

Viscoelastic behaviour of carboxyl-terminated (butadiene-co-acrylonitrile)-based composite propellant binder containing polyglycidyl-type bonding agent

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Abstract

The influence of tris(2,3-epoxypropyl) isocyanurate as