# Furoic Acid-Based (Non)Energetic Plasticizers for Solid Composite Propellants Production

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This paper presents the development of high-performance energetic plasticizers based on furan-2,5-dicarboxylic acid (FDCA) as a renewable bio-material, resulting in bis(2-ethylhexyl) furan-2,5-dicarboxylate (FDC) and bis(1,3-diazidopropan-2-yl) furan-2,5-dicarboxylate (FDAC). The structural characterization was performed using FTIR spectroscopy. The effects of FDCA-based plasticizers were analyzed in the binder component of composite rocket propellants (CRP) as well as in ammonium perchlorate-based CRP, and the results were compared with those obtained for the commercial plasticizer dioctyl adipate (DOA). Mechanical properties were assessed through uniaxial tensile tests. The relaxation behavior, as well as the temperature and frequency dependence of the developed plasticizers, were studied using dynamic mechanical analysis (DMA). The presence of two relaxation processes was observed in the temperature dependence curves of  $\tan(\delta)$ . The primary relaxation process was detected in the temperature range of -70 °C to -55 °C, while the secondary process was observed in the range of -40 °C to 40 °C. Activation energy values for viscoelastic relaxation were calculated. This research highlights advancements in the development of composite rocket propellants through innovative plasticizer design.

Key words: propellants, plasticizers, energetic materials, mechanical properties, rocket technology.

## Introduction

OMPOSITE rocket propellants (CRP) are valued in rocket/aerospace development due to their exceptional stability, energetic, mechanical and inner-ballistic properties. These characteristics, combined with relatively simple manufacturing processes and long service life, make them an ideal choice for various aerospace applications. The main challenges of CRP development are achieving acceptable viscoelastic properties of uncured CRP [1], adjusting their energetic and mechanical properties. Viscoelastic properties, processability (e.g. pot life) and mechanical properties as well are significantly influenced by the chemical structure of plasticizer [1]. Plasticizers, lowmolecular weight compounds, improve the processing properties of solid propellant by physically inserting between binder chains, which reduces their interactions, *i.e.* decreasing the cohesive forces and  $T_g$  of the system. Commonly used plasticizers, such as dioctyladipate (DOA), not only facilitate the manufacturing process, but also impart desirable mechanical properties to the propellants. The main goals in developing plasticizers are to improve thermal stability and energy content, enhance the oxygen balance in the formulation, reduce the glass transition temperature  $(T_g)$  and improve other mechanical properties of the propellant matrix. Incorporating energetic groups such as azido (-N<sub>3</sub>), nitro (-

 $NO_2$ ), and nitrate (- $NO_3$ ) into organic molecules represents one of the sustainable strategies for producing energetic plasticizers [2], [3]. Among energetic plasticizers, azide compounds have recently garnered increasing attention. The primary combustion product of azide-based plasticizers is nitrogen, a highly stable molecule that shows minimal reactivity even at the high temperatures encountered in rocket motors [4], [5].

Both, energetic and non-energetic plasticizers can be prepared from bio-based raw materials, which preserve fossilbased resources respecting principles of circular economy and sustainable development. Some of those natural resources are carbohydrates such as fructose, maltose or cellulose based derivatives. Natural sugar, glucose, is starting materials for furan-2,5-dicarboxylic acid (FDCA), which represents a potential substitute for terephthalic acid (TPA), used in producing polyesters like poly(ethylene terephthalate) - PET and poly(buthylene terephthalate) - PBT. FDCA is a key building block for the synthesis of polymers like poly(ethylene furanoate) (PEF), offering an alternative to petrochemical materials such as terephthalic acid (PTA). The PEF has better mechanical strength, higher thermal stability and high gas barrier than petroleum-based PET [6], [7].

The aim of this study is to investigate the structural and dynamic-mechanical characteristics of the CRP binder mixture and composite rocket propellant based on hydroxy-

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terminated poly(butadiene) (HTPB) prepolymer and isocyanate crosslinker, using newly developed plasticizers derived from FDCA. This research highlights the potential of advanced composite rocket propellants achieved through innovative plasticizer design, paving the way for more efficient, sustainable, and high-performance propulsion systems [8].

