Effect of Tris(2,3–Epoxypropyl)Isocyanurate on Dynamic Modulus of CTBN-Based Composite Rocket Propellant

Saša Brzić[1)]
Marica Bogosavljević[1)]
Gordana Ušćumlić[2)]
Ljiljana Jelisavac[1)]

The influence of tris(2,3–epoxypropyl)isocyanurate as a bonding agent on viscoelastic dynamic modulus of carboxyl–terminated (butadiene–co–acrylonitrile)–based composite propellant was investigated. Strain amplitude sweep tests have been run at the room temperature. Frequency dependencies of rheological behaviour parameters (storage and loss modulus) were also analyzed. Based on the frequency dependencies of the storage and loss modulus, in the temperature range from –80 °C to 40 °C, the master curves were created, reaching broader frequency interval in comparison to that used in the measurements. This enables a prediction of the material response at various frequencies, usually unobtainable experimentally. Williams–Landell–Ferry (WLF) equation constants were determined for different reference temperatures. Further, material constants, fractional free volume at the glass transition temperature and thermal coefficient of free volume expansion were calculated. The data obtained from WLF analysis of the tested composite propellants showed that the values of the thermal coefficient of expansion of free volume and the fractional free volume at the glass transition temperature decrease with increasing content of tris(2,3–epoxypropyl)isocyanurate. Also, the apparent energy for viscoelastic relaxation increases, because of the increased intermolecular hydrogen interactions

Key words: composite propellant, rheological behaviour, butadiene co acrylonitrile, isocyanurate, glass transition temperature, test results.

Nomenclature

HTPB – hydroxyl–terminated poly(butadiene)
CTBN – carboxyl–terminated (butadiene–co–acrylonitrile)
LX 112 – polyglycidyl–ether of glycerol and epichlorhydrin
TEIC – tris(2,3–epoxypropyl)isocyanurate
AP – ammonium–perchlorate
DMTA – dynamic–mechanical thermal analysis
G' – the storage shear modulus
G'' – the loss shear modulus
$tan(\delta)$ – loss factor
T_g – glass transition temperature
γ_c – limiting shear strain value of linear viscoelastic range
a_T – shift factor
C_1 – WLF constant for reference temperature T_0
C_2 – WLF constant for reference temperature T_0
$C_{1,g}$ – WLF constant for reference temperature T_g
$C_{2,g}$ – WLF constant for reference temperature T_g
α_f – thermal coefficient of free volume expansion
f – fractional free volume
f_g – fractional free volume at the T_g
B – constant of Doolittle equation

E_a *(WLF)* – activation energy of viscoelastic relaxation based on WLF equation

Introduction

COMPOSITE solid rocket propellants consist of solid rigid fillers (usually ammonium–perchlorate) embedded in a rubbery polymeric matrix [1,2]. The binder, as the name implies, holds the composition together and acts as an auxiliary fuel. Hydroxyl–terminated poly(butadiene) (HTPB)–based composite rocket propellants have at present become the worldwide workhorse propellants in solid–fuel rocket motor [3]. The polyurethane network obtained by curing HTPB with a suitable diisocyanate provides an adequate polymeric matrix for inorganic oxidizer and metallic fuel that are dispersed in the propellant grain. Mechanical properties of these materials are related to the macromolecular structure of the binder as well as to the content and nature of the fillers [4]. Due to the physical and chemical properties of the binder and the filler, links are not spontaneously formed between the polymer chains of the binder and the filler surface. Ammonium–perchlorate (AP) as a filler is denoted as an active or reinforcing filler [4]. As dewetting is the main damage mechanism in composite rocket propellants, bonding agents are added to the composition to promote the adhesion

[1)] Military Technical Institute (VTI), Ratka Resanovića 1, 11132 Belgrade, SERBIA
[2)] University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, SERBIA
Correspondence to: Saša Brzić; e–mail: sasabrzic@gmail.com

of binder polymer chains to the surface of fillers. In other words, in order to improve the mechanical characteristics, an interaction between the ammonium–perchlorate 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 (–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 show that tris(2,3–epoxypropyl)isocyanurate (TEIC) as the bonding agent significantly improves the mechanical characteristics [6]. Dynamic mechanical thermal analysis (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 [7]. Since the bonding agent is an ingredient that is added to modify the mechanical properties of the propellant, precise knowledge of the dynamic mechanical behaviour is extremely important.

We have performed a comprehensive study of the viscoelasticity of the CTBN–based composite propellant and corresponding binder included tris (2,3–epoxypropyl) isocyanurate (TEIC) as a bonding agent. The results are reported in our previous papers [6-9]. Regarding the loss factor evolution according to the temperature, it was observed that all the tested materials have shown two relaxation processes. The first one, structural relaxation (α–transition) related to the transition (T_g) and the position of this peak remains unchanged as the TEIC content increases (Fig.1).
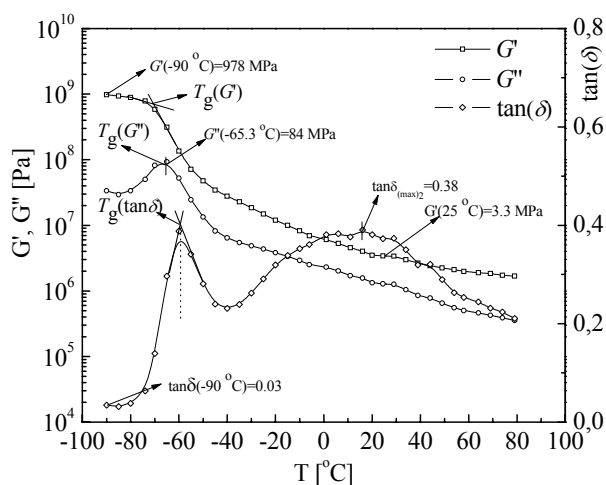

Figure 1. Characteristic values of the CP00 baseline composition shown by the DMA thermogram of ω=6.28 rads^{-1} =1 Hz [ref.9]

The second one, secondary relaxation process, appears at much higher temperatures. The peak (designated as $T_g^{restricted}$) is assigned to the glass transition of polymer chains experiencing mobility restrictions due to interactions with ammonium–perchlorate particles. As the TEIC content increases, the size of the second peak increases, while its maximum shifts to a higher temperature.

The objective of this paper is to describe viscoelastic properties of the CTBN–based composite propellant in details. Also, the goal of this study is to widely explore the influence of the composition containing TEIC on the mechanical behaviour of composite propellant. To our knowledge, there is no publication in the extensive literature,

except our previous investigation, that has surveyed not only the viscoelastic properties of CTBN–based composite propellant but also the effect of tris (2,3–epoxypropyl) isocyanurate on the relaxation processes exhibited in these composite materials.

Experimental part

Materials

Six 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 μm and 10 μm) 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). These values are shown in parentheses in Table 1, column 2.

