U.P.B. Sci. Bull., Series B, Vol. 86, Iss. 4, 2024 ISSN 1454-2331

INSIGHTS INTO POLYMERIC BINDER–DRIVEN VARIATIONS OF CHEMICAL, VISCOELASTIC PROPERTIES AND COMPATIBILITY IN NOVEL PYROTECHNIC COMPOSITES

Cristiana EPURE[1], Tudor-Viorel ȚIGĂNESCU[2], Gabriel EPURE[3], Ovidiu IORGA[4,*], Gabriela TOADER[5], Mihail MUNTEANU[6], Alexandru MARIN[7], Daniela SANDU[8], Florin-Marian DÎRLOMAN[9]

The issues related to the mechanical loadings of energetic materials during storage or handling directly influence their safety in use. Therefore, in the structure of an energetic composite formulation, an appropriate binder is introduced in order to obtain adequate mechanical behavior. In this context, this study aims to highlight the influence of a polymeric binder, consisting of a polyurethane-chlorinated rubber mixture, on the mechanical properties of a new composite pyrotechnic mixture based on an inorganic oxidizer (potassium perchlorate) and micrometric metallic fuel (aluminum-magnesium alloy powder), designed for thermal decoy aviation countermeasures. Dynamic mechanical analysis (DMA) was used to demonstrate the importance of the presence of the two binders on the mechanical properties of the pyrotechnic composite, while Fourier transform infrared spectroscopy (FT-IR) and heat flux calorimetry (HFC) were used to observe the chemical compatibility of the polymer matrix with the fuel and oxidizer.

Keywords: chlorinated rubber, composite pyrotechnic mixture, mechanical analysis, polyurethane, polymeric binder

1. Introduction

The solvent-free PU binders are a favorable alternative to develop a pyrotechnic composition used as an energetic load for thermal decoy

---

[1] PhD Student., Military Technical Academy „FERDINAND I", Bucharest, Romania, Romania, e-mail: cristiana.epure@nbce.ro

[2] Prof. Eng. Ph.D., Military Technical Academy "Ferdinand I", Romania, e-mail: tiganescu.viorel.t@gmail.com

[3] CS III Eng. Ph.D., Research and Innovation Center for CBRN Defense and Ecology, Romania, e-mail: gabriel.epure@nbce.ro,

[4] CS III Eng. Ph.D., Research and Innovation Center for CBRN Defense and Ecology, Romania, e-mail: ovidiu.iorga@nbce.ro, corresponding author

[5] Assoc. Prof. Eng. Ph.D., Military Technical Academy „FERDINAND I", Bucharest, Romania, e-mail: gabriela.toader@mta.ro

[6] Ph.D. Student, Military Technical Academy „FERDINAND I", Bucharest, Romania, e-mail: mihail.munteanu@nbce.ro

[7] Ph.D. Student, Military Technical Academy „FERDINAND I", Bucharest, Romania, e-mail: alexandru.marin@nbce.ro

[8] Eng., Energetic Materials Department, CBRN Defence and Ecology Research and Innovation Center, Bucharest, Romania, e-mail: daniela.sandu@nbce.ro

[9] Eng. Ph.D., Military Technical Academy „FERDINAND I", Bucharest, Romania, e-mail: florin.dirloman@mta.ro

countermeasures (FLARE) ammunition because, during thick layer polymerization they do not form reaction products that would cause the appearance of gas bubbles trapped inside, which would eventually serve as nucleation sites promoting the transition from combustion to the undesirable phenomena of deflagration and ultimately, detonation. The addition of a binder based on chlorinated rubber to the mixture results in improvements to the viscoelastic behavior and pyrotechnic grain molding process [1]. These composite materials comprise two different types of polymeric matrices. The first one is a polyurethane matrix, which is obtained by the reaction of an aromatic polyisocyanate based on diphenylmethane diisocyanate with a castor oil-based branched polyol. The second polymer is a commercial chlorinated polybutadiene rubber. To achieve the desired properties in pyrotechnic composites, it is essential to bind the powdered energetic materials together effectively. The polymeric binders serve this purpose by holding the materials together, thereby enhancing the overall performance of the pyrotechnic composites. These binders also have a crucial role to play in ensuring the safety, stability, and optimal use of the materials.

In this study, the authors investigated the performance of pyrotechnic composite formulations designed for FLARE thermal decoys. By employing spectrometric (FT-IR), thermal (HFC), and mechanical (DMA) analysis techniques, they aimed to understand the chemical properties, compatibility between components, and mechanical performances.