# **Experimental part**

#### Materials and methods

For plasticizers synthesis, following chemicals, supplied from MERCK, Germany, were used: 2,5-furan dicarboxylic acid (FDCA), thionyl chloride (SOCl<sub>2</sub>), dimethylformamide (DMF), 1,3-dichloropropan-2-ol, and sodium azide (NaN<sub>3</sub>). All chemicals were used without further purification. HTPB, commercial name R-45M (USA, viscosity at 30 °C: 5500 mPa·s, OH value: 44-51 mg KOH g<sup>-1</sup>, hydroxyl functionality: 2.4, average molecular weight, Mn: 2900 g·mol-1, glass transition temperature,  $T_g$ : -80 °C), was used as a binder. Dioctyladipate (DOA) and bonding agent, triethylenetetramine (TETA), were purchased from Merck, Germany. Antioxidant AO2246 (2,2'-bis(4-methyl-6tertbutyl) phenol, was supplied from Sigma Aldrich, Germany. Curing agent, isophorone diisocyanate (IPDI) was supplied from Acros Organics, Belgium. Ammonium perchlorate oxidizer (AP - grade IZ-200-TCP) was procured from Eruca Technologies, Czech Republic. Aluminum with average particle sizes of 15 and 30 µm (X-71 and X-86) was procured from Alcan Toyo.

#### Synthesis of furoic acid-based plasticizers

The synthesis of non-energetic plasticizers was carried out in a two-step process. In the first step, furan-2,5-dicarbonyl dichloride and 1,3-diazidopropan-1-ol precursors were synthesized according to the procedure:

*furan-2,5-dicarbonyl dichloride:* In a 250 cm<sup>3</sup> three-neck flask equipped with a condenser, magnetic stirrer, and thermometer, 15.6 g (0.1 mol) of FDCA, 0.22 g (0.002 mol) of SOCl<sub>2</sub> and 60 cm<sup>3</sup> of DMF solvent were measured. The reaction mixture was continuously stirred under reflux at 80 °C for 5 hours. Unreacted SOCl<sub>2</sub> and the DMF solvent were removed by vacuum distillation. The isolated and purified product was a white crystalline solid with a yield of 98% (Figure 1 – chemical structure 1).

**1,3-diazidopropane-2-ol:** In a 250 cm<sup>3</sup> three-neck flask equipped with a thermometer, condenser and magnetic stirrer, 5 g (38.8 mmol) of 1,3-dichloropropan-2-ol, 5.05 g (77.5 mmol) of sodium azide (NaN<sub>3</sub>) and 100 cm<sup>3</sup> of DMF solvent were measured. The reaction mixture was heated to 80 °C and continuously stirred for 5 hours. After the reaction was completed, the organic phase that contained the product was extracted with 50 cm<sup>3</sup> of ethanol and dried over anhydrous MgSO<sub>4</sub>. The remained solvent was removed by vacuum distillation, yielding a colorless oily product (4.58 g, 32.23 mmol, 83%) (Figure 1 – chemical structure 2).



Figure 1. Schematic illustration of the synthesis of turan-2,5dicarbonyldichloride (structure 1) and 1,3-diazidopropane-2-ol (structure 2)

In the second step, esterification of 2,5-dicarbonyl dichloride with 2-ethylhexanol was carried out to obtain the bis(2-ethylhexyl) furan-2,5-dicarboxylate (FDC) plasticizer. Afterward, the esterification was performed using 1,3diazidopropan-1-ol to obtain the bis(1,3-diazidopropan-2-yl) furan-2,5-dicarboxylate (FDAC) plasticizer. In a 250 cm<sup>3</sup> three-neck flask equipped with a thermometer, condenser, dropping funnel, and magnetic stirrer, 20 g of 2,5-furan dicarbonyl dichloride was dissolved in 50 cm<sup>3</sup> of toluene. 13.6 g of 2-ethylhexanol or 1,3-diazidopropan-1-ol was added dropwise over 20 minutes at 0 °C with vigorous stirring. The reaction mixture was then heated to 80 °C and stirred for 5 hours (Figure 2). Upon completion of the reaction, the mixture was cooled to room temperature, and anhydrous CaCl<sub>2</sub> was added to remove moisture. Finally, the product was filtered. The yield was 98% for FDC (structure 3) and 72% for FDAC as a pale-yellow liquid (structure 4) (Figure 2).