The binder composition consisted of 100 phr of CTBN (commercialy designated as 1300×15, viscosity at 25ºC: 66.2 Pas , carboxyl functionality: 1.9, number–average molecular weight: 3800 g/mol, specific gravity at 23ºC: 0.931 gcm^{-3}, glass transition temperature, Tg: –63.3ºC), 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)$_3$). Quantity of curing agent (Epoxy) with respect to the quantity of carboxyl functions (COOH) is the E/COOH ratio.

This value measures the relative amount of curing agent available to form a polymer network. The E/COOH ratio was 1.20. The curing of CTBN was achieved by an epoxid using LX 112 (polyglycidyl ether of glycerol and epichlorhydrin, EW: 145).

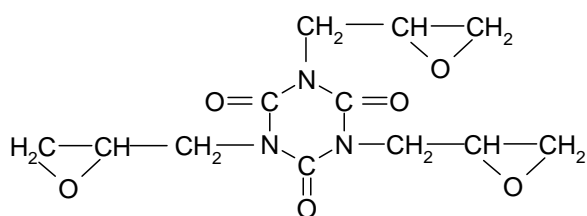**Table 1.** Tested composite propellant compositions

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)
CP04	100(13.92)	8.7(1.21)	(0.40)
CP05	100(13.85)	8.7(1.20)	(0.50)

Tris(2,3–epoxypropyl)isocyanurate (TEIC) was prepared by dehydrohalogenating the reaction of cyanuric acid and epichlorohydrin with dispersions of alkali metal hydroxides in non-reactive organic media [10]. Composite propellant samples differed in a bonding agent content. Composition CP00 was a baseline propellant composition containing no bonding agent. TEIC content varied from 0.1 to 0.5 wt.% of the total mass of the tested propellant.
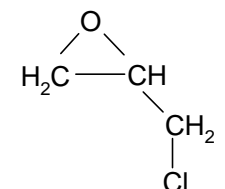
The chemical structures of the propellant ingredients are shown in Fig.2.
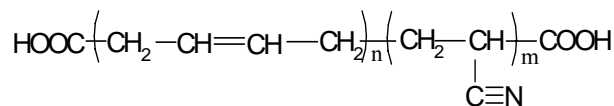
a) carboxyl-terminated (butadiene-*co*-acrylonitrile) (CTBN)

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

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

Figure 2. The chemical structures of the ingredients of the investigated propellants[9]

The tested propellant compositions were mixed in a 1–gallon Baker–Perkins planetary mixer at the temperature of 60ºC. All of the binder ingredients, except the curing agent and the cure catalyst, were blended thoroughly for 15 min at the 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 the ambient pressure and then vacuum mixed for a further 10 min. Finally, the cure catalyst was added to the mixture and the same procedure was repeated. Then, the mixture was cured for 5 days at 77±2ºC.

Methods

Dynamic mechanical thermal analysis (DMTA)

DMTA study of the tested propellant samples was performed in 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 (±0.1) and liquid nitrogen with automated cooling accessories [11]. The DMTA tests, in order to evaluate the influence of TEIC on rheological properties of tested composite propellants, have included the strain sweep and frequency sweep tests. Strain sweeps are oscillatory tests performed at variable amplitudes, while keeping the frequency at constant value (also, the measuring temperature). These tests were performed at T=20°C, while shear strain, γ was varied from 0.001% up to 10%, i.e. from 0.00001 up to 0.1, with 41 equidistant values on a linear scale. Frequency was held constant at 6.28 rads^{-1}.

Frequency sweeps represent the oscillatory tests performed at variable frequencies, keeping the amplitude at a constant value (also, the measuring temperature). These tests are used to investigate time-dependent deformation behaviour since the frequency is the inverse value of time. Short-term behaviour is simulated by a rapid motion, i.e. at high frequencies and long-term behaviour by a slow motion, i.e. at low frequencies.

This paper includes the access from the microscopic point of view. Possibility of increasing or decreasing dynamic modulus of the viscoelastic rocket propellant is considered, and thus the mobility of the polymer chains. The way the modulus affects the properties of the propellant grain under the loads, from macroscopic point of view, is an area which deals with structural analysis.

Finally, the components of propellant dynamic modulus were measured over three decades of frequency in the temperature range from −80°C to 40°C, scanned with a heating rate of 5°C min^{-1}. Shear strain, γ was constant at 0.01% (0.0001). Temperature step was 10°C. At each test temperature, frequency was varied from 0.1 to 100 rads^{-1}, with 16 equidistant values on a logarithmic scale (0.1, 0.158, 0.251, 0.398, 0.631, 1, 1.58, 2,.51, 3.98, 6.31, 10, 15.8, 25.1, 39.8, 63.1 and 100 rads^{-1}).

The samples for the DMTA 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 $\tan(\delta) = G''/G'$. A molecular interpretation of the viscoelastic behaviour can be given considering the $\tan(\delta)$, which describes molecular rearrangement regions, corresponding to the binder fractions with different mobility. 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 [12]. At the maximum intensity of the $\tan(\delta)$, the molecular rearrangement process from glassy to rubbery and vice versa is at its maximum. These values were reported in our previous paper [9].

Results

Strain sweep analysis

Strain sweep tests are mostly carried out for the sole purpose of determining the limit of the **L**inear **V**isco**e**lastic (LVE) range. As long as the strain amplitudes are still below the limiting value, γ_c, the curves of G' and G'' are remaining on a constant value, i.e. the structure of the tested sample shows no significant change at these low deformations [13]. When measuring in the LVE range, practical users speak of "non-destructive testing". The result of the strain sweep test, i.e. variation of the storage and loss shear moduli with the strain amplitude for the baseline propellant sample CP00, is shown in Fig.3.
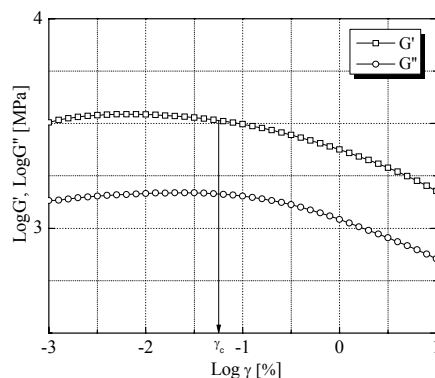
Figure 3. Strain sweep test for the baseline propellant sample CP00

