

# Viscoelastic Properties of Carboxyl-Terminated (Butadiene-co-Acrylonitrile)-Based Composite Rocket Propellant Containing Tris(2,3-Epoxypropyl) Isocyanurate as Bonding Agent

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The influence of tris(2,3-epoxypropyl) isocyanurate as a bonding agent on the polymer network characteristics as well as rheological properties of [carboxyl-terminated (butadiene-co-acrylonitrile)/polyglycidyl ether of glycerol and epichlorhydrin]-based composite propellant was investigated. Amplitude sweep tests have been run above the glass transition temperature to establish the linear viscoelastic range (LVR) in a rubbery phase of the composite propellant for the correct physical interpretation of DMTA data. Temperature dependencies of rheological behaviour parameters (storage modulus, loss modulus, loss factor and glass-rubber transition temperature) were analyzed. It was observed that all the tested propellants have shown two relaxation processes in the temperature range  $-80^{\circ}\text{C}$  to  $+80^{\circ}\text{C}$ . The first one, structural relaxation ( $\alpha$ -transition) related to glass transition and the other one, secondary relaxation process. The activation energy for glass transitions was determined by the Arrhenius plot from dynamic properties measured at three frequencies (1, 5 and  $10\text{ rad s}^{-1}$ ). The dynamic mechanical analysis showed that the tris(2,3-epoxypropyl) isocyanurate content did not affect the glass transition temperature of the tested propellants

*Key words:* composite rocket propellant, butadiene-co-acrylonitrile, isocyanurate, glass transition temperature.

## Nomenclature

CTBN	– carboxyl-terminated (butadiene-co-acrylonitrile)
LX 112	– polyglycidyl ether of glycerol and epichlorhydrin
TEIC	– tris(2,3-epoxypropyl) isocyanurate
AP	– ammonium perchlorate
$C$	– cross-link density
$G'$	– the storage shear modulus
$G''$	– the loss shear modulus
$\tan(\delta)$	– loss factor
$T_g$	– glass transition temperature
$\sigma_m$	– tensile strength
$\varepsilon_m$	– strain at maximum load
$\varepsilon_b$	– strain at break
$E$	– Young's modulus
$E_a$	– activation energy

## Introduction

THE essential ingredients of a composite propellant are a crosslinked binder (an organic polymer) and an oxidizer (usually ammonium perchlorate). The binder, as the name implies, holds the composition together and acts as an auxiliary fuel. The use of hydroxyl-terminated (HTPB) and carboxyl-terminated (CTPB) polybutadienes as prepolymers for composite propellants is the most common choice of

polymeric materials to achieve the desired mechanical properties of the propellant in rocket motors [1,2,3]. The composite propellant grain undergoes high stresses induced by a rapid acceleration, sharp turn, or rapid chamber pressure rise during launch and flying. A proper propellant must possess mechanical properties that prevent these stresses [4]. In order to improve mechanical characteristics, an interaction between the ammonium perchlorate (AP) particles and the polymeric binder is necessary, which is achieved by bonding agents added to composite propellant composition. Bonding agents are typically used in HTPB-based composite propellants since these polymers are weakly polar [5]. Due to the highly polar carboxyl ( $-\text{COOH}$ ) group, carboxyl-terminated prepolymers (CTPB) do not require the use of bonding agents. If for a composite propellant production carboxyl-terminated (butadiene-co-acrylonitrile), known as CTBN, is taken, experiments have shown that tris(2,3-epoxypropyl) isocyanurate (TEIC) as the bonding agent significantly improves mechanical characteristics [6].

The molecular structure of the polymer based composite propellant is the largest factor in determining the mechanical properties of the cured propellant. The mechanical properties of composite propellants depend strongly on the time, temperature, loading procedure and loading history [7]. Dynamic mechanical thermal analysis (DMTA) is one of the most versatile techniques available for the characterization of

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time-, frequency-, and temperature-dependent mechanical properties of polymers. No other characterization method provides more information in a single test [8]. The technique may be used to characterize various polymers including thermoplastics, thermosets, elastomers and polymer based composites. Moreover, DMTA is often considered as the most accurate test method for determining the glass transition temperature and other structurally related phase transformation temperatures in polymers [9].

Since the bonding agent is an ingredient that is added to modify the mechanical properties of the propellant, precise knowledge of the dynamic mechanical behavior is extremely important.

The main objective of this paper is to broaden our knowledge of applying dynamic mechanical analysis to the study of CTBN-based propellant. As far as we are aware, there are no publications in the extensive literature, except our previous investigation, that have surveyed not only the viscoelastic properties of CTBN-based composite propellant but also the effect of this type of bonding agent on the CTBN-based composite propellant behavior.

## 2. Experimental part

### 2.1 Materials

Four CTBN-based composite propellant compositions (Table 1) were selected for this study. They consisted of 80 wt.% of solids loading including AP (oxidizer, with two particle sizes, 200  $\mu\text{m}$  and 10  $\mu\text{m}$ ) and 20 wt.% of a polymeric binder, whose mix ratio of ingredients is expressed in phr (parts per hundred of resin based on 100 parts of CTBN). The binder composition consisted of 100 phr of CTBN (1300 $\times$ 15, viscosity at 25 $^{\circ}\text{C}$ : 66.2 Pa $\cdot$ s, carboxyl functionality: 1.9, number-average molecular weight: 3800 g/mol, specific gravity at 23  $^{\circ}\text{C}$ : 0.931 g/cm $^3$ , glass transition temperature,  $T_g$ : -63.3 $^{\circ}\text{C}$ ), 30 phr of plasticizer (dioctyl adipate, DOA), 1.7 phr of antioxidant (2,2'-bis (4-methyl-6-tertbutyl) phenol, commercially available as a product called AO 2246) and 0.44 phr of cure catalyst [iron(III) acetylacetonate] (Fe(acac) $_3$ ). Preferred curing agents for carboxyl functional prepolymers are multifunctional epoxides. When carboxy terminated prepolymer is employed, the epoxy curing agent is added in an amount sufficient to generate a ratio of epoxy groups to carboxy groups, known as E/COOH ratio. The E/COOH ratio between the epoxy groups E of the curing agent to the carboxyl groups COOH of the CTBN was 1.20. The curing of CTBN was achieved by an epoxid curing using LX 112 (polyglycidyl ether of glycerol and epichlorhydrin, EW: 145).