Figure 2. Schematic illustration of the synthesis of bis(2-ethylhexyl) furan-2,5-dicarboxylate and bis(1,3-diazidopropan-2-yl) furan-2,5dicarboxylate

#### Homogenization of the binder and propellants

Homogenization of the binder mixture was performed in a vertical DRAIS FH mixer (Figure  $3a - 1.5 \text{ dm}^3$  working volume). HTPB prepolymer, plasticizer, TETA bonding agent and AO2246 antioxidant were measured and homogenized 30 minutes at 60 °C, after which IPDI curing agent was added and homogenized further for 15 minutes. Separation of the plasticizer-prepolymer phases was not observed during the homogenization. The mass was then cast into Teflon molds with dimensions of 200x130x4 mm and cured in an oven for five days at 70 °C.

In order to analyze the effects of the synthesized novel furoic acid-based non-energetic plasticizers on the mechanical properties of the solid rocket propellants, following propellant compositions were homogenized and cast (Table 1). Propellants were homogenized using a laboratory 1-gallon Baker-Perkins planetary mixer (Figure 3b) at a temperature of 60 °C. The homogenization process started with a premix phase where HTPB prepolymer, plasticizer, TETA bonding agent AO2246 antioxidant and metal fuel (50/50 bimodal

aluminum mixture) were placed in a mixer and homogenized for 30 minutes at 60 °C. The next step included adding the AP oxidizer (30/70 bimodal AP mixture of 10 and 200 µm average particle size) in three equal portions. The mixture was homogenized for 90 minutes at 60 °C under vacuum (10-14 mbar). Finally, IPDI curing agent was added and homogenized for 15 minutes. Selected binders and propellants are marked according to the used plasticizers as shown in Table 1, where P and B represent propellant and binder, respectively. The numbers in the index indicate the ratio of plasticizers within the selected sample. For example, BFDAC/DOA<sub>50-50</sub> represents a binder sample containing FDAC-based and DOA-based plasticizers in a 50/50 mass ratio. The B<sub>Ref</sub> sample does not contain a plasticizer, but only the HTPB prepolymer cross-linked with IPDI. The amount of the main premix ingredients is shown in Table 1.

| Table 1. Selected binders and | propellants samples <sup>a</sup> |
|-------------------------------|----------------------------------|
|-------------------------------|----------------------------------|

| Samples                    | DOA<br>[phr <sup>b</sup> ] | FDC<br>[phr] | FDAC<br>[phr] | TETA<br>[phr] | AO2246[phr] | IPDI<br>[phr] |
|----------------------------|----------------------------|--------------|---------------|---------------|-------------|---------------|
| PDOA                       | 15.00                      | -            | -             | 0.35          | 1.50        | 8.41          |
| PFDAC                      | -                          | -            | 15.00         | 0.35          | 1.50        | 8.41          |
| B <sub>Ref.</sub>          | -                          | -            | -             | -             | 1.50        | 8.41          |
| BFDC <sup>c</sup>          | -                          | 15.00        | -             | -             | 1.50        | 8.41          |
| BFDAC                      | -                          | -            | 15.00         | -             | 1.50        | 8.41          |
| BFDAC/DOA <sub>50-50</sub> | 7.50                       | -            | 7.50          | -             | 1.50        | 8.41          |

<sup>a</sup> - all samples contain 100 phr of HTPB; 75 wt.% AP i 7 wt.% Al; <sup>b</sup> - phr - parts per hundred of rubber; <sup>c</sup> - unsuccessful curing;



Figure 3. (a) Vertical DRAIS FH mixer, and (b) laboratory 1-gallon Baker-Perkins planetary mixer

#### Characterization methods

The viscosity of the uncured propellants was measured at the 60 °C by HBT type Brookfield viscometer with a T-C spindle at a rotation speed of 5 rpm.