Dependencies of the storage and loss modulus values on TEIC content, for different strain amplitude level, are shown in Figures 4 and 5. It is observed that the values of G' and G''

decrease with an increase of the strain amplitude. This effect, often called the "Payne" effect is attributed to the destruction of the filler structure in the highly filled elastomers [14]. In a composite propellant, the particle–polymer interactions, as well as physical confinement effects, have a significant influence on the polymer chain mobility. Although molecular segments are almost free to move in the rubbery region, the incorporation of highly active fillers such as aluminum and ammonium–perchlorate, significantly modifies the molecular mobility [6].
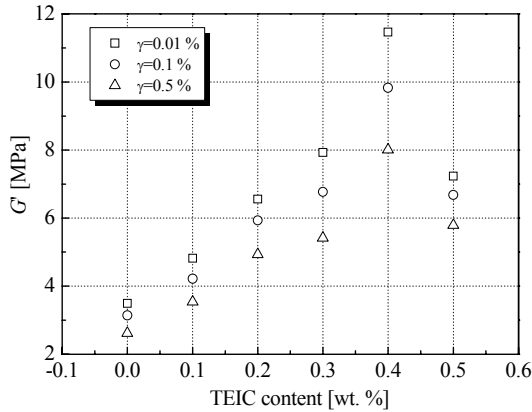

Figure 4. Influence of TEIC content on the values of shear storage modulus at different shear strain levels

Increasing the strain amplitude is favorable to microstructural cooperative movements. The macromolecular polymer chains position around the filler particles is modified, which limits the constraint imposed by such a high filler fraction on the polymer network. Also, the G' value increases with increasing TEIC content, regardless of the strain amplitude level (Fig.4). The maximum of the value is observed for 0.4 wt.% of TEIC.
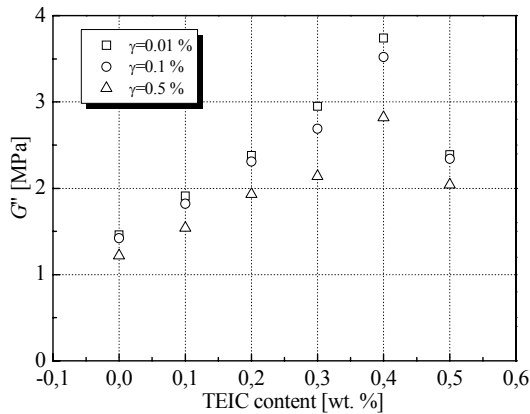

Figure 5. Influence of TEIC content on the values of shear loss modulus at different shear strain levels

TEIC affects the links between the polymer network chains and AP particles surface, which act as a giant cross–links disturb the strain distribution in the binder. In this way the TEIC causes the increase of G' values. The G' value is a measure of a deformation energy stored by the composite propellant during the shear process, showing completely reversible deformation behaviour. The increase of the G' value is connected with a reduction of polymer chain mobility, regardless of whether it is caused by increasing the degree of cross-linking or binder-filler interactions [6]. Finally, this increase leads to an increase in tensile strength and Young's modulus value.

The same trend can be seen by observing the change of the G'' values with increasing the TEIC content (Fig.5). Increase of the G'' values indicates the increase of dissipation energy within microstructure of the tested composite propellant compositions. This can be explained by the influence of TEIC on creating the reinforcing layer around the filler particles [15]. Thus, the resulting polymer layer increases the effective volume of the filler particles and links the polymer network to the surface of the fillers. This could be regarded as a constraint imposed on the polymer network which increases with increasing of the TEIC content.

Frequency dependence of the composite propellant samples

Fig.6 shows the frequency dependencies of the storage shear modulus for CP00 propellant sample at different test temperatures. Storage modulus increases in a regular fashion with increasing frequency or decreasing temperature, suggesting that time–temperature superposition of data is possible. Similar results were obtained for each of the six tested propellant samples.
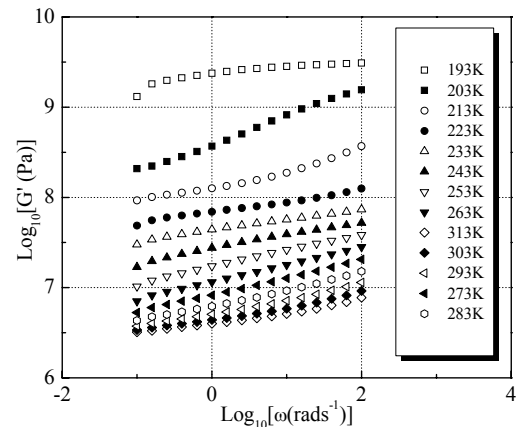

Figure 6. Storage modulus

The storage modulus *versus* temperature curves at various frequencies were shifted using the time–Temperature Superposition Principle (tTSP), based on the assumption of the equivalence loading in temperature and time [16]. The amount of shifting along the horizontal (*x*-axis) of each curve to align with the reference temperature curve is generally described by the Williams–Landel–Ferry (WLF) equation [17], which defines the shift factor a_T, in dependence of the temperature change, Eq.(1).

$$\log(a_T(T)) = \frac{-C_1 \cdot (T - T_0)}{C_2 + T - T_0} \qquad (1)$$

where: a_T – shift factor (representing the ratio between the time needed for some phenomenon to be developed at certain temperature T and the time for the same phenomenon at reference temperature, T – test temperature, T_0 – reference temperature, C_1, C_2 – WLF constants, which depend on the reference temperature.

In the first application of the WLF equation, the average values of $C_{1,g}$ and $C_{2,g}$ (WLF constants obtained by choosing the glass transition temperature, T_g as a reference temperature) were obtained by fitting data on a large number of different polymer materials and estimated to be $C_1=17.44$ and $C_2=51.6°C$, respectively [18]. These values were originally thought to be "universal" and are still widely used. But surely this is a rough approximation. For more accurate calculations it is necessary to determine the values of a shift factor a_T, and constants C_1 and C_2 for each material in consideration. Based

on the values of the storage modulus, G', experimentally determined at different temperatures, a single isothermal curve is constructed. In making the master curve from the experimental data, the storage shear modulus $G'(\omega)$ must first be multiplied by a temperature correction factor, T/T_0. Next, the corrected moduli curves are then shifted one by one along the $\log(\omega)$ scale until they superpose. Curves at the temperatures above T_0 are shifted to the left and those below T_0 are shifted to the right. The amount of horizontal shift of the $\log(\omega)$ is given by $\log a_T$.

This, so-called "master" curve, covers a much wider frequency interval compared to that in which the measurement was done. In this way, the frequency dependence of the dynamic moduli G' and G'' were expanded from 3 to 16 decades of frequency.

Storage modulus (G') as a function of frequency for the tested propellant sample CP00 and corresponding master curve created with the reference curve obtained at $T_0 = -20°C$ is shown in Fig.7.
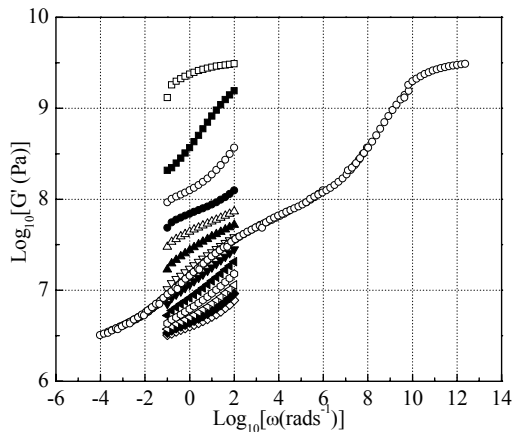

Figure 7. Storage modulus (G')

In practise, it is best to choose a reference temperature at the midpoint of the data and superpose the data to this temperature [19].