2. Experimental section

2.1. Materials

For the development of energetic heterogeneous mixtures, the following solid materials were involved: potassium perchlorate ($KClO_4$, powder, average particle size 30 – 50 µm, purity >99%, Pyrogarage, Poland), as oxidizer and magnesium-aluminum alloy (Mg-Al alloy 1:1 weight ratio, amorphous powder, particle size <63 µm, Pyrogarage, Poland) as metallic fuel. Setathane D1160, hydroxyl content 5.4%, (SET, Allnex, Brussels, Belgium), polymeric isocyanate based on diphenylmethane-4,4'-diisocyanate, -NCO content 31.5% (MDI, solvent-free, technical product Desmodur® 44V20L, Covestro, Leverkusen, Germany) and polybutadiene-derived chlorinated rubber binder (Parlon™, ~70% degree of chlorination, powder state, particle size < 30 µm, Pyrogarage, Poland) were used as received. Dioctyl phthalate (DOP, purity min. 98%, Merck) was used as received as a plasticizer.

2.2 Methods - *Preparation of the pyrotechnic mixture*

Taking into account the solid and liquid components of the pyrotechnic formulation, the preparation was executed in two phases. In the first step, the oxidizer was vacuum-dried at 60°C for 24 hours, then granulometrically sorted and dosed. Only the 200 µm fractions were further used. Small amounts of oxidizer were added to the plasticizer under continuous stirring before adding the metallic fuel powder and chlorinated rubber, and mixing was continued until complete homogenization. In the second phase, the polyurethane binder was prepared separately by mixing the commercial polyol (Setathane®) with the aromatic polyisocyanate (Desmodur®) for approximately 15 minutes before being added to the heterogeneous mixture to obtain the final pyrotechnic composite. The composition of the pyrotechnic formulation is illustrated in Table 1. In addition, acetone was added to the composition in a volumetric ratio of 1:4 in relation to Parlon™ powder to solubilize it. The slurry mixture was poured into molds and cured for 24 hours at 60 °C to yield pyrotechnic grains for further testing.

Table 1 - Pyrotechnic composite formulation

	Component	Composition (wt. %)
1	Sethatane D1150 (ricin oil ester polyol)	4,66
2	Desmodur VL (MDI prepolymer) 31,5% NCO	2,34
3	Potassium perchlorate	40,50
4	Magnalium (Al-Mg 50/50%)	40,50
5	Parlon (chlorinated rubber)	7,00
6	Diethyl hexyl phthalate (DOF) plasticizer	5,00

2.3. Characterization

FT-IR characterization

The polymerization process of the polyurethane binder was observed by using FTIR spectrometry with a Bruker Tensor 37 instrument equipped with a Specac Golden Gate ATR device. The ATR diamond window was coated with a freshly prepared blend of Sethatane and Desmodur (polyurethane mixture). Spectra were collected every 5 minutes for the first 24 hours and every 3 hours in the following 7 days. The baseline was acquired once before loading the reactive mixture in the ATR as a 64 scan average, and afterward, the spectrum represented the averaging of 64 consecutive spectrums. The reaction temperature was constant at 25°C. In order to determine the kinetics of the polyurethane polymer formation reaction and the influence that the other components of the pyrotechnic formulation have on it, both the polyurethane and the pyrotechnic mixture were subjected to HFC analysis. The analysis was performed with the thermal flow calorimeter TAM IV, TA Instruments, according to the standard STANAG 4515 ed. 2 [2]. An isothermal analysis was conducted for both polyurethane and the entire pyrotechnic mixture. The viscoelastic properties of the developed pyrotechnic formulation (specimens measuring 35×10×2 mm) were studied with a dynamic mechanical analyzer (DMA Discovery 850) from TA Instruments, in single cantilever mode, on a temperature ramp ranging from -90°C to +50°C, with a heating rate of 5°C/min at a frequency of 1 Hz. Rectangular specimens with dimensions of 45×10×2 mm and 10×10×2 mm were cut from pyrotechnic grains for bending and shear analyses. Samples were cut from fully cross-linked pyrotechnic grains. The three-point bending test at constant temperature (25°C) was performed by sweeping the deformation amplitude with the frequency of 1 Hz, the sweep interval being between 1 and 250 µm, and the frequency sweep mode is with logarithmic increment. Shear tests were conducted at a constant temperature of 25°C with a strain of 0.1% and a sweeping mode of frequency from 0.1 to 100 Hz with logarithmic increment.