Structural characterization of synthesized plasticizers was determined by Nicolet<sup>TM</sup> iS<sup>TM</sup> 10 FTIR Spectrometer (Thermo Fisher SCIENTIFIC) with Smart iTR<sup>TM</sup> Attenuated Total Reflectance (ATR) Sampling accessories, United States of America. Spectrum was recorded in transmittance mode, within a range of 400-4000 cm<sup>-1</sup>, at a resolution of 4 cm<sup>-1</sup> and in 20 scan mode.

The dynamic mechanic analysis (DMA) of cured binders and propellants (rectangular bar with dimensions as follow: length: 54.0 mm, width: 10.0 mm, and thickness: 4.0 mm) was done by Modular Compact Rheometer MCR-302 (Anton Paar GmbH, Austria) equipped with standard fixtures SRF12, temperature chamber (CT S620) which has high temperature stability ( $\pm 0.1$  °C) and with automated cooling accessories using liquid nitrogen. DMA measurements were performed at a temperature range of -85 °C to +40 °C with a heating rate of 5 °C min<sup>-1</sup> and a single angular frequency of 6.28 rad<sup>-1</sup>s.

The mechanical characteristics of cured binders and propellants were determined according to the standard tensile tests performed using an Instron 1122 Universal Testing Instrument at 20 °C with a force loading rate of 50 mm min<sup>-1</sup>. The tensile properties were determined using seven standard JUS (for binder testing) and JANNAF C specimens (dog-bone shape for propellant testing). The average value is presented.

#### **Results and Discussion**

The effect of plasticizer on the end-of-mix (EOM) viscosity of the uncured propellants depends on its chemical structure, *i.e.* the interactions established with the prepolymer. Figure 4 and Table 2 show that the increase in viscosity of propellant containing FDAC as a plasticizer is substantially greater compared to that with DOA. FDAC has a significant amount of polar domain within its structure which is capable of establishing hydrogen bonding interactions with the free hydroxyl groups of HTPB. In addition, its bulky conformation reduces the free volume for cooperative motions of macromolecule segments of HTPB. However, the remarked increase in viscosity for the FDAC plasticizer does not affect the pot life, *i.e.* the time when the propellant slurry remains liquid, which allows easy manipulation and casting into rocket motor chamber [9] (Table 2). Namely, compositions with viscosity up to 500 Pa s are completely acceptable for casting propellants. Numerical models of viscosity dependence on time are derived by regression analysis (equations in Figure 4,  $y = a \cdot X + b$ ), where y is the maximum viscosity value (500)  $Pa \cdot s$ ), X is the pot-life, and a and b are coefficients. According to the above equations, the obtained pot-life is 185 min and 422 min for PFDAC and PDOA, respectively. A DOA propellant indicates poor reactivity, requiring a long curing time and high electric energy consumption. Contrary to this, the introduction of FDAC instead of DOA reduces the curing time, but provides sufficient space for propellant casting.

Table 2. Viscosity of the analyzed propellants

| Samples | η [Pa·s] |        |        |        |        |        |
|---------|----------|--------|--------|--------|--------|--------|
|         | 15       | 30     | 45     | 60     | 75     | 90     |
| PFDAC   | 127.79   | 159.51 | 191.81 | 223.41 | 264.48 | 287.88 |
| PDOA    | 71.50    | 89.87  | 108.13 | 126.86 | 137.15 | 149.02 |



Figure 4. Time dependences of viscosity of the following propellants: (a) PFDAC and (b) PDOA

Table 3 shows the vibration frequencies at which IR absorption occurs (absorption maxima).

Table 3. FTIR spectrum values of synthesized plasticizers

| Plasticizers | Vibration frequencies ( $v_{max}$ [cm <sup>-1</sup> ])   |  |  |
|--------------|--|--|--|
| FDAC         | 2958 $v_{as}(-CH_3)$ , 2929 $v_{as}(-CH_2)$ , 2860 $v_s(-CH_3)$ , 1719 $v_s(C=O)$ , 1270 and 1220 $v_{as}(C-O)$ , 1127 $v_s(C-O)$ , 764 $v_s(C-H)$ |  |  |
| FDC          | 2962 $v_{as}(-CH_2)$ , 2098 $v_s(C=N)$ , 1721 $v_s(C=O)$ , 1265<br>and 1220 $v_{as}(C-O)$ , 1126 $v_s(C-O)$ , 760 $v_s(C-H)$                       |  |  |