Some authors stated that the regression curve of the WLF equation has exactly the same form for a large number of materials (C_1=8.86 and C_2=101.6) if the reference temperature is chosen such that $T_0 \sim (T_g + 50)°C$, where T_g is the glass transition temperature [20]. The same principle is used in this paper. The T_g values of the tested propellant samples varied from $-60°C$ to $-70°C$, regardless of the rheological parameter whose maximum value is taken as the nominal glass transition temperature.

Certainly, the choice of the reference temperature affects the position of master curve but not its form.
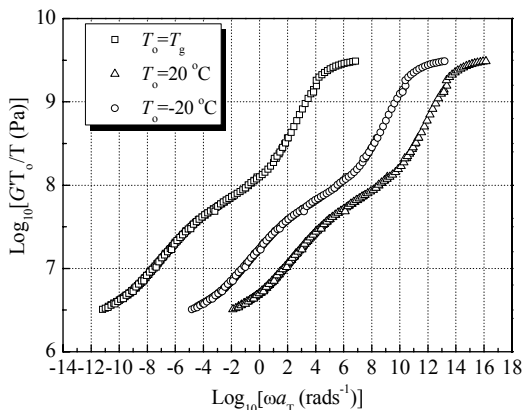

Figure 8. Master curves of the storage modulus

Master curves of the storage modulus (G') for the tested propellant sample CP00 shown for three referent temperatures, $T_0 = T_g$, $T_0 = -20°C$ and $T_0 = 20°C$, is shown in Fig.8.

Master curves for the storage and loss modulus of CP00 composite propellant sample at the reference temperature $T_0 = -20°C$ are presented in Fig.9.
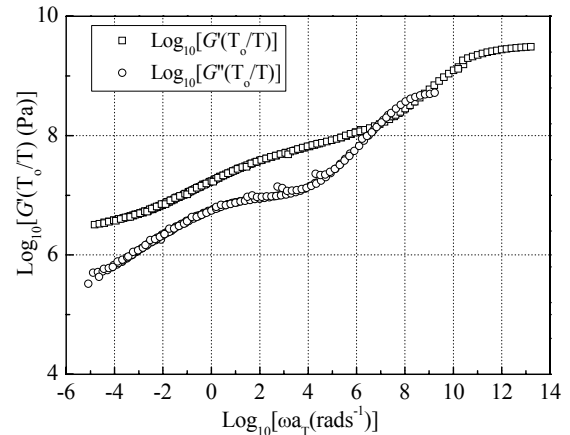

Figure 9. Master curves of the storage and loss moduli

Fig.9 shows several important features concerning the viscoelastic response of the tested propellant sample. At low temperatures or high frequencies, slope in G' curve is maximized. This temperature/frequency region of the viscoelastic spectrum is commonly termed the transition region, referring to the material transition from a soft elastomer to a hard glassy solid. At higher temperatures or lower frequencies, the value of G' is observed to approach the equilibrium value. This portion of the curve is termed the rubbery plateau.

The horizontal shift factor values a_T, used to superpose the G' and G'' experimental data into a master curve for tested propellants, are shown in Table 2.

A typical form of temperature dependence of $\log a_T$ for the tested composite propellant sample CP00 is shown in Fig.10.
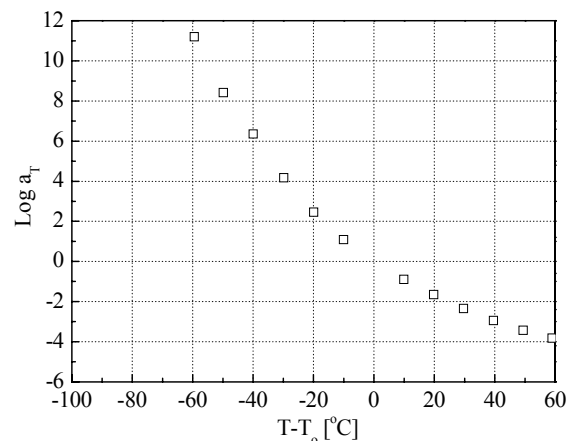
Figure 10. Temperature dependence of $\log a_T$ for the tested propellant sample CP00

Linearization of the experimentally obtained a_T values was performed in accordance with the WLF equation, using its transformed form, i.e. $(T-T_0)/\log a_T$ vs $(T-T_0)$. Linearization of the experimental shift factors values in accordance with the WLF equation, in order to calculate the values of constants C_1 and C_2 for tested propellant sample CP00, is shown in Fig.11.

Figure 11. Linearization of the shift factors values

The WLF constants, C_1 and C_2, are calculated from the slope "s" and the intersept "i" of a straight line through a plot of $(T-T_0)/\log a_T$ *vs* $(T-T_0)$, using the Eq. (1) and Eq. (2):

$$C_1 = \frac{-1}{s} \qquad (1)$$
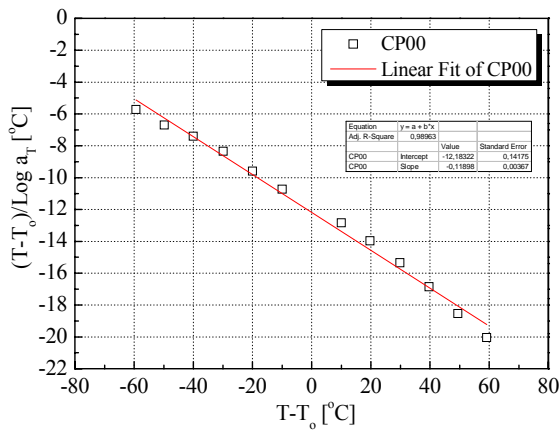
and

$$C_2 = \frac{i}{s} \qquad (2)$$

Exact form of the WLF equation for the tested propellant sample CP00 is obtained by substituting the values of experimentally obtained constants C_1 and C_2 into the Eq. (3), noting that the reference temperature is $T_0 = -20°C$, Eq.(3):

$$\log a_T = -\frac{11.42 \cdot (T+20)}{115.26 + T + 20} \qquad (3)$$

Substituting the corresponding absolute values of the test temperature in Eq. (3), calculated and experimental values of $\log a_T$ are obtained in accordance with the WLF equation. The values are presented in Fig.12.
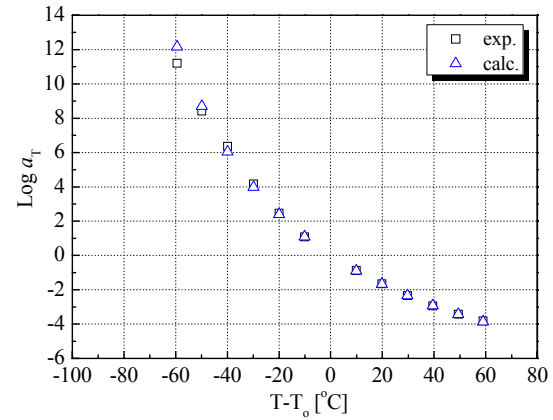

Figure 12. Experimental and calculated values of a shift factor, a_T for the tested propellant sample CP00

The remarkable agreement is evident between the experimental and calculated values of $\log a_T$, except for the test temperature $T = -80°C$, where a significant deviation is observed. This test temperature is below the T_g, regardless of the rheological parameter whose maximum value is taken as the nominal glass transition temperature.