3. Results and discussion

3.1. Investigations on the formation of the polyurethane matrix

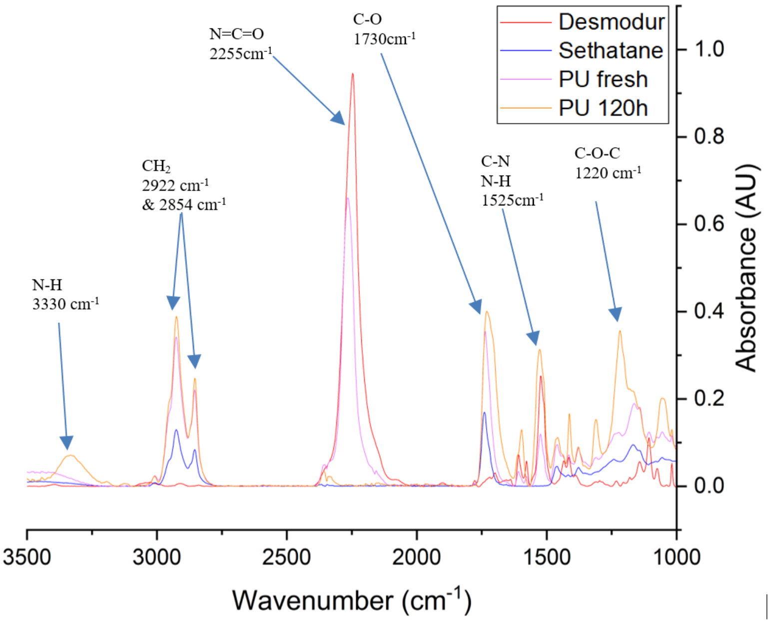
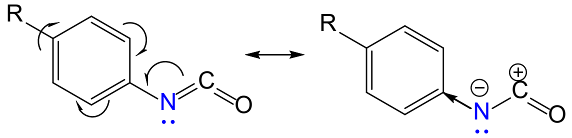


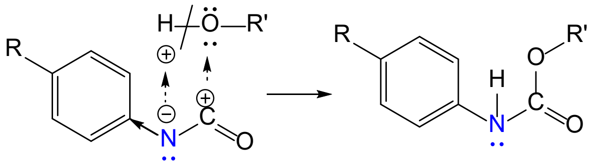
Fig. 1. FTIR-ATR spectra of Sethatane (polyol) and Desmodur (isocyanate) precursors together with the resulting cured (PU 120h) and uncured (PU fresh) polyurethanes.

The FTIR analysis conducted on the precursors and resulting polyurethane has revealed that the chemical structure conforms to the precursor data sheet. The polyol, namely Sethatane, shows absorption bands at 2922 cm^{-1} and 2854 cm^{-1}, conforming with the CH_2 asymmetric/symmetric stretch and a specific C-O band at 1739 cm^{-1}, corresponding with the hydroxyl-terminated chains. The isocyanate-based compound (Desmodur) displays two significant absorption bands: at 2255 cm^{-1} (N=C=O) and at 1525 cm^{-1} (C-N), corresponding with the phenyl-isocyanate bond. The uncured polyurethane (PU fresh) presents the characteristic peaks of both Desmodur and Sethatane. The fully cured polyurethane, after 120h at 25°C, presents polyurethane-specific absorption bands, respectively 1220 cm^{-1} (C-O-C) form the ester bond and 3330 cm^{-1} and 1525 cm^{-1} (N-H bond). Also, the depletion of desmodur can be observed through the absence from the spectrum of the characteristic N=C=O band 2255 cm^{-1}. This demonstrates that the polyaddition reaction between the polyisocyanate and the polyol occurs within the first 120 hours after mixing. The polyaddition reaction mechanism can be explained as follows: within the aromatic diisocyanate molecule, there is a permanent electron transfer between the π electrons of benzene nucleus and the non-participating electron pair of nitrogen in the -N=C=O group [3], which attracts the π electrons of the C=O double bond to the nitrogen atom, generating a partial negative charge on the nitrogen atom and a partial positive charge on the carbon atom. This occurs in the absence of any other reactant [4, 5].



(1)

In the presence of the polyol (R-OH), the O–H group on the macromolecular chain, through the non-participating electron pair belonging to oxygen, orients towards the positively charged carbon atom of the isocyanate group, initiating the formation of a new single C–O bond, followed by the loss of the proton through the breaking of the bond between oxygen and hydrogen. This represents the first stage of the polyaddition reaction. The second stage is the attraction of protons from the system by the nitrogen atom with a negative charge, forming the new N–H bonds, which, along with the C–O bonds, are characteristic of the urethane group.