The peaks at 2929 cm<sup>-1</sup>, 2958 cm<sup>-1</sup>, and 2962 cm<sup>-1</sup> correspond to the asymmetric and symmetric stretching of C-H bonds in -CH<sub>2</sub> and -CH<sub>3</sub> groups [10], [11]. Peaks around 1719 cm<sup>-1</sup> (FDAC) and 1721 cm<sup>-1</sup> (FDC) are indicative of C=O stretching in the FDCA structure, as it contains two carbonyl groups. Peaks near 1270 cm<sup>-1</sup>, 1220 cm<sup>-1</sup>, and 1127 cm<sup>-1</sup> suggest the presence of ester bonds within plasticizers chemical structure. C-H deformations within the furan ring structure often appear in the region between 750-800 cm<sup>-1</sup>, which could explain peaks such as 764 cm<sup>-1</sup> (FDAC) and 760 cm<sup>-1</sup> (FDC), respectively. Additionally, the presence of a nitrile group in FDC is attributed to the peak at 2098 cm<sup>-1</sup>.

#### DMA analysis of the cured binder

Determination of the glass transition temperature,  $T_g$  is of great importance for the exploitation of solid rocket propellants (Figure 5). On temperatures below  $T_g$  the propellant becomes very brittle and the rocket motor may fail during the firing and exploitation. The motor failure occurs due to propellant cracking which is caused by its inability to remain mechanically stable at operational pressure. The following rheological parameters were recorded: G' - storage modulus, G'' - loss modulus and  $tg(\delta)$  mechanical damping factor defined as the ratio of loss and storage modulus. The G' is an elastic response of the tested material and determines its ability to store energy [12], while G'' is related to viscous response of a material, *i.e.* its ability to release thermal energy [13].



Figure 5. (a) Storage modulus (G'), loss modulus (G''), and mechanical loss modulus ( $tg(\delta)$ ) as a function of temperature for the PDOA propellant; (b), (c) and (d) temperature dependences of G', G'' and  $tg(\delta)$  for PDOA and PFDAC propellants, respectively

The resulting DMA curves (Figure 5a) are typical of solid viscoelastic HTPB-based rocket propellants [13]. Storage modulus decreases with temperature from 3023 MPa at -90 °C and to 7.5 MPa at 25 °C. The loss modulus curve shows a single peak in the wide temperature range from -80 °C to -55 °C. Plasticizer type has not significantly affected decreasing of the G' with temperature increase, but its influence is more evident in G" curve shape and values of the  $T_{\rm g}$  obtained from G'' and tg( $\delta$ ) peaks maxima (Table 4). The PDOA sample has the lowest G' value, indicating lower elasticity, while the G'' and  $tg(\delta)$  values are moderate, suggesting medium viscoelastic properties. The PFDAC sample shows the highest G'' value, indicating higher viscosity, while its lowest  $tg(\delta)$  value suggests the least viscous behavior compared to elastic properties. The glass transition temperature region is shifted to slightly lower values for the PDOA propellant compared to the one containing PFDAC (Figure 5c and 5d).

Two peaks can be observed in the  $tg(\delta)$  curve  $[tg(\delta) =$ f(T)], Figure 5d. The first peak is observed in the temperature range from -70 °C to -55 °C with a maximum of -63.5 °C. The second peak, observed in the temperature range from -40 °C to 40 °C, reaches its maximum -15.0 °C. The second peak is wide and has a lower intensity than the first peak. This behavior is related to the presence of hard and soft segments in polyurethane based propellant. The first peak is a  $T_{
m g}$  of the soft segments ( $T_{
m g}^{
m soft}$ ) which determines the beginning or the end of the movement of the segments of the main HTPB chain. The second peak is related to a complex process involving two mechanisms: the interactions of the HTPB polymer itself and the interactions of the heterogeneous material. It is a  $T_{\rm g}$  of hard and/or soft segments, with the mobility significantly reduced due to solid content and interactions between the binding agent and the solids  $(T_{g}^{hard})$ . The polyurethanes have a segmented structure - the hard segments being the urethane groups (-N=C=O), and the polybutadiene chain being the soft segment [5].