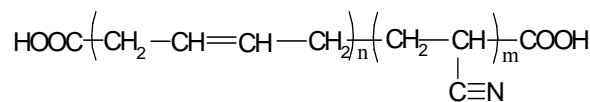
**Table 1.** Investigated propellant compositions

Sample	phr (wt. % of the total mass of the tested propellant sample)		
	CTBN 1300x15	LX 112	TEIC
CP00	100(14.20)	8.7(1.24)	(0)
CP01	100(14.13)	8.7(1.23)	(0.10)
CP02	100(14.06)	8.7(1.22)	(0.20)
CP03	100(13.99)	8.7(1.22)	(0.30)

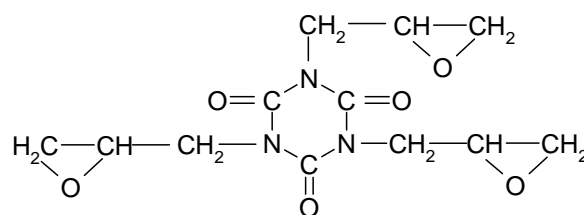
Tris(2,3-epoxypropyl) isocyanurate (TEIC) was prepared by the reaction of cyanuric acid and epichlorhydrin in accordance with a modified literature method [10]. Investigated composite propellant samples differ from each other in the bonding agent content. Composition CP00 is a

baseline propellant composition containing no bonding agent. In most of the currently used propellants, an amount from 0.1 to 0.3 is the preferred amount of the bonding agent [11]. TEIC content varied from 0.1 to 0.3 wt. % of the total mass of the investigated propellant.

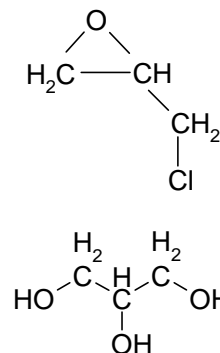
The chemical structures of the propellant ingredients are shown in Fig.1.



a) carboxyl-terminated (butadiene-co-acrylonitrile) (CTBN)



b) tris(2,3-epoxypropyl) isocyanurate (TEIC)



c) polyglycidyl ether of glycerol and epichlorhydrin (LX-112)

**Figure 1.** The chemical structures of the ingredients of the investigated propellants

The tested propellant formulations were mixed in a 1-gallon Baker-Perkins planetary mixer at a temperature of 60 $^{\circ}\text{C}$ . All of the binder ingredients, except the curing agent and the cure catalyst, were blended thoroughly for 15 min at an ambient pressure and then vacuum mixed for 30 min. The AP blend (fine and coarse fractions) was added portionwise and after each portion the mixture was blended for 10 min. The mixture was then vacuum mixed for 60 min. The curing agent was then added to the mixture, mixed for 10 min at an ambient pressure and then vacuum mixed for further 10 min. Finally, the cure catalyst was added to the mixture and the same procedure was repeated. The mixture thus prepared was cured for 5 days at 77 $\pm$ 2 $^{\circ}\text{C}$ .

### 2.2 Methods

#### Sol-Gel measurements

The sol content of the propellant binder is the weight of the soluble fraction of the propellant, obtained by the extraction with a solvent, as described in STANAG 4581 [12]. The extraction was carried out in three Soxhlet extraction units (with refluxing solvent) for 16 hours using approximately 150 mL of dichloromethane (CH $_2$ Cl $_2$ ) in each. The formula for the sol fraction evaluation was modified [13] and, in accordance with Equation (1), the polymeric part  $S_{\text{poly}}$  of the

total soluble part  $E_{total}$  of the propellant sample was determined with respect to the polymeric part of the formulation  $A_{k-p}$ .

$$S_{poly} = \frac{E_{poly}}{A_{k-p}} = \frac{E_{total} - A \cdot P_{DOA} - A \cdot P_{AO2246} - A \cdot P_{Fe(acac)_3}}{A \cdot (1 - P_{AP} - P_{DOA} - P_{AO2246} - P_{Fe(acac)_3})} \quad (1)$$

where:

- $S_{poly}$  – the polymeric part of the soluble (extractable) part of the propellant composition,
- $E_{total}$  – the total amount of the extract [g], obtained by the method,
- $E_{poly}$  – the polymeric part of the total extract [g], corrected for the nominal parts of DOA, AO 2246 and  $Fe(acac)_3$ ,
- $A$  – amount of the propellant sample weighed-in for the extraction [g],
- $A_{k-p}$  – amount of the propellant sample weighed-in for the extraction [g], corrected for the nominal parts of AP, DOA, AO 2246 and  $Fe(acac)_3$ ,
- $P_{AP}$  – nominal part of AP in the propellant composition (e.g. 80 wt.% mean 0.80) [-],
- $P_{DOA}$  – nominal part of DOA in the propellant composition [-],
- $P_{AO2246}$  – nominal part of AO 2246 in the propellant composition [-],
- $P_{Fe(acac)_3}$  – nominal part of  $Fe(acac)_3$  in the propellant composition [-]

#### Uniaxial tensile properties of the composite propellant binder samples

The uniaxial tensile properties of the cured propellant samples were evaluated at 20°C using INSTRON 1122 tensile test machine fitted with a 5000 N load cell. «JANNAF C» dog bone samples (120 mm length, 25 mm width, 8 mm thickness) were used. Crosshead speed of the tensile machine was 50 mm/min, while the effective gauge length of the JANNAF C samples was 68.6 mm.