(2)

All these types of bonds coexist in the system until the complete consumption of the isocyanate groups and hydroxyl groups. It should be noted that these functional groups tend to react with any H–O group in the system, including the one presented in the H_2O molecule, which is much more reactive than the H–O group in the polyol chain. It is crucial that the mixture does not contain any moisture or polar solvents. Such impurities can block the isocyanate groups, leading to a reduction in the viscoelastic properties of the final polymer matrix. Additionally, they can generate secondary reaction products (CO_2), which will remain in the system and create centers that promote the transition from combustion to deflagration or detonation. Therefore, it is essential to ensure that the mixture is free from moisture/polar solvents. The polyaddition reaction was monitored in real-time using live FTIR-ATR spectrum acquisition immediately after mixing the reactants in the ATR device.

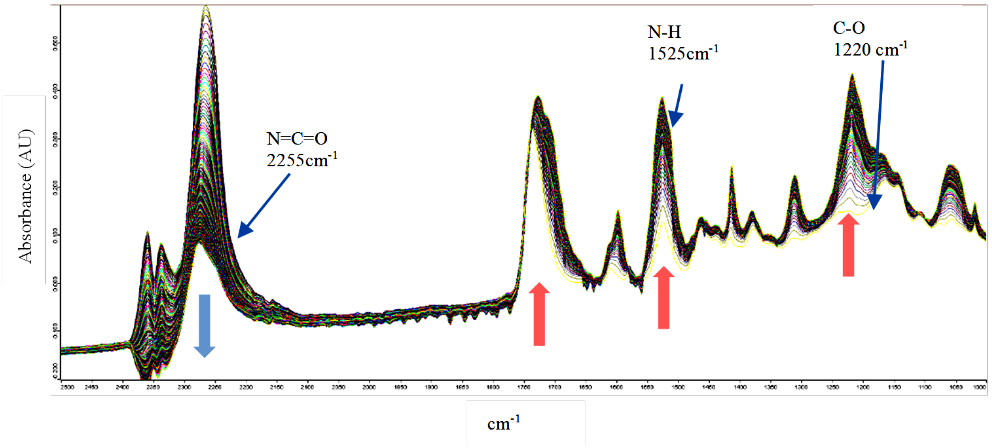
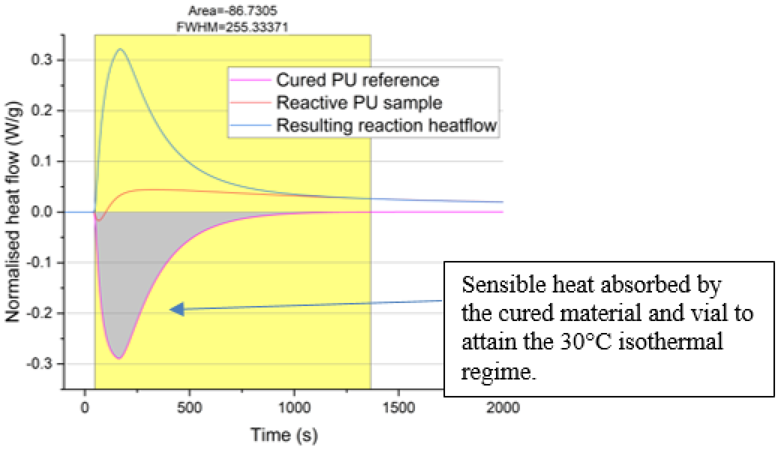


Fig. 2. FTIR-ATR spectra of the curing process of polyurethane (24 hours, every 5 minutes, 300 superimposed spectra)

The curing process of the polyurethane film was observed based on the real-time FTIR-ATR signals (Fig. 2). Confirmation of the formation of the urethane linkage was achieved through the depletion of Desmodur, which led to a decrease in the peak located at 2255 cm^{-1} (specific for the N=C=O group). This was accompanied by an increase in the peaks that are characteristic of the urethane group, in particular νN-H at approximately 1525 cm^{-1}, and carbonyl group via νC=O around 1700 cm^{-1}, and νC-O at 1220 cm^{-1} (C-O-O).

