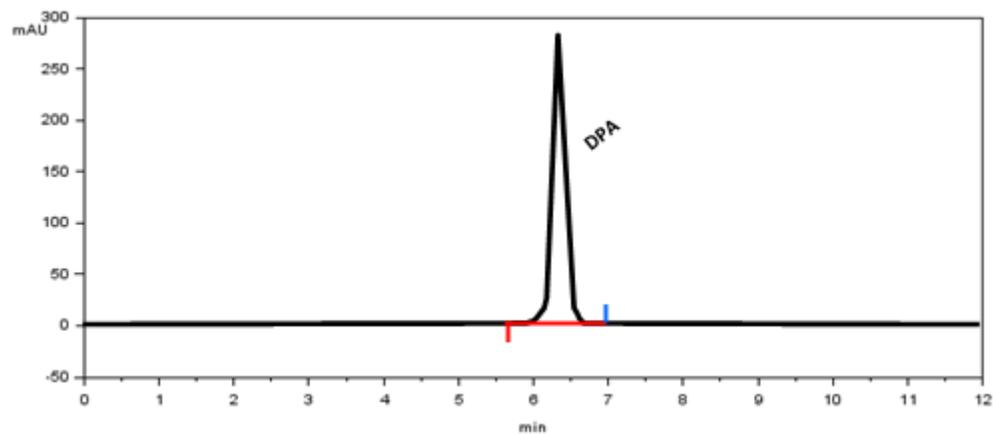


Figure 8

DPA standard peak (Tr = 6.31 minutes).

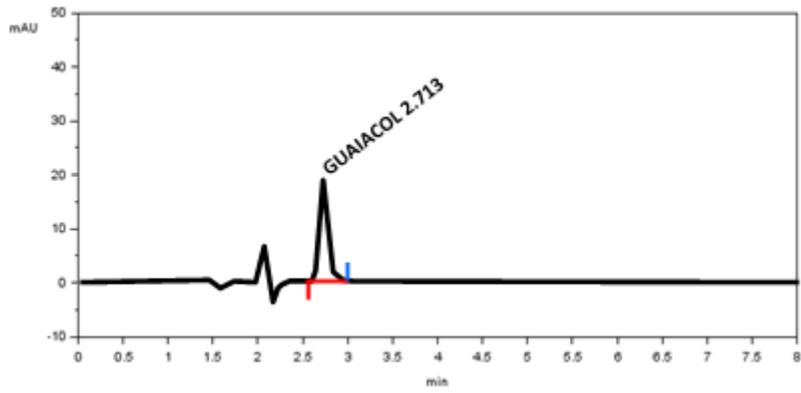


Figure 9

Guaiacol standard peak (Tr = 2.73 minutes).

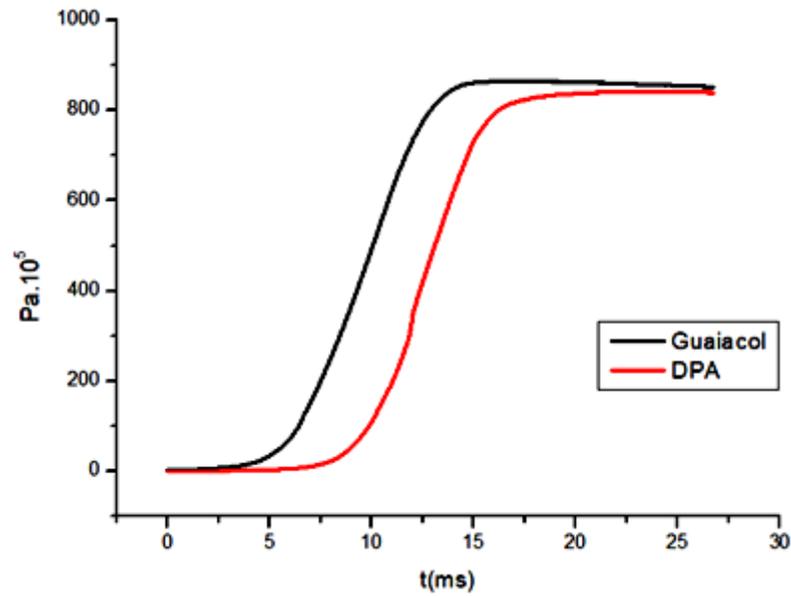


Figure 10

Closed vessel results.

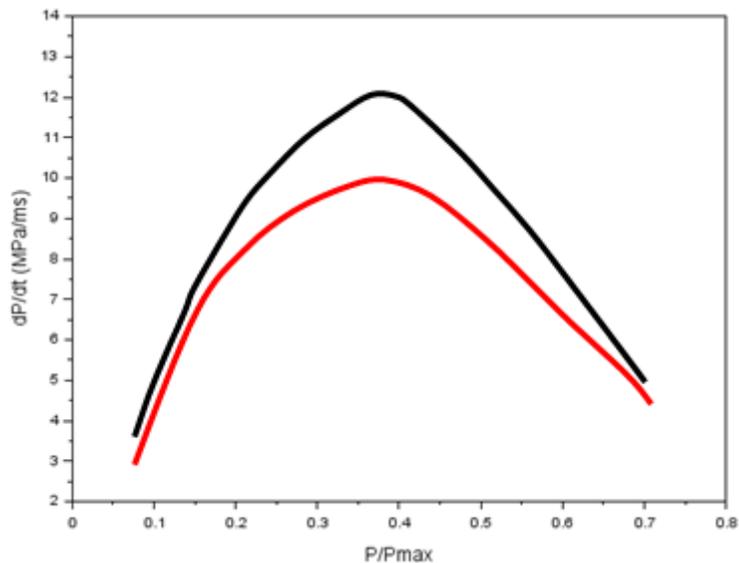


Figure 11

Vivacity results for propellants stabilized by DPA and guaiacol.