#### Differential scanning calorimetry (DSC)

DSC analyses were carried out using the DSC Q20 manufactured by TA Instruments with liquid nitrogen cooling. The temperature scale is calibrated using the melting temperature of high purity indium. These measurements were made with the purpose to investigate the thermal based glass transition temperature ( $T_g$ ) of the tested samples. The small amount of the samples (~5 mg) was scanned with a heating rate of 10°C min<sup>-1</sup>, in a range from -90°C to +50°C. The  $T_g$  of the samples were determined from the midpoints of the transitions.

#### Dynamic mechanical thermal analysis (DMTA)

DMTA study of the investigated propellant samples was performed in a torsion deformation mode using the Modular Compact Rheometer MCR-302 (Anton Paar GmbH) equipped with standard fixtures (SRF12) for rectangular bars, temperature chamber (CTD-620) having high temperature stability ( $\pm 0.1$ ) and liquid nitrogen with automated cooling accessories [14]. The DMTA tests, in order to evaluate the influence of TEIC on viscoelastic properties of the tested composite propellant, have included the following specific experiments:

- strain amplitude sweep tests, in order to determine the linear viscoelastic range (LVR) for the tested propellant,

- o  $T=20^\circ\text{C}$ ,
- o shear strain,  $\gamma$  from 0.001 up to 10 %.
- temperature sweep tests at different frequencies, with the aim to evaluate viscoelastic relaxation processes,
  - o temperature range from -80 to +40°C,
  - o the heating rate was 2°C/min,
  - o shear strain,  $\gamma=0.01\%$ ,
  - o angular frequencies 1, 5 and 10 rads<sup>-1</sup>.
- temperature sweep tests in heating mode,
  - o temperature range from -80 to +80°C,
  - o the heating rate was 5°C/min,
  - o shear strain,  $\gamma=0.01\%$ ,
  - o single frequency point of 1 Hz.

The equipment and details of a fixed specimen are shown in Fig.2.



Figure 2. The Modular Compact Rheometer MCR-302 equipped with the temperature chamber

The samples for the DMA tests were of a rectangular bar shape (54×10×3-4 mm). The complex shear modulus was determined,  $G^*(\omega) = G'(\omega) + iG''(\omega)$ . The extracted data were the storage shear modulus ( $G'$ ), the loss shear modulus ( $G''$ ) and the loss factor  $\tan(\delta) = G''/G'$ . The glass transition temperature ( $T_g$ ), determined by the dynamic mechanical measurements, was estimated as the temperature at which the loss factor,  $\tan(\delta)$  reached its maximum value.

### 3. Results

#### Sol-gel analysis

Knowing the soluble fraction content ( $S_{poly}$ ), the crosslink density ( $C$ ) of the propellant binder (Table 2) can also be estimated following the modified version of the Charlesby-Pinner [15], see Equation (2).

$$C = \frac{(1 - S_{poly}) \cdot (2 - (S_{poly} + \sqrt{S_{poly}}))}{(S_{poly} + \sqrt{S_{poly}})} \quad (2)$$

Table 2.  $S_{prop}$ ,  $S_{poly}$  and  $C$  values for the tested propellant samples

Sample	$S_{prop}$	$S_{poly}$	$C$
CP00	0,09538	0,31371	0,88453
CP01	0,09769	0,33061	0,80895
CP02	0,08697	0,26067	1,17798
CP03	0,10454	0,37651	0,63593

The soluble or extractable content is a useful parameter to characterize the extent of cross-linking within a cross-linked polymer [13]. The greater the fraction of not cross-linked

polymer chains, the higher is the soluble fraction. A soluble fraction equal 1 means that the material is not cured and that all can be extracted. In contrast, a value of  $S_{\text{poly}}$  tending to 0 means that nothing can be extracted. For a propellant formulation, the soluble fraction  $S_{\text{poly}}$  should be in the range 0.15 to 0.2 to get an elastomer with a low cross-link density to achieve a suitable rubbery state.

For the specified TEIC content in the tested propellant compositions sol fraction in the polymer network is from 26 up to 37 %. With an introduction bonding agent into propellant composition (CP01), an increasing in the soluble fraction is evident, as well as the decrease in the crosslink density value. The percentage increasing in the soluble fraction was 5.39 % in CP01 (0.1 wt.% TEIC). But with a TEIC content of 0.2 wt.% the cross-link density value reached its maximum. Further increase of TEIC content resulted in a decrease of polymer network cross-link density. Decrease of the crosslink density can be explained by an increase in physical crosslinking due to the high concentration of epoxy curing agent. However, the highest percentage reduction in the soluble fraction was 16.91 % in CP02 (0.2 wt.% TEIC).

We conclude that the cross-link density of a polymer network cannot be determined definitely using this method alone. However, the increase in  $C$  value suggests that the degree of cross-linking should increase.

### Uniaxial tensile mechanical characteristics

The average and standard deviation [SD] values of uniaxial tensile mechanical properties, *i.e.* the tensile strength ( $\sigma_m$ ), the strain at maximum load ( $\varepsilon_m$ ), the strain at break ( $\varepsilon_b$ ) and the Young's modulus ( $E$ ) for the investigated propellant samples are listed in Table 3.

**Table 3.** Values of uniaxial tensile characteristics of tested CTBN-based propellant samples at  $T=20^\circ\text{C}$ .

Sample	$\sigma_m$ (MPa), [SD]	$\varepsilon_m$ (%), [SD]	$\varepsilon_p$ (%), [SD]	$E$ (MPa), [SD]
CP00	0.57 [0.09]	47.99 [0.12]	63.21 [2.62]	1.86 [0.52]
CP01	0.62 [0.07]	45.10 [0.70]	57.81 [2.97]	2.23 [0.79]
CP02	0.71 [0.04]	45.39 [1.24]	55.19 [2.63]	2.65 [0.69]
CP03	0.64 [0.11]	41.66 [0.91]	50.23 [2.13]	2.60 [0.95]

SD – standard deviation.