Table 2. Shift factor a_T, temperature dependences determined through G' and G'' superposition

T [°C]	log a_T											
	CP00		CP01		CP02		CP03		CP04		CP05	
	G'	G''	G'	G''	G'	G''	G'	G''	G'	G''	G'	G''
-80	10.38	5.15	11.05	5.79	11.56	5.60	10.89	5.66	11.88	5.85	11.65	6.17
-70	7.44	6.75	9.06	8.30	8.74	7.60	9.02	7.66	9.13	7.48	8.70	7.21
-60	5.40	4.82	6.82	6.12	6.63	5.59	6.55	5.32	7.06	5.58	6.63	5.33
-50	3.58	3.42	4.92	4.66	4.20	3.83	4.53	3.92	4.58	3.95	4.58	4.00
-40	2.08	2.14	3.12	3.45	2.52	2.62	2.62	2.67	2.71	2.78	2.67	2.79
-30	0.93	0.96	1.27	1.63	1.10	1.23	1.13	1.33	1.17	1.43	1.19	1.39
-20	0	0	0	0	0	0	0	0	0	0	0	0
-10	-0.78	-0.83	-0.88	-0.95	-0.90	-0.97	-0.95	-1.00	-0.99	-1.07	-0.97	-1.04
0	-1.41	-1.52	-1.61	-1.76	-1.66	-1.78	-1.76	-1.82	-1.85	-1.93	-1.77	-1.90
10	-1.94	-2.13	-2.26	-2.48	-2.36	-2.51	-2.51	-2.53	-2.64	-2.65	-2.47	-2.60
20	-2.35	-2.66	-2.81	-3.11	-2.96	-3.15	-3.19	-3.24	-3.35	-3.37	-3.07	-3.26
30	-2.67	-3.10	-3.27	-3.70	-3.46	-3.71	-3.72	-3.86	-3.88	-4.02	-3.52	-3.81
40	-2.95	-3.53	-3.64	-4.15	-3.85	-4.21	-4.11	-4.29	-4.29	-4.53	-3.88	-4.30

Discussing the concept of the frequency–temperature superposition, the assumption in constructing master curves is that the mechanism of relaxation for the tested propellants remains unchanged and that the temperature changes only lead to changes in the rate of relaxation. In other words, the assumption is that the tested composite propellants are thermorheologically simple materials. Nevertheless, the evidence of the thermorheological complex behaviour was observed as indicated by slightly different shift factors for G' and G''. This difference is more pronounced comparing to the tested HTPB-based composite propellants reported in our previous paper [21].

WLF equation is based on the concept of free volume, which at temperatures below the T_g remains unchanged due to

a frozen conformational structure of the polymer chain, so it is logical that the glass transition temperature limits the lowest temperature of the temperature interval of application of the WLF equation.

Also, the WLF theory was developed to describe the temperature dependence of rheological properties close to the polymer glass transition temperature (in the temperature range T_g to $T_g+100°C$) [19].

The upper limit of the measuring range was 40°C, which represents the upper temperature limit of the composite propellant usage.

For the tested composite propellant samples, this means that the upper test temperature is 100–120°C above the glass transition temperature, depending on the rheological

parameter whose maximum value is taken as the nominal glass transition temperature. This criterion can be seen as a condition of using the WLF equation with the universal values of its constants.

However, limiting the interval of application of the WLF equation to the tested composite propellant samples, despite deviation of the calculated values of log a_T from those obtained by the experimental measurements, was not carried out due to the lowest values of the T_g which was recorded on temperature dependence of the storage modulus ($T_g = -74,5$°C).

According to the time-Temperature superposition principle, the strain rate (frequency) at a given reference temperature, at which cooperative movement of macromolecular chains is not possible, is called the glass transition frequency, ω_g (analog T_g). The ω_g value was determined as the frequency boundary between transition and equilibrium or plateau zone, as described in [4]. Its value could be estimated by the intersection of the tangents corresponding to the equilibrium zone and transition region of the master curve [4].

Also, the ω_g value can be determined based on the obtained master curves of the storage modulus as a value on the abscissa which corresponds the values of $G'=10^8$ Pa [22]. The same procedure was followed in this paper.

The constants of the WLF equation varied with the structure, i.e., content of TEIC, because of different contributions of the free volume, which is expected to depend on the mobility of the macromolecules. The fractional free volume in the temperature range above the glass transition temperature [18,23], T_g, is a linear function of temperature, Eq.(4):

$$f = f_g + \alpha_f \left(T - T_g \right) \tag{4}$$

where f is the fractional free volume at temperature T, f_g is the fractional free volume at T_g and α_f is the thermal expansion coefficient of the free volume above T_g. The values of f_g and α_f, related to the constants C_1 and C_2, by the following equations [18]:

$$f_g = B\left[1 + \left(T_g - T_0\right)/C_2\right]/2.303C_1 \tag{5}$$

$$\alpha_f = B / 2.303 C_1 C_2 \tag{6}$$

where B is the empirical constant of the Doolittle equation, the value of which is close to 1. In these transformations, the highest determined value of the T_g was used, i.e., the one determined as the maximum in the temperature dependence of the loss factor.

From the relation between the WLF equation constants obtained with two reference temperatures the relation given in Eq.(7) and (8) can be obtained. In one case the glass transition temperature T_g is reference, and in the other case the reference temperature is named T_0 [18].

$$C_{1,g} = \frac{C_1 \cdot C_2}{C_2 + T_g - T_o} \tag{7}$$

$$C_{2,g} = C_2 + T_g - T_o \tag{8}$$

The calculated values of $C_{1,g}$, $C_{2,g}$, f_g and α_f for the tested composite propellant samples are given in Table 3.

C_1 and C_2 values describe the state of a material, in relation to its free volume. So, the changes in free volume are reflective of the changes at the molecular level.