It is observed from Table 4 that, depending on the plasticizer type, the Tg shifts to higher values. This occurs due to the increased mobility of segments of the polymer chains.  $T_g$  is shifted to higher values for BFDAC and BFDAC/DOA<sub>50</sub>-<sub>50</sub> samples compared to the BDOA, but the intensity of the tg( $\delta$ ) has not affected with plasticizer type. BFDAC has polar azido groups within the structure capable to establish hydrogen bonds with hydrogen atoms from HTPB which is manifested in a slight increase of  $T_g$ .

| <b>Table 4.</b> $T_g$ values determined from the G''= f(T), G'= f(T), and | $tg(\delta) =$ |
|---|----------------|
| f(T)  |                |

| Sample                     | $T_{g}^{1}[^{\circ}C]$ |        |              |  |
|----------------------------|------------------------|--------|--------------|--|
| Sampto                     | G"                     | G'     | $tg(\delta)$ |  |
| PDOA                       | -70.20                 | -74.30 | -63.80       |  |
| PFDAC                      | -66.60                 | -73.80 | -58.60       |  |
| BDOA                       | -78.60                 | -80.60 | -68.90       |  |
| BFDAC                      | -71.80                 | -75.50 | -61.00       |  |
| BFDAC/DOA <sub>50-50</sub> | -71.80                 | -78.40 | -63.50       |  |

The sample with the best balance of elastic and viscous properties, PFDAC, could be the best choice as it has the lowest  $tg(\delta)$  and appropriate G' and G'' values, suggesting stable viscoelastic properties.

# Mechanical analysis of the cured binder and propellant formulations

The mechanical properties of solid rocket propellants depend on the characteristics of the polymer used in the premix phase, type of cross-linking agent and its ratio with the polymer, the structure and amount of the solid phase [13]. The tensile characteristics of analyzed binders and corresponding propellants, expressed as tensile strength ( $\sigma_t$ ), strain at maximum load ( $\varepsilon_m$ ), strain at break ( $\varepsilon_b$ ) as well as Young's modulus (E) are shown in Table 5. These mechanical properties depend on the content of hard segments, which is dictated by the amount of curing agent. Since the ratio of IPDI and HTPB is the same within all binders/propellants, the nature of plasticizer makes a difference in the mechanical behavior as remarked in Table 5. The plasticizers used in this study have different structures, and therefore the mechanical properties are influenced by the formed polymer network, as well as secondary bonds in the polymer itself and with solid filler particles (oxidizer and metal fuel). It is noted that the binders have significantly lower values of tensile strength and higher strain at maximum load as well as strain at break. This is expected since binders are unreinforced materials in which the constraint of cooperative motion of the macromolecule segment is not hindered by solids. However, the effect of the type of plasticizer on the mechanical characteristics is evident as the presence of DOA reduces  $\sigma_t$  by 14.7% compared to the binder with the same amount of FDAC. In contrast,  $\varepsilon_m$  and  $\varepsilon_b$ are higher for 37.2% and 33.8%, respectively. Such phenomenon is caused by the weaker interaction between DOA and HTPB, which leads to easier collapse and deformability of the material. Substitution of 50% of DOA with FDAC exhibits similar tensile strength to the BFDAC binder, but the resulting material is stiffer, as manifested by lower values  $\varepsilon_m$  and  $\varepsilon_b$ . These results are potentially a reflection of the stronger interaction between FDAC and HTPB within BFDAC and rigid furan ring structure, providing the material with the ability to withstand an external force for higher stresses before cracking. High values of the elongation (maximal and fracture strain) of the binder matrix are desirable in terms of propellant lifetime [14]. The introduction of solids in corresponding propellants exhibits the same phenomena remarked with binders where  $\sigma_t$  is quite higher and  $\varepsilon_m$  and  $\varepsilon_b$  lower. FDAC in propellant composition (PFDAC) leads to an increase in the strain at maximum load and strain at break by 19.2% and 18.5%, respectively, compared to the PDOA composition.