All of the values listed in Table 3 were obtained as an average of five specimens. The uniaxial tensile properties of composite propellant depend on the tensile properties of the propellant binder, which in turn determines the strain capability of the propellant. High strain capability of the binder network is favorable considering long shelf life of the propellant system [16]. The uniaxial test data showed that the values of the tensile strength and the Young's modulus increase as the TEIC content increases. Increasing the tensile strength and Young's modulus is caused by a larger amount of hard segments. The most pronounced improvement in the uniaxial tensile strength is shown by the propellant CP02. TEIC content at 0.2 wt. % causes an increase in tensile strength of 24.6% with a simultaneous decrease in the strain at maximum load value of 5.4%.

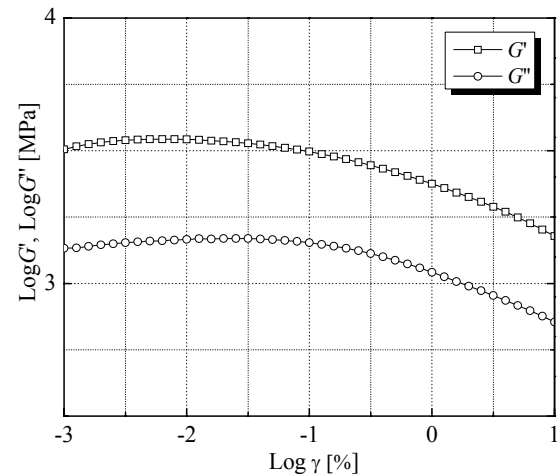
The incorporation of TEIC into the propellant formulation decreases the value of the strain at maximum load as a consequence of the decreased molecular weight of the polymer chains between the crosslink points. The same tendency can be seen in the strain at break values as a function of the effective polymer chains between the crosslink points [6].

### Dynamic mechanical thermal analysis

#### Strain amplitude sweep test

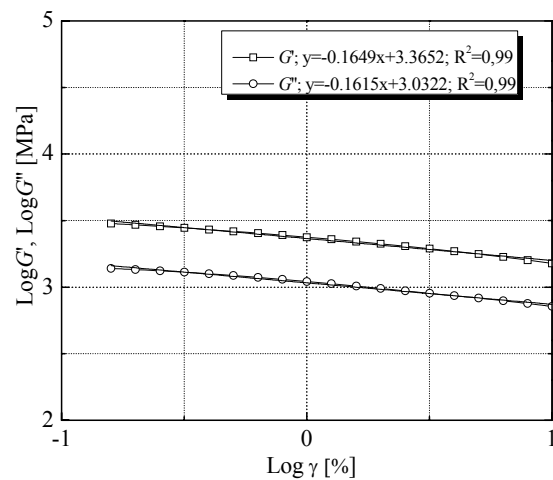
In order to use the DMTA technique to accurately determine rheological properties of materials, a tested polymer must be deformed at the amplitudes that remain within the linear viscoelastic region (LVR). Within LVR, the viscoelastic response of the polymer is independent of the magnitude of deformation [17]. As a general rule, this region must be determined for every type of polymer by DMTA amplitude sweep tests, in which a frequency is fixed and the strain amplitude is incrementally increased.

Fig.3. shows the dependence of the shear storage modulus,  $G'$ , on the strain amplitude for the baseline propellant sample CP00.



**Figure 3.** Amplitude sweep test: variation of the storage and loss shear moduli with the strain amplitude for the baseline propellant sample CP00

The logarithm of the storage modulus decreases linearly with the logarithm of increasing the shear strain level, indicating some form of damage function exists which increases with deformation (Figure 4). Similar behavior was exhibited by the loss modulus. This phenomenon of strain-dependent material properties, termed nonlinear viscoelastic behavior, is often associated with the presence of the filler particles.



**Figure 4.** The effect of the strain amplitude on the shear storage modulus for tested propellant sample for the baseline propellant sample CP00

Data in Fig.4, representing CTBN-based composite propellant as a material utilizing predominately reinforcing filler, show that the logarithm of modulus is linearly dependent on the strain over approximately 2 decades of

strain. This suggests that over the strain range examined in this work, constitutive relationships can be developed of the form:

$$G' = A \cdot \gamma^m \quad (3)$$

and

$$G'' = B \cdot \gamma^n \quad (4)$$

where A and B are the shear storage and loss moduli at 1 % strain, respectively.  $\gamma$  is the strain amplitude and the exponents m and n are the factors representing the degree of nonlinear response [18].

Table 4 lists the factors obtained by fitting the data in Fig. 4 using equations (3) and (4). Agreement between these equations and data is very high as indicated by the linear regression correlation coefficients, given in Fig. 4.

**Table 4.** Nonlinear factors and reference moduli

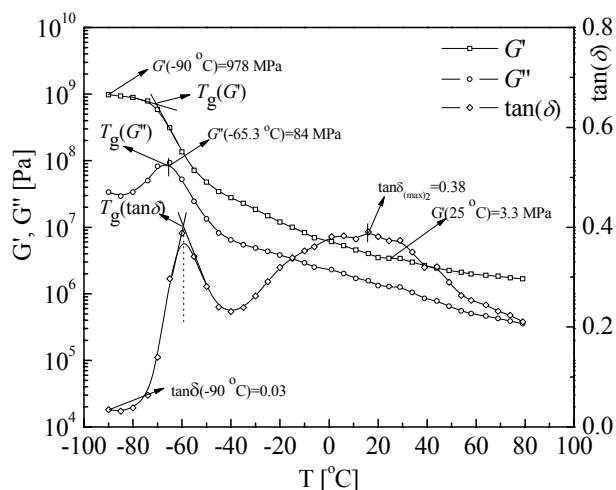
Sample	$\gamma_c$ [%]	m, Pa	Log A, MPa	n, Pa	Log B, MPa
CP00	0.045	-0.165	3.375	-0.162	3.042
CP01	0.036	-0.156	3.506	-0.162	3.139
CP02	0.059	-0.175	3.650	-0.185	3.236
CP03	0.037	-0.174	3.693	-0.182	3.286

For all tested propellants except the propellant CP00, the absolute value of n is greater than m. Relative values of these nonlinear factors are most likely dependent on the region of the strain investigated.