3.2. HFC characterization

The HFC analysis (Fig. 3) has offered significant insights into the process involved in obtaining the PU binder by investigating the thermal evolution of the polyaddition reaction. This analysis is based on the principle that materials undergo physical or chemical transformations that cause them to either absorb or generate heat when kept at a constant temperature. After preparation, the thermal evolution of the PU binder was analyzed in isothermal analysis at 25°C. In order to further explore the reaction kinetics and its temperature dependence, additional calorimetric analyses were conducted at 30°C and 35°C. The heat of reaction (J/g) and the relative peak intensities measured on FTIR-ATR are represented in Fig. 4 as time-dependent graphs. The heat release due to polyaddition and crosslinking was calculated using as a baseline a reference ampule loaded with the same amount (≈0.1g) of cured polyurethane to compensate for the sensible heat exchange in order for the sample to attain analysis temperature as shown in Fig. 3.



Sensible heat absorbed by the cured material and vial to attain the 30°C isothermal regime.

Fig. 3. Heat flow measurements in isothermal mode (30°C) for a Desmodur-Sethatane reactive system

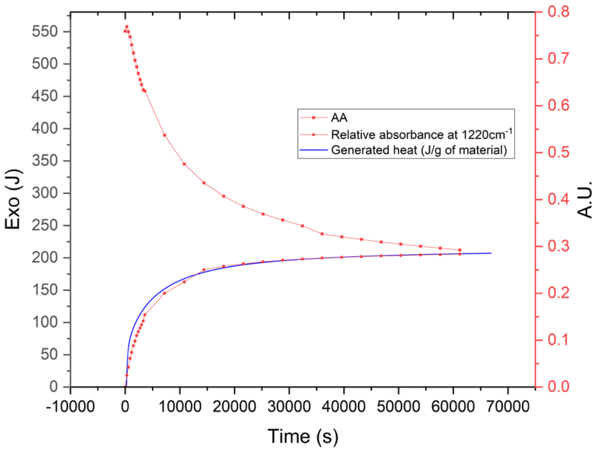


Fig. 4. Heat released by the curing reaction in relation to 1220 cm^{-1} (C-O-C) polyurethane ester formation and isocyanate depletion (N=C=O 2255cm^{-1}).

It can be observed that the heat generated is directly related to the formation of the polyurethane bond, and the heat release rate is proportional mainly to the cured product concentration and not to the quantity of available isocyanate. This could indicate that excess Desmodur is present in the composition.

The reaction's temperature dependence was analyzed by measuring the heat flow as a time-dependent variable at 25°C, 30°C, and 35°C. The measurements were only considered viable after the ampule reached thermal equilibrium with the calorimeter since thermal stabilization heat flow saturated the heat flow sensor. The results can be observed in Figs. 5 and 6, respectively.

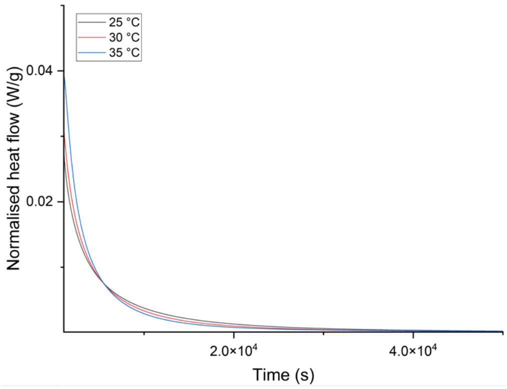


Fig. 5. Heat flow measurement at different temperatures for the polyurethane curing

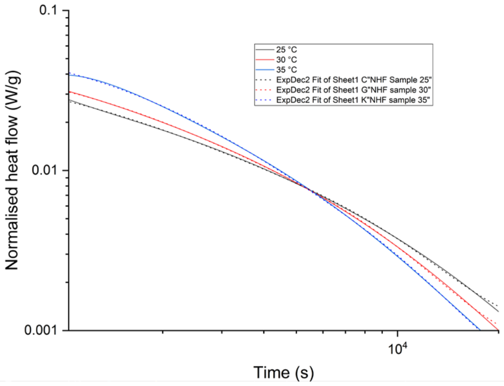


Fig. 6. Double exponential decay fitting of the reaction heat flow shown in double logarithmic scale.

In Fig. 5, it can be observed that in the 2 hours (6400s), there is a direct proportionality of the heat flow with the temperature. In the time left until the final curing of the reaction, the heat flow is inversely proportional to temperature, explained by the fact that the conversion is higher, and thus, the kinetics slows down. The double decay exponential fitting can be used to explain the kinetics of curing, mainly a higher rate polymerization reaction (chain extension), which is consumed in the first 6000s, and a slower rate crosslinking with a slower rate, as shown in Fig. 7.