Obtained results confirm that the WLF equation constants $C_{1,g}$ and $C_{2,g}$, are not "universal", but roughly approximated by the universal values. If the "universal" constants are used, significant mistakes would be made for estimating how composite propellant behaves at different temperatures and strain rates. According to the literature data, there are moderate deviations from the given $C_{1,g}$ value depending on the polymer type, while with the constant $C_{2,g}$ deviations are larger [24]. This also applies to our tested composite propellant samples. α_f/B values are lower than the one derived from the WLF equation. Obtained f_g/B values are within the boundaries found in the literature for the most of polymer systems.

Table 3. Experimental values of the WLF equation and free volume constants for the tested propellant samples

Sample	C_1	C_2 [°C]	$C_{1,g}$	$C_{2,g}$ [°C]	$f_g/B \cdot 10^{-2}$	$\alpha_f/B \cdot 10^{-4}$ [K⁻¹]
universal values*	–	–	17.44	51.60	2.50	4.80
CP00	8.40	102.38	13.55	63.50	3.20	5.05
CP01	9.92	99.54	16.24	60.81	2.67	4.40
CP02	11.24	112.31	17.59	71.72	2.47	3.44
CP03	12.42	117.59	18.46	79.13	2.35	2.97
CP04	12.95	117.45	19.63	77.49	2.21	2.85
CP05	11.55	110.78	18.00	71.07	2.41	3.39

*– experimental values determined by averaging the values of a wide variety of polymers [18]

Apparent activation energy of viscoelastic relaxation

From the WLF equation, an apparent activation energy for viscoelastic relaxation, E_a, was determined using the Eq.(9)[18]:

$$E_a = R\left(\frac{d \ln a_T}{d(1/T)}\right) = 2.303R\left[\frac{C_1 C_2 T^2}{\left(C_2 + T - T_o\right)^2}\right] \tag{9}$$

The physical meaning of the activation energy is a measure of energy barrier that must be overcome when molecular motion of the polymer network segments of composite propellant binder, as a viscoelastic material, is to occur. The obtained values of E_a for the temperatures related to relaxation processess (T_g and $T_g^{restricted}$) are presented in Fig.13.
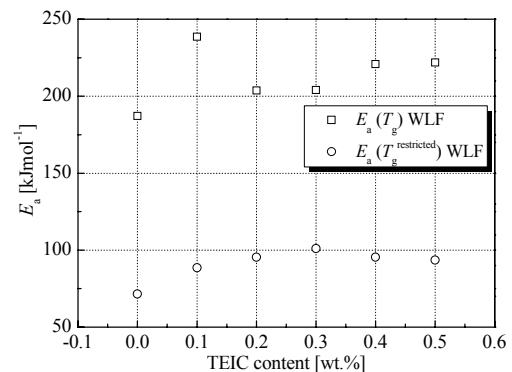

Figure 13. Influence of TEIC content on an apparent activation energy values for both relaxation processes

The values of E_a for two temperatures, related to the main and secondary relaxation processes, for tested composite propellant samples are in the range from 187 to 220 kJmol^{-1}, 70 to 100 kJmol^{-1}, respectively. The first peak of the loss factor curve is attributed to the main glass transition temperature in the soft–segment regions (CTBN main chain elements) where the main chain molecular motion ceases or starts. The second peak in tan(δ) that appears at a much higher temperature is referred to as the glass transition of the mobility restricted segments ($T_g^{restricted}$) and it is assumed to be related to the filler–binder interactions [9, 25]. The different nature of the two observed relaxation mechanisms is reflected in the values of E_a. The value $E_a(T_g^1)$ of the sample CP00 is slightly higher than the value of this parameter for HTPB–based composite propellant composition ($E_a(T_g)$=160 kJmol^{-1} and $E_a(T_g^{restricted})$=75 kJmol^{-1}) [1]. Higher E_a values indicate decreased chain mobility, which in the case of the CTBN–based composite propellant can be attributed to the presence of bulky and polar acrylonitrile group [26]. The results show that the activation energy of the both peaks is affected by the incorporation of TEIC into the propellant composition.

The apparent activation energy of the process associated with the cooperative motions of long soft segments (T_g process) is higher than that associated with the motions in by filler-matrix interactions mobility restricted segment.

E_a values related to the secondary relaxation process increase with incraesing TEIC and reach the maximum for 0.3 wt.% of this bonding agent. Further increase of the TEIC leads to the decrease of E_a value, but the value is still higher than the one obtained for the baseline CP00 composition.
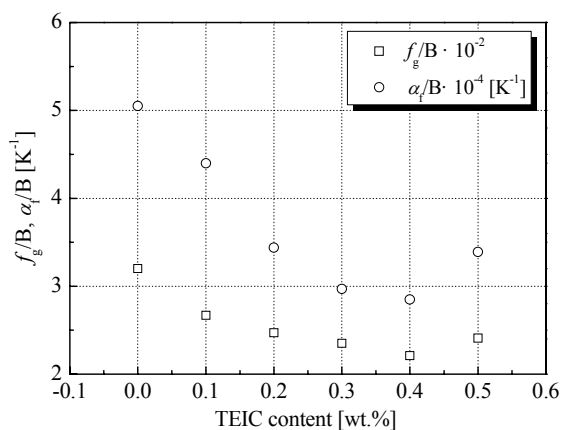

Figure 14. f_g and α_f dependences on TEIC content for the tested composite propellant samples

It is observed that the values of f_g/B and α_f/B decrease with increasing the TEIC content as a result of reduction in the degree of freedom of movement of macromolecular chains (Fig.14). Change of α_f/B with the increase of TEIC content is the same as the corresponding change of f_g/B, but the rate of change is intensified.

These differences could be explained by the fact that the free volume is directly controlled by the structure of the composite propellant. Such a trend is in accordance with the observed decrease in E_a with the increase of TEIC content and suggests that the flexibility is decreased because the hydrogen bonding is more pronounced. All this is reflected on physical properties of the tested propellant samples. TEIC as the bonding agent was found to alter the uniaxial tensile properties of the tested composite propellants. Both the tensile strength and Young's

modulus increased with increasing the TEIC content. Maximum values of these characteristics are recorded for 0.3 wt.%, of TEIC [9].
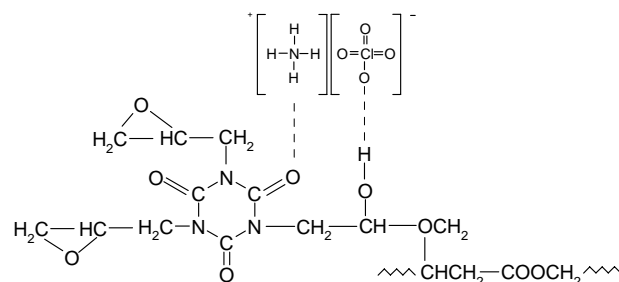

Figure 15. Hydrogen bonds between TEIC as a part of a polymer network and ammonium–perchlorate[27]

Formation of hydrogen bonds between the TEIC as a part of a polymer network on one side, and ammonium–perclorate particles on the other side can be a reason for the mobility restrictions.