The composite propellant sample CP02 displays the greatest nonlinear behavior (largest absolute values of m and n). The effect of crosslinking or crosslink density appears to increase the nonlinear behavior.

#### Temperature dependence of rheological parameters

Based on a weakly crosslinked polymeric matrix, composite rocket propellants show very large changes in mechanical properties with temperature [19,20]. Figure 5 shows the viscoelastic response of a baseline composite propellant sample CP00 in terms of  $G'$ ,  $G''$  and  $\tan(\delta)$  as a function of temperature.



**Figure 5.** Characteristic values of the CP00 baseline composition shown by the DMA thermogram of  $\omega=6.28 \text{ rad}\cdot\text{s}^{-1}=1 \text{ Hz}$

It follows from Fig. 5 that the  $G'$  is almost constant at low temperatures and it reaches the maximum value in the region

below the glass transition ( $-90^\circ\text{C}$  to  $-80^\circ\text{C}$ ). The transition from the glassy to the rubbery state (the onset point on the  $G'$ - $T$  curve at  $T=-73^\circ\text{C}$ ) has, as a consequence, a drop in the  $G'$  value by a factor of about 35 (from 978 MPa at  $-90^\circ\text{C}$  to 27 MPa at  $-40^\circ\text{C}$ ). With increasing the temperature (between  $T=-60^\circ\text{C}$  and  $T=20^\circ\text{C}$ ) the  $G'$  curve exhibits a two-step character, indicative of two separate relaxation processes. Similar temperature dependence of  $G'$  curve was observed in the CTBN-based composite propellant binder composition [21]. Thus, the existence of two relaxation process observed in the composite propellant composition could not be attributed only to the influence of AP solid particles on the polymer network mobility. Copolymers often show a broadening of the transition region with a decrease in the slope of the modulus curve. Part of broadening of the transition region could be due to the heterogeneity in the molecular weight between cross-links. Also, the reason for a slow decrease of the storage modulus could be crystallinity within a polymer structure of the tested propellant binder samples [22].

A molecular interpretation of the viscoelastic behavior can be given considering the  $\tan(\delta)$ , which describes molecular rearrangement regions, corresponding to the binder fractions with different mobility. There is a question what the glass transition temperature is. According to one group of authors the  $T_g$  is the maximum of the  $G''$ . The other choice for assigning a  $T_g$  is the maximum of the  $\tan(\delta)$ . At the maximum intensity of the  $\tan(\delta)$ , the molecular rearrangement process from glassy to rubbery and vice versa is at its maximum. Therefore, in order to characterize the transition between these two states, the maximum of the  $\tan(\delta)$  must be taken as glass (to rubber) transition temperature. Also,  $\tan(\delta)$  is much more sensitive than the  $G''$  in showing the different temperature regions of molecular rearrangements in order to change the basic state from energy to entropy elasticity [23]. Polybutadiene-based elastomers contain soft and rigid segments [7]. The soft segments consist of large flexible non-crystalline polymer chains, in this case, polybutadiene, while rigid (hard) segments consist of crosslinking units.

The peak of  $\tan(\delta)$  positioned between  $T=-65^\circ\text{C}$  and  $T=-55^\circ\text{C}$  (its temperature location is designated as  $T_g$ ), is attributed to the glass-rubber transition temperature. This relaxation process involves cooperative motions of prepolymer (CTBN) main chains between the crosslinks within the soft segment regions. These polymer network segments have a very low density of ester groups and are the polybutadiene part of binder which reorient at very low temperatures. The  $T_g$  value for the baseline propellant composition, CP00, is  $-59.1^\circ\text{C}$ .

Being **reinforcing** (filler strongly interacts with the binder) or **non reinforcing** (filler interact only weakly with the binder), viscoelastic properties of composite propellants are strongly affected by the inclusion of solid fillers. Particle-polymer interactions as well as physical confinement effects, have a significant influence on the polymer chain mobility. Although the molecular segments are almost free to move in the rubbery region, the incorporation of highly active fillers such as AP, significantly modifies the molecular mobility. Such systems indicate the appearance of a second, higher  $T_g$ , reflecting a constrained population of polymer chain segments in the vicinity of the filler particle surface [24].

The second peak (its temperature location is designated as  $T_g^{\text{restricted}}$ ), broader than the first one, is located 60-100 deg higher than the first. The peak is assigned to the glass transition of polymer chains experiencing mobility restrictions due to the interactions with ammonium perchlorate particles.

The Fig.6 shows temperature dependencies of the loss factor,  $\tan(\delta)$ , loss modulus,  $G''$  and storage modulus,  $G'$  of the tested composite propellant samples.

CP01 propellant sample (0.1 wt.% TEIC) has the lowest values of  $G'$  in the plateau of glassy state. Modulus in the glassy state is determined primarily by the strength of the intermolecular forces and the way the polymer chains is packed [25]. The increase in storage modulus values with increasing TEIC content suggests that a tougher, more rigid network is obtained at higher TEIC concentrations. The transition from the glassy to the rubbery state has as a consequence a drop in the  $G'$  value, also the  $G''$  maximum value. The loss modulus in the transition region is higher for propellants with higher TEIC content, which may be due to an increase in internal friction, creating energy dissipation. Although a broadening of the loss modulus peak was not observed, this may be attributed to the inhibition of the relaxation process within the composition as a consequence of a higher number of chain segments upon TEIC addition.