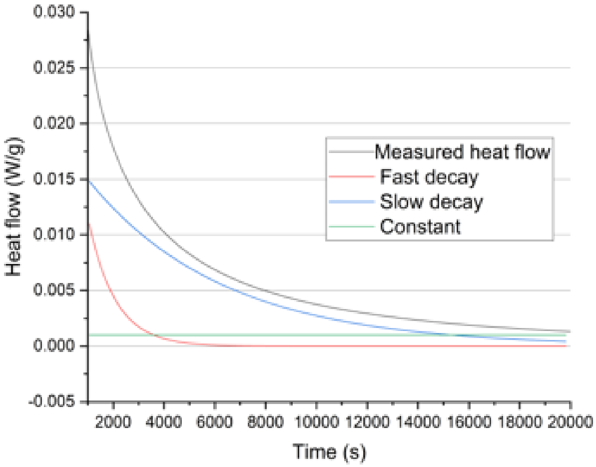


Fig. 7. Fast and slow decay fitting of the curing reaction of PU

Material compatibility was analyzed using heat flow calorimetry as a component analysis and whole pyrotechnic composition analysis. The heat flow measurements are shown in Fig. 8. Each component of the flare composition was analyzed separately, in individual ampoules, in 1g quantity, while in the graph, the individual component heat flow is normalized to its proportion in composition. A theoretical resulting heat flow is represented as the sum of the individually normalized heat flow of components. The actual heat flow of the flare composition is represented separately, and the difference between the theoretical heat flow and the actual heat flow is considered to be the interaction of the components. The results show an apparent interaction in the first three days. The integral of the interaction represents 10% (0,16J) of the integral of the pyrotechnic composition heat flow (1.74J). Also, the interaction graph drops to negative values after 3 days of analysis, meaning that the PU does not chemically interact with other components, but these components catalyze the curing reaction. The negative value of the interaction graph in the 60°C isotherm is related to the air oxidation of magnalium in the ampule, giving an artificial high heat flow.

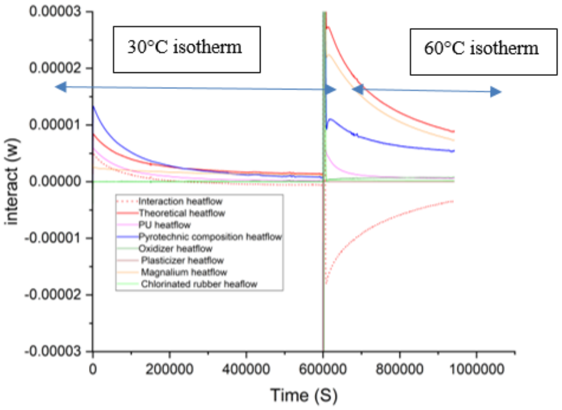


Fig. 8. Material compatibility analysis

3.3. DMA characterization

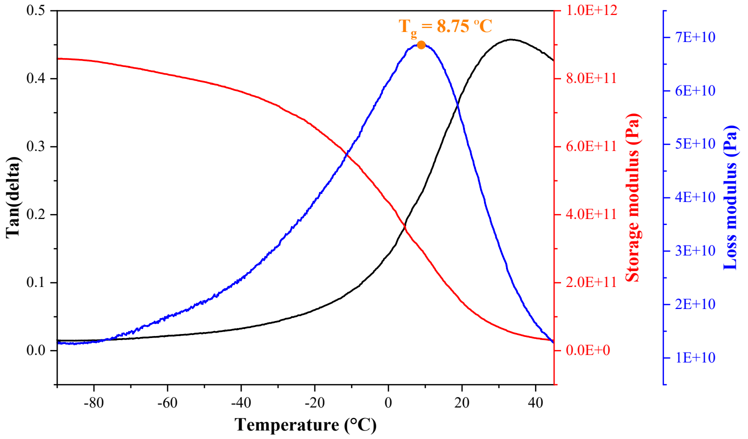


Fig. 9. Single-point bending behavior of the pyrotechnic composite material (*storage modulus E' - purely elastic component, loss modulus E'' - purely viscous component, loss tangent – tan(δ) and glass transition temperature Tg)*

To determine the viscoelastic properties, the developed pyrotechnic formulations were subjected to dynamical mechanical analysis, recording their behavior in the form of the deformation modules – E or G and the loss factor – tan(δ) (module ratio). The deformation modulus of a material can be either the modulus of elasticity (E) or the shear modulus (G), depending on the type of mechanical stress it experiences. The glass transition temperature (Tg) can be determined by DMA results. Based on storage modulus, E′, loss modulus, E″ and tan(δ) curves obtained in single cantilever mode presented in Fig. 9, it is observed that glass transition temperature appears at 8.75 °C. At this temperature, the structure of the pyrotechnic composition changes the state from the semi-crystalline, hard and relatively fragile, to the viscous (elastic), resistant to deformation.