Conclusion

Composite propellant based on carboxyl–terminated (butadiene–*co*–acrylonitrile) cured with polyglycidyl–ether of glycerol and epichlorhydrin containing tris (2,3–epoxypropyl) isocyanurate as a bonding agent was investigated with the dynamic mechanical analysis. Time–temperature superposition was used to construct modulus-frequency master curves that have been created for the temperature range from –80°C to 40°C considering the curve at –20°C as a reference. The experimental frequency range of three logarithmic decades measured between –80 °C to 40°C, is extended to 16 logarithmic decades. By choosing the glass transition temperature of the tested propellant samples to be the reference temperature in the WLF equation, based on C_1 and C_2 constants values at reference temperature of –20°C of the same equation, not only the values of "universal" constants $C_{1,g}$ and $C_{2,g}$ have been calculated, but also the fractional free volume at the glass-rubber transition temperature and the thermal coefficient of free volume expansion. The former is in agreement, while the latter is lower than the literature data.

Analyses of the master curves of the tested composite propellants showed that with increasing the TEIC content, the apparent energy for viscoelastic relaxation increased, because the chains were less flexible and the impact of hydrogen bonding was more pronounced.

References

[1] CERRI,S., BOHN,M.A., MENKE,K., GALFETTI,L.: Ageing Behaviour of HTPB Based Rocket Propellant Formulations. *Central European Journal of Energetic Materials*, 2009, Vol.6, No.2, pp. 149–165.

[2] RODIĆ,V., DIMIĆ,M., BRZIĆ,S., GLIGORIJEVIĆ,N.: *Cast Composite Solid Propellants with Different Combustion Stabilizers.* Scientific Technical Review, ISSN 1820-0206, 2015, Vol.65, No.2, pp. 3–10.

[3] KOHGA,M.: *Viscoelastic Behaviour of Hydroxyl Terminated Polybutadiene Containing Glycerin.* Journal of Applied Polymer Science, 2011, 122, pp.706–713.

[4] FUENTE, de la J.L., GARCIA,M.F., CERRADA,M.L.: *Viscoelastic Behaviour in a Hydroxyl-Terminated Polybutadiene Gum and Its Highly Filled Composites: Effect of the Type of Filler on the Relaxation Processes.* Journal of Applied Polymer Science, 2003, Vol.88, pp.1705–1712.

[5] CONSAGA,P.J.: *Bonding Agent for Composite Propellant*, US patent, 4 214 928. 1980-07-29.

[6] BRZIĆ,S., DIMIĆ,M., JELISAVAC,LJ., DJONLAGIĆ,J., UŠĆUMLIĆ,G., BOGDANOV,J.: *Influence of Polyglycidyl-type Bonding Agents on the Viscoelastic Properties of a Carboxyl–Terminated Poly(butadiene–co–acrylonitrile)–based Composite Rocket Propellant*. Central European Journal of Energetic Materials, 2014, Vol.68, No.4, pp.435–443.

[7] KAZAKEVIČIUTE–MAKOVSKA,R., MOGHAREBI,S., STEEB,H., EGGELER,G., NEUKING,K.: *A Critical Assessment of Experimental Methods for Determining the Dynamic Mechanical Characteristics of Shape Memory Polymers*. Advanced Engineering Materials, 2013, Vol.15, No.8, pp.732–739.

[8] BRZIĆ,S., UŠĆUMLIĆ,G. DIMIĆ,M., TOMIĆ,M., RODIĆ,V., FIDANOVSKI,B.: *Viscoelastic Behaviour of Carboxyl–Terminated (butadiene–co–acrylonitrile)-based Composite Propellant Binder Containing Polyglycidyl–type Bonding Agent*. Chemical Industry, 2015, DOI:10.2298/HEMIND150918062B

[9] BRZIĆ,S., UŠĆUMLIĆ,G., MILOJKOVIĆ,A., RODIĆ,V., BOGOSAVLJEVIĆ,M.: *Viscoelastic Properties of Carboxyl–Terminated (Butadiene–co–Acrylonitrile)–Based Composite Rocket Propellant Containing Tris(2,3–Epoxypropyl)Isocyanurate as Bonding Agent*. Scientific Technical Review, ISSN 1820-0206, 2015, Vol.65, No.4, pp.28–36.

[10] PRICE,H.: *Triglycidyl Isocyanurate Preparation*, US patent, 3 910 908. 1975–10–7.

[11] Anton Paar Germany GmbH, MCR: The Modular Compact Rheometer Series, 2016.

[12] BOHN,M.A.: *Impacts on the Loss Factor Curve and Quantification of Molecular Rearrang*ement Regions from it in Elastomer Bonded Energetic Formulations, In Energetics Science & Technology in Central Europe, ed. R. Armstrong, J. Short, and D.K. Anand, University of Maryland: CALCE EPSC Press, 2012, pp.195-235.

[13] MEZGER,G.T.: *The Rheology Handbook*, 4th Edition, Vincentz Network, Hanover, 2014.

[14] STACER,R.G., HUSBAND,D.M., STACER,H.L.: *Viscoelastic Response and Adhesion Properties of Highly Filled Elastomers*. Rubber chemistry and technology, 1987, Vol. 60, No. 2, pp. 227–244.

[15] AZOUG,A., NEVIERE,R., PRADEILLES,R-M., CONSTANTINESCU,A.: *Influence of Fillers and Bonding Agents on the Viscoelasticity oh Highly Filled Elastomers*. Journal of Applied Polymer Science, 2014, DOI:10.1002/APP.40664

[16] MENARD,K.P.: Dynamic Mechanical Analysis: A Practical Introduction. CRC Press, Washington, D.C., 1999.

[17] WILLIAMS,L.M., LANDEL,F., FERRY,J.: *The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids*. J. Am. Chem. Soc., 1955, Vol. 77, pp. 3701-3707.

[18] FERRY,J.D.: *Viscoelastic properties of polymers*, 3rd ed., John Wiley&Sons, New York, 1980.

[19] LANDEL,F.R., NIELSEN,E.L.: *Mechanical Properties of Polymers and Composites*, 2nd Edition, Marcel Dekker, New York, 1994.

[20] JEREMIĆ,R. *Some Aspects of Time–Temperature Superposition Principle Applied for Predicting Mechanical Properties of Solid Rocket Propellants*. Propellants, Explosives, Pyrotechnics, 1999, Vol.24, pp. 221–223.

[21] BRZIĆ,S., JELISAVAC,Lj., GALOVIĆ,J., SIMIĆ,D., PETKOVIĆ,J.: *Viscoelastic Properties of Hydroxyl–Terminated poly(butadiene)–based Composite Rocket Propellants*. Hemijska Industrija, 2014, Vol.68, pp.435–443.