Considering the  $\tan(\delta)$  curves of tested propellants, no change in the main glass-rubber transition temperature was observed on varying the content of TEIC.

The  $T_g$  values determined by  $G''$ ,  $G'$  and  $\tan(\delta)$  are listed in Table 5. According to the temperature dependencies of the loss factor,  $T_g^{\text{restricted}}$ ,  $\tan(\delta)_{\text{max1}}$  and  $\tan(\delta)_{\text{max2}}$  values were determined, also temperature intervals ( $W_1$  and  $W_2$ ) corresponding to these values. These are parameters used to analyze the influence of applied bonding agent on tested propellant compositions.

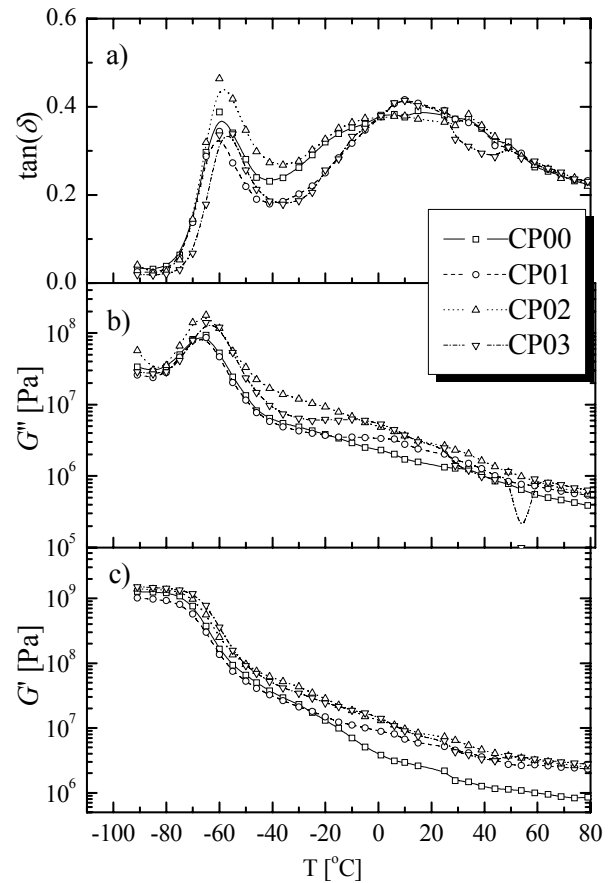
For the tested propellant samples only quite small variations in  $T_g$  values were observed. Regardless the TEIC content, the  $T_g$  values are located in the narrow temperature range ( $T_g \sim -60^\circ\text{C}$ ). The reason is the concentration of crosslink points apart from the polybutadiene parts, which are responsible for the main glass-rubber transition at low temperatures.

**Table 5.**  $\tan(\delta)_{\text{max}}$  values and  $T_g$  values determined by  $G''$ ,  $G'$  and  $\tan(\delta)$

Sample	$T_g$ [ $^\circ\text{C}$ ]			$T_g^{\text{restricted}}$ [ $^\circ\text{C}$ ]	$\tan(\delta)_{\text{max2}}$	$\tan(\delta)_{\text{max2}}$	$W_1$ [ $^\circ\text{C}$ ]	$W_2$ [ $^\circ\text{C}$ ]
	T in max of $G''$	Tangens method with $G'$	T in max. of $\tan(\delta)$					
CP00	-65.8	-73.0	-59.1	16.3	0.37	0.38	16.9	63.4
CP01	-66.2	-74.7	-60.3	11.0	0.34	0.42	15.5	50.6
CP02	-65.8	-71.6	-58.8	9.8	0.46	0.38	18.1	47.5
CP03	-65.8	-72.4	-59.4	11.0	0.33	0.41	17.8	41.4

The invariance in  $T_g$  values indicates that distances between the crosslink points within the polymer network of tested propellant samples are such that the restrictions affected by the presence of the bonding agent during the crosslink process do not contribute to differences in  $T_g$  value. In other words, cooperative motions of polymer network segments, related to main relaxation transition are not influenced. The corresponding relaxation time is only changed minor by the structural changes in propellant binder cross-link structure due to the TEIC addition.

It is observed that, as the TEIC content increases, the width of the second  $\tan(\delta)$  peak (designated as  $W_2$ ), which corresponds to  $\tan(\delta)_{\text{max2}}$  value, gets smaller. This can be explained by the glass transition of polymer chains experiencing more mobility restrictions due to the interactions with the ammonium perchlorate particles. Formation of hydrogen bonds between the TEIC as a part of a polymer network on one side, and ammonium perchlorate particles on



**Figure 6.** Temperature dependencies of a) loss factor ( $\tan(\delta)$ ), b) loss modulus ( $G''$ ) and c) storage modulus ( $G'$ ) for the investigated propellant samples

the other side can be a reason for the mobility restrictions. This is the most pronounced in the CP03 propellant composition. In comparison with the CP00 composition, reduction in  $W_2$  value is 53.1%.