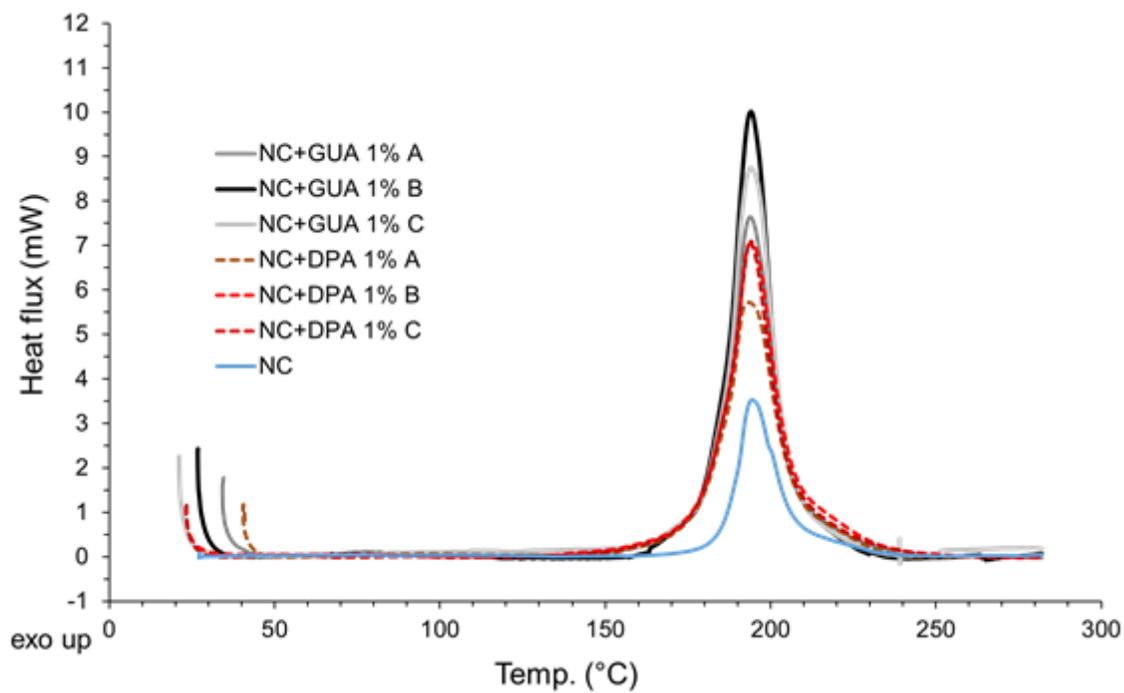


Figure 12

DSC analysis of the NC and NC-stabilizers samples.

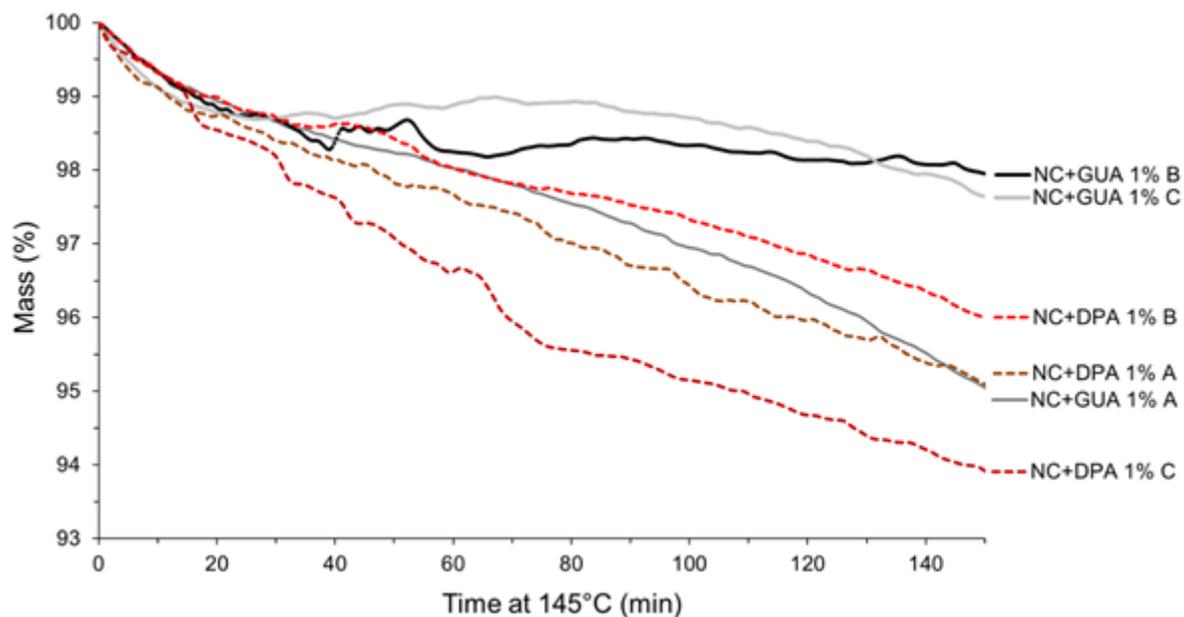


Figure 13

Isothermal TGA at 145 °C of the NC and NC-stabilizers samples.

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