From the graphical representation of the storage modules E′ and loss module E″, depicted in Fig. 10, it can be seen that the values of the elastic component are higher than those of the viscous component and, at the same time, during the analysis. Based on the results, the storage modulus G′ is greater than the loss modulus G″, indicating that the pyrotechnic formulation has an elastic behavior rather than a viscous (rigid) behavior.

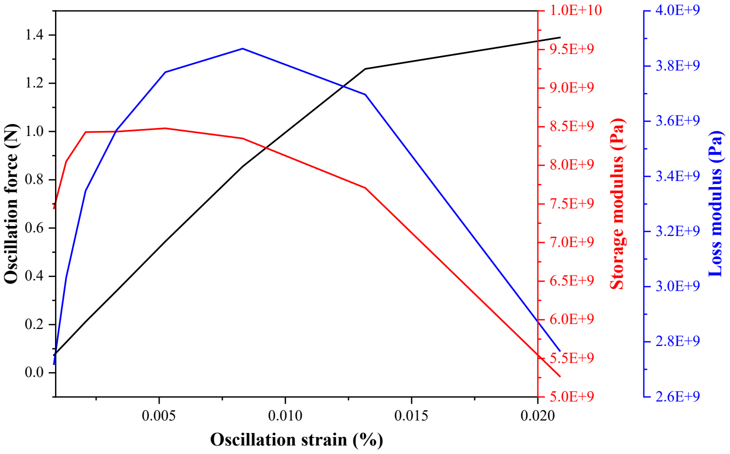


Fig. 10. Three-point bending behavior of the FLARE composition

Additionally, shear tests were conducted with oscillating frequency. The resulting data for G′, G″ and tan(δ) was plotted in Fig. 11.

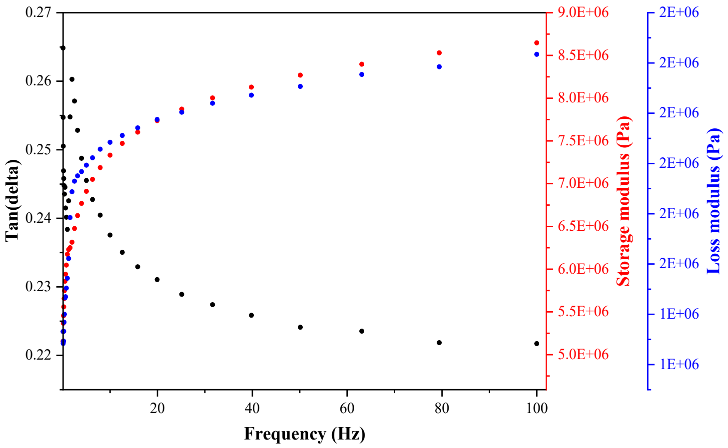


Fig. 11. Shear storage modulus, shear loss modulus, and tan delta profiles vs. frequency for developed pyrotechnic mixture

4. Conclusions

The purpose of the study was to verify the viscoelastic properties and chemical compatibility of a new pyrotechnic mixture developed for use as an energetic charge in the FLARE thermal decoy ammunition.

The curing reaction follows a double exponential decay kinetics, with a faster link extension addition and a slower crosslinking curing, as observed by both FTIR-ATR spectroscopy and Heat flow calorimetry. The compatibility measurements, performed by heat flow calorimetry revealed that the presence of the other compounds in the pyrotechnic mixture will accelerate the curing process but does not generate additional stable compounds. The analysis showed that the polyurethane binder is compatible with the other components of the pyrotechnic composition.