#### Effect of TEIC on activation energy of relaxation events

Dynamic mechanical analysis is one of the most appropriate methods to investigate relaxation events. Bihari et al. in their article have demonstrated that the interpretation of viscoelastic relaxation strength in polymers depends on the tangent of the phase lag angle ( $\tan \delta$ ) or real (in-phase) or imaginary (out-of-phase) components of the storage and loss modulus, respectively [26]. The glass transition temperature ( $T_g$ ) of a material also referred as  $\alpha$ -transition is normally observed as a peak of  $\tan(\delta)$  considering the variation of  $\tan(\delta)$  with temperature (Figure 7). At this point the material absorbs energy and the modulus of the material decreases as it passes through the glass transition phase. Normally, at a lower



temperature, sometimes other relaxation processes are observed for polymeric materials. The secondary transition, known as  $\beta$ -relaxation, is normally attributed to the polymer backbone configuration reorganization. The activation energy ( $E_a$ ) represents the energy barrier of the material of which has to overcome in order to undergo the structural reorganization of the relaxation process. The  $E_a$  activation energy corresponding to  $\alpha$ -transition was determined by the Arrhenius equation, see Equation (5).

$$\ln(F) = \ln(A) - \frac{E_a}{R} \frac{1}{T} \quad (5)$$

where  $F$  is frequency (Hz),  $A$  is the preexponential factor,  $E_a$  is the activation energy ( $\text{kJmol}^{-1}$ ),  $R$  is the gas constant ( $\text{kJ}(\text{molK})^{-1}$ ) and  $T$  is the temperature (K).

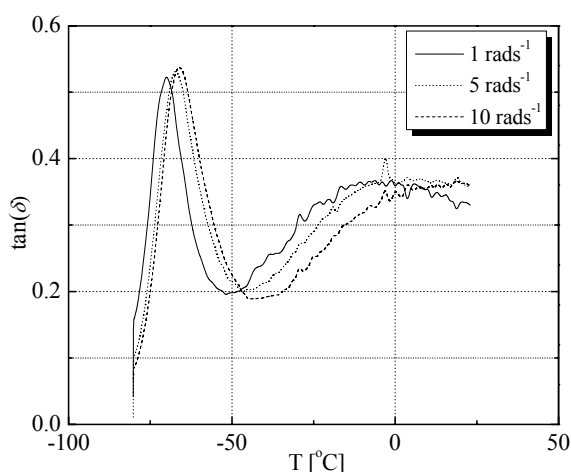


Figure 7. Variation of  $\tan(\delta)$  with temperature at different frequencies

The activation energies were calculated from  $\tan(\delta)$  peaks and onset values of dynamic properties measured at frequencies 1, 5 and  $10 \text{ rad s}^{-1}$  using the Arrhenius plots for each tested propellant.

The  $E_a$  values corresponding to  $\alpha$ -transition are given in Table 6.

Table 6. Activation energy of main relaxation process for tested propellants

Sample	$\alpha$ -transition [ $\text{kJmol}^{-1}$ ]
CP00	197.5
CP01	190.6
CP02	160.2
CP03	199.3

It is found that the  $E_a$  for  $\alpha$ -transition of tested propellants is from 160 up to 199  $\text{kJmol}^{-1}$ .

The  $E_a$  associated with the  $T_g$  process, which is attributed to the cooperative motions of long soft segments, is higher for a baseline propellant composition (CP00) compared to the propellant compositions CP01 and CP02. This result suggested that the relaxation of CTBN was made easier by the addition of 0.1 and 0.2 wt.% of TEIC. In other words, lower contents of TEIC affect the concentration of short linking hard segments, whereas 0.3 wt.% of TEIC can readily interfere with soft segment motions in CTBN polymer network.

#### DSC measurements

As an essential ingredient, the binder largely determines the mechanical properties of the composite solid propellants. Low glass transition temperature is preferred for the

composite propellant binder, so that it can withstand a large spectrum of stress transients in operation. Therefore, the glass transition temperature ( $T_g$ ) of elastomer bonded composite propellant is one of the most important properties determining their in-service application [27].  $T_g$  values of the tested propellant binder samples determined through DSC are shown in Table 7.

Table 7. Glass transition temperature values of the tested propellant binder samples

Sample	$T_g$ , [°C]
CP00	-76.24
CP01	-75.47
CP02	-75.75
CP03	-75.56

The differences between  $T_g$  values of tested propellant samples determined through DSC are within experimental error. Obtained  $T_g$  values show that it cannot be observed any regularity in its change with increasing TEIC content in the tested propellant formulations.

Glass transition temperatures, determined by DSC, are significantly lower than the ones determined by DMA. The reason is the "static" determination, which means no mechanical deformation causing strain hardening is applied, neglecting the volume change by thermal expansion [28]. The invariance in  $T_g$  values, regardless of the method of determining, indicates that distances between the crosslink points within the polymer network of the tested binder samples are such that the restrictions affected by the presence of the bonding agent during the crosslink process do not contribute to differences in  $T_g$  value. In other words, cooperative motions of polymer network segments, related to main relaxation transition are not influenced. The corresponding relaxation time is only changed minor by the structural changes in binder cross-link structure due to TEIC addition.

#### Conclusion

Samples of the composite propellant based on carboxyl-terminated (butadiene-co-acrylonitrile) cured with polyglycidyl ether of glycerol and epichlorhydrin (LX-112) containing the bonding agent tris(2,3-epoxypropyl) isocyanurate (TEIC) were investigated with sol-gel analysis, dynamic mechanical analysis and uniaxial testing. The temperature dependences of rheological parameters disclose that the glass-rubber transition temperature of the investigated propellants do not change by the addition of tris(2,3-epoxypropyl) isocyanurate. The glass transition temperature,  $T_g$ , of all propellant samples was about  $-60^\circ\text{C}$ . TEIC as the bonding agent was found to alter uniaxial tensile properties of the tested composite propellants. Both the tensile strength and Young's modulus increased, while the strain at maximum load and the strain at break decreased.