[22] POPOVIĆ,R.: *Inhibitorski materijali na bazi elastomera*, Naučnotehnička Informacija (NTI), VTI, Beograd, 1996, Vol.30, No.6.

[23] JEREMIĆ,R.: *Strukturni integritet raketnih g*oriva, Vojnoizdavački zavod, Beograd, 2009.

[24] EMRE,I.: *Rheology of Solid Polymers*, The British Society of Rheology, 2005.

[25] TSAGAROPOULOS,G., EISENBERG,A.: *Dynamic Mechanical Study of the Factors Affecting the Two Glass Transition Bahavior of Filled Polymers*. Similarities and Differences with Random Ionomers. Macromolecules, 1995, Vol. 28, pp.6067–6077.

[26] PETRIĆ,M.: *Uticaj tipa umreživača na viskozitet kompozitnih raketnih goriva na bazi karboksiterminiranih polibutadienskih prepolimera*. Naučnotehnički pregled, ISSN 0350-0667, 2000, Vol.L, No.4–5, pp. 70–74.

[27] PETKOVIĆ,J., WALI,A., MIJIN,D., UŠĆUMLIĆ,G.: *The Influence of Bonding Agents in Improving Interactions in Composite Propellants*, Determined Using the FTIR Spectra. Scientific Technical Review, ISSN 1820-0206, 2009, Vol.59, No.3-4, pp.12–16.

Uticaj tri(2,3–epoksipropil)izocijanurata kao vezujućeg agensa na dinamički modul kompozitnog raketnog goriva na bazi CTBN

Ispitivan je uticaj tri(2,3–epoksipropil)izocijanurata u funkciji vezujućeg agensa na reološka svojstva kompozitnog raketnog goriva na bazi karboksiterminiranog kopolimera (butadien-akrilonitril) umreženog sa poliglicidil-etrom glicerola i epihlorhidrina. Ispitivanje zavisnosti viskoelastičnih svojstava od amplitude deformacije izvršeno je na sobnoj temperaturi. Analizirane su frekvencione zavisnosti parametara reološkog ponašanja (modula sačuvane energije, G' i modula izgubljene energije, G''). Na osnovu reoloških parametara, eksperimentalno određenih u temperaturnom opsegu od -80°C to 40°C, konstruisane su zbirne (master) krive, koje prekrivaju znatno širi interval frekvencija (16 logaritamskih dekada) u odnosu na onaj u kome je vršeno merenje. Odabirom temperature ostakljivanja kao referentne temperature, određene su "univerzalne" konstante WLF jednačine, na osnovu kojih su izračunate vrednosti frakcione slobodne zapremine na temperaturi ostakljivanja f_g/B, i koeficijent toplotnog širenja slobodne zapremine α_f/B.

Dobijeni rezultati pokazuju da vrednosti f_g/B i α_f/B opadaju sa porastom udela tri(2,3–epoksipropil)izocijanurata u okviru ispitivanih sastava goriva. Takođe, vrednosti prividne energije aktivacije viskoelastične relaksacije rastu sa porastom udela ovog vezujućeg agensa, što ukazuje na povećanje intermolekulskih vodoničnih interakcija.

Ključne reči: **kompozitno raketno gorivo, reološke osobine, butadienakrilonitril, izocijanurat, temperatura ostakljivanja, rezultati ispitivanja.**

Действие трёх (2,3-эпоксипропил) изоцануратов в роли связующих материалов на динамический модуль композитных ракетных топлив на основе ctbn

В настоящей работе испытыван эффект трёх (2,3-эпоксипропил) изоцануратов в функции связующего вещества на реологические свойства композитных ракетных топлив на основе карбокситерминированного кополимера (бутадиен-акрилонитрил), с поперечными связями с полиглицидил-эфиром глицерина и эпихлоргидрина. Исследование зависимости вязкоупругих свойств от амплитуды деформации проводят при комнатной температуре. Проанализированы частоты в зависимости от параметров реологического поведения (модуля запасенной энергии, G' и модуля потерянной энергии, G''). На основании реологических параметров, экспериментально определённых в температурном диапазоне от -80°C до 40°C, таким образом сконструированы компилирующие (мастер) кривые, которые охватывают гораздо более широкий частотный интервал (16 логарифмических декад) по сравнению с тем, в котором измерение выполняется. Выбором температуры остекления в качестве эталонной температуры, определены "универсальные" постоянные WLF-уравнения, на основе которых вычисляются значения долей свободного объёма при температуре остекления f_g/B, и коэффициент термического расширения свободного объёма α_f/B.

Полученные результаты показывают, что значения f_g/B и α_f/B уменьшаются с увеличением долей трёх-(2,3-эпоксипропил) изоцануратов в рамках исследуемых составов топлива. Кроме того, значения кажущейся энергии активации вязкоупругой релаксации увеличиваются с увеличением доли связующего вещества, что свидетельствует об увеличении связей межмолекулярных водородных взаимодействий.

Ключевые слова: **композитное ракетное топливо, реологические свойства, бутадиенакрилнитрил, изоцианурат, температура стеклования, результаты испытаний.**

Influence de tri(2,3 – époxy propyle) iso cyanure comme l'agent de liage sur le module dynamique du propergol composite à la base de CTBN

L'influence de tri(2,3 – époxy propyle) iso cyanure comme l'agent de liage sur les propriétés rhéologiques du propergol composite à la base de copolymère carboxyle terminé (butadiène acrylonitrile) a été examiné. L'examen de dépendance des propriétés viscoélastiques de l'amplitude de déformation a été effectué à la température de chambre. On a analysé les dépendances fréquentielles des paramètres de comportement rhéologiques (module de l'énergie conservée G' et le module de l'énergie perdue G''). A la base des paramètres rhéologiques déterminés expérimentalement aux températures de -80ºC jusqu'à 40ºC on a construit les courbes magistrales qui comprenaient une intervalle de fréquence beaucoup plus large (16 décades logarithme) par rapport à celle ou le mesurage a été effectué. Par le choix de la température de vitrification comme la température de référence on a déterminé les constantes universelles WLF de l'équation à la base desquelles on a calculé les valeurs du volume libre à la température de vitrification et le coefficient de la croissance thermique de volume libre . Les résultats obtenus démontrent que les valeurs citées diminuent avec l'augmentation de tri(2,3- époxy propyle) iso cyanure chez les compositions des propergols examinées. Les valeurs de l'énergie apparente de l'activation de relaxation viscoélastique augmentent si la part de cet agent de liage croit ce qui indique la croissance des interactions intermoléculaires hydrogènes.

Mots clés: **propergol composite, propriétés rhéologiques, butadiène acrylonitrile, iso cyanure, température de vitrification, résultats des recherches.**