| Sample                         | σ <sub>m</sub> (MPa),<br>[SD] | <i>ɛ</i> <sub>m</sub> (%), [SD] | &p (%), [SD]  | E (MPa),<br>[SD] |
|--------------------------------|-------------------------------|---------------------------------|---------------|------------------|
| PDOA                           | 0.96 [0.09]                   | 14.60 [0.38]                    | 18.40 [0.77]  | 10.11 [2.35]     |
| PFDAC                          | 0.98 [0.23]                   | 17.40 [0.17]                    | 21.80 [0.70]  | 8.02 [1.35]      |
| BFDAC                          | 0.34 [0.27]                   | 162.4 [17.11]                   | 164.5 [16.78] | 0.32 [0.19]      |
| BFDAC/DOA <sub>50-</sub><br>50 | 0.35 [0.19]                   | 143.0 [13.58]                   | 144.8 [13.56] | 0.46 [0.40]      |
| BDOA                           | 0.29 [1.43]                   | 222.8 [9.69]                    | 220.1 [9.41]  | 0.22 [0.16]      |

**Table 5.** Values of  $\sigma_{m}$ ,  $\varepsilon_{m}$ ,  $\varepsilon_{p}$  and *E* at T=20 °C (SD - standard deviation)

# Conclusion

In the presented study novel FDCA-based plasticizers, bis(2-ethylhexyl) furan-2,5-dicarboxylate and bis(1,3diazidopropan-2-yl) furan-2,5-dicarboxylate, were synthesized. Propellants with DOA and FDAC have similar  $\sigma_m$  values (a slight increase of 2.08% was recorded for the PFDAC composition). The highest tensile strength values at room temperature were achieved with FDAC. FDAC in propellant composition (PFDAC) leads to an increase in the elongation at maximum and break force by 19.2% and 18.5%, respectively. Compared to the PDOA composition, which can be considered as the reference, the elongation values obtained for the FDAC-based composition are also acceptable. Rheological analysis revealed two relaxation processes in the temperature range from -70 °C to 40 °C. The first process, occurring between -70 °C and -55 °C with a  $T_g$  peak at -63.8 °C for PDOA, while the second process, spanning -40 °C to 40 °C with a peak at -15.0 °C. The glass transition temperature for the PFDAC propellant slightly increases and it is around -58.6 °C. Obtained results indicate that synthesized FDCA-based plasticizer preserves the rheological and mechanical properties of the binder and composite rocket propellant in the range of the standard values, making this additive suitable for the production of such energetic materials.

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# Plastifikatori na bazi furoinske kiseline za proizvodnju čvrstih kompozitnih pogonskih goriva (energetski i ne-energetski)

U ovom radu prikazan je razvoj energetskih plastifikatora na bazi furanske-2,5-dikarboksilne kiseline (FDCA) kao obnovljivog bio-materijala, čime su dobijeni bis(2-etilheksil) furan-2,5-dikarboksilat (FDC) i bis(1,3-diazidopropan-2-il) furan-2,5-dikarboksilat (FDAC). Strukturna karakterizacija izvedena je korišćenjem FTIR spektroskopije. Efekti plastifikatora na bazi FDCA analizirani su u vezivnoj komponenti kompozitnih raketnih goriva (KRG), a rezultati su upoređeni sa vrednostima dobijenim za komercijalni plastifikator dioktiladipat (DOA). Mehanička svojstva ispitana su jednoosnim testovima zatezanja. Reološke karakteristike razvijenih plastifikatora proučavane su pomoću dinamičkog mehaničkog analizatora (DMA). Prisutnost dva relaksaciona procesa primećena je na krivama temperaturne zavisnosti  $tan(\delta)$ . Primarni relaksacioni proces zabeležen je u temperaturnom intervalu od -70 °C do -55 °C, dok je sekundarni proces uočen u intervalu od -40 °C do 40 °C. Izračunate su vrednosti energije aktivacije za viskoelastičnu relaksaciju. Ovo istraživanje naglašava napredak u razvoju kompozitnih raketnih goriva kroz inovativan dizajn plastifikatora.

Ključne reči: pogonska goriva, plastifikatori, energetski materijali, mehanička svojstva, raketna tehnologija.