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## Viskoelastična svojstva kompozitnog raketnog goriva na bazi karboksiterminiranog kopolimera (butadien-akrilonitril) i tri (2,3-epoksi)propil) izocijanurata kao vezujućeg agensa

Ispitivan je uticaj tri(2,3-epoksi)propil) izocijanurata u funkciji vezujućeg agensa na karakteristike polimerne mreže kao i na reološka svojstva sastava kompozitnog raketnog goriva na bazi karboksiterminiranog kopolimera (butadien-akrilonitril) umreženog sa poliglicidil etrom glicerola i epihlorhidrina. Oblast linearne viskoelastičnosti (LVR) određena je za ispitivane sastave goriva "amplitude sweep" testovima, iznad temperature ostakljivanja, u cilju korektno fizičke interpretacije podataka dobijenih dinamičko-mehaničkom analizom. Analizirane su temperaturne zavisnosti parametara reološkog ponašanja (modul sačuvane energije,  $G'$ , modul izgubljene energije,  $G''$  i tangens ugla gubitaka,  $\tan(\delta)=G''/G'$ ). Kod svih ispitivanih sastava goriva, u temperaturnom opsegu od  $-80^{\circ}\text{C}$  do  $+80^{\circ}\text{C}$ , uočava se pojava dva relaksaciona procesa. Prvi kao strukturna relaksacija ( $\alpha$ -prelaz) koji se odnosi na oblast ostakljivanja i drugi, sekundarni relaksacioni proces. Za ispitivane sastave goriva određene su energije aktivacije viskoelastične relaksacije, na osnovu Arrheniusove jednačine, merene na tri različite frekvencije ( $1, 5$  i  $10$   $\text{rads}^{-1}$ ) u temperaturnom opsegu od  $-80^{\circ}\text{C}$  do  $+40^{\circ}\text{C}$ . Rezultati dobijeni dinamičko-mehaničkom analizom pokazali su da sadržaj tri(2,3-epoksi)propil) izocijanurata ne utiče na vrednost temperature ostakljivanja ispitivanih sastava goriva.

*Ključne reči:* kompozitno raketno gorivo, butadienakrilonitril, izocijanourat, temperatura ostakljivanja.



## Високоупругие свойства композитного твёрдого ракетного топлива на основе карбоновых предельных сополимеров (бутадиен-акрилонитрил) и трёх (2,3-эпоксипропил) изоцианурата в качестве связывающего вещества

В этой работе исследован эффект трёх (2,3-эпоксипропил) изоциануратов в функции связывающего вещества к характеристикам полимерной сетки, а также и к реологическим свойствам композитного твёрдого ракетного топлива на основе карбонового предельного сополимера (бутадиен-акрилонитрил) поперечно-сшитого с полиглицидил эфиром глицерина и эпихлоргидрина. Область линейной вязкоупругости (LVR) определяется для испытаний тестируемого состава топлива „амплитуды развертки“ (“amplitude sweep”), выше температуры стеклования, для того, чтобы исправить физическую интерпретацию данных, полученных с помощью динамическо-механического анализа. Мы проанализировали температурные зависимости параметров реологических свойств и поведений (модуль сохранения энергии,  $G'$ , модуль потери энергии,  $G''$  и тангенс угла потерь, тангенс  $(\delta)=G''/G'$ ). Во всех испытанных составах топлива, в интервале температур от  $-80^{\circ}\text{C}$  до  $+80^{\circ}\text{C}$ , можно наблюдать возникновение двух релаксационных процессов. Первая такая структурная релаксация ( $\alpha$ -переход) относится к области стеклования и вторая – это вторичный процесс релаксации. Для получения результатов тестируемого состава топлива определялись энергии активации вязкоупругой релаксации, основанные на уравнении Аррениуса, как измерено при трёх различных частотах (1, 5 и 10 рад-1) в интервале температур от  $-80^{\circ}\text{C}$  до  $+40^{\circ}\text{C}$ . Результаты, полученные с помощью динамическо-механического анализа, показали, что содержание трёх (2,3-эпоксипропил) изоциануратов не влияет на величину температуры стеклования испытываемых составов топлива.

*Ключевые слова:* композитное ракетное топливо, бутадиен акрилонитрил, изоцианурат, температура стеклования.

## Propriétés viscoélastiques du propergol composite à la base de copolymère carboxyle terminé (butadiène –nitrile acrylique) et tri (2,3 – époxy propyle) iso cyanure comme agent liant

L'influence de tri (2,3 époxy propyle) iso cyanure en fonction de l'agent liant sur les caractéristiques du réseau polymère ainsi que les propriétés rhéologiques du propergol composite à la base du carboxyle terminé copolymère (butadiène acrylonitrile) durci avec polyglycidyl éther de glycérol et épichlorhydrin) ont été examinés. Le domaine de la viscoélasticité a été déterminé pour les compositions examinées de propergol au moyen des tests „amplitude sweep“ au dessus de la température de vitrification dans le but de l'interprétation correcte physique des données obtenues par l'analyse dynamique mécanique. On a analysé les dépendances de la température des paramètres de comportement rhéologique (module de l'énergie conservée,  $G'$ , module de l'énergie perdue,  $G''$  et tangence de l'angle de perte,  $\tan(\delta)=G''/G'$ ). Chez toutes les compositions du propergol examinées, dans le portée de température de  $-80^{\circ}\text{C}$  jusqu'à  $+80^{\circ}\text{C}$  on peut observer l'apparition de deux processus relaxants. Le premier comme la relaxation de structure (passage) lié au domaine de vitrification et le deuxième, le processus secondaire de relaxation. Pour les compositions examinées de propergol on a déterminé les énergies d'activation de relaxation viscoélastique à la base de l'équation d'Arrhenius mesurées à trois fréquences différentes (1,5 et 10 rads<sup>-1</sup>) dans la portée de température de  $-80^{\circ}\text{C}$  jusqu'à  $+40^{\circ}\text{C}$ . Les résultats de l'analyse dynamique mécanique démontrent que le contenu de tri (2,3 – époxy propyle) iso cyanure n'affecte pas la valeur de température de vitrification des compositions examinées de propergol.

*Mots clés:* propergol composite, butadiène acrylonitrile, iso cyanure, température de vitrification.