The dynamic mechanical analysis highlighted the importance of the binder based on chlorinated rubber. It helped determine the glass transition temperature of the pyrotechnic composite material, which was found to be 8.75 °C. Considering that the Tg of the binder based on chlorinated rubber is -36 °C, it can be deduced that it contributes significantly to the decrease in Tg of the composite, giving the composite a predominantly elastic behavior. It can be said that the pyrotechnic composite material developed will maintain its elastic behavior throughout the storage period of the FLARE thermal decoys, but also in the case of thermal and mechanical shocks to which they may be subjected. Although the ammunition can reach negative temperatures, when returning to positive temperatures the pyrotechnic composite will regain elastic behavior.

It was also proven that the storage modulus (elastic component) of the composite has higher values than the loss modulus (viscous component), thus confirming crosslinking. Yet, during the mechanical analysis, the elastic and viscous components were found to contribute equally to maintaining the material's integrity.

Altough both Parlon™ and polyurethane binders are long known to be used in pyrotechnic mixtures as binders [6, 7, 8, 9, 10] the novelty of this work consists in the use of a mixture of polyuretane- Parlon™ rubber mixture as binder for pyrotehnic formulations. This combination presents superior performance in terms of parameters of combustion (burn rate, combustion temperature) [21], while this work demonstrates that the use of the mixture will improve the mechanical properties of the composite material, compared with formulations based on singe polymer formulations.

Acknowledgement

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CCCDI-UEFISCDI, project number PN-III-P2-2.1-PTE-2021-0157, within PNCDI.

REFERENCES

[1]. Epure, C., Ţigănescu, T.V., Iorga, O., Marin, A., Munteanu, M., Zecheru, T., Şchiopu, A., Pulpea, B., Fuel Ratio and Additives Influence on the Combustion Parameters of Novel Polyurethane-based Flares, Mater. Plast., 75 (4), 2020, p. 109 – 124, https://doi.org/10.37358/MP.20.4.5411

[2]. STANAG 4515 ed. 2 – Explosives: thermal analysis using differential thermal analysis (DTA), differential scanning calorimetry (DSC), heat flow calorimetry (HFC), and themogravimetric analysis (TGA).

[3]. Toader, G., Diacon, A., Rusen, E.; Rizea, F.; Teodorescu, M., Stanescu, P.O.; Damian, C.; Rotariu, A.; Trana, E., Bucur, F.; et al., A Facile Synthesis Route of Hybrid Polyurea-Polyurethane-MWCNTs Nanocomposite Coatings for Ballistic Protection and Experimental Testing in Dynamic Regime, Polymers, 13, 2021. https://doi.org/10.3390/polym13101618

[4]. Toader, G., Rusen, E., Teodorescu, M., Diacon, A., Stanescu, P.O., Rotariu, T., Rotariu, A., Novel polyurea polymers with enhanced mechanical properties, Journal of Applied Polymer Science, 133 (38), 2016, https://doi.org/10.1002/app.43967

[5]. Toader, G., Diacon, A., Axinte, S.M., Mocanu, A.; Rusen, E., State-of-the-Art Polyurea Coatings: Synthesis Aspects, Structure–Properties Relationship,and Nanocomposites for Ballistic Protection Applications, Polymers, 16, 2024, https://doi.org/10.3390/polym16040454

[6]. Moulai Karim Boulkadida, Sabri Touidjinea , Djalal Tracheb , and Samir Belkhiri, Analytical Methods for the Assessment of Curing Kinetics of Polyurethane Binders for High-Energy Composites, CRITICAL REVIEWS IN ANALYTICAL CHEMISTRY, 2020, doi.org/10.1080/10408347.2020.1863768

[7]. Pietron, J.J., Mirkarimi, P.B., Review of the Effects of Polymer Binder Properties on Microstructure and Irreversible Volume Growth of Plastic Bonded Explosives Formulations, PEP, 2022, doi.org/10.1002/prep.202100379

[8]. GABRIELA TOADER, TRAIAN ROTARIU, EDINA RUSEN, JEREMIE TARTIERE, SORIN ESANU, TEODORA ZECHERU, IZABELA CRISTINA STANCU, ANDRADA SERAFIM, BOGDAN PULPEA, New Solvent-free Polyurea Binder for Plastic Pyrotechnic Compositions, MATERIALE PLASTICE, 1 (54), 2017

[9]. S. Kanitkar, Y. Zhou, D. Haynes, E. M. Sabolsky, B. Chorpening, Can. J. Chem. Eng. 2023, 101(7), 3798. https://doi.org/10.1002/cjce.24727

[10]. S. Kanitkar, D. Haynes, E. M. Sabolsky, B. Chorpening, Prop., Explos., Pyrotech. 2023, 48, e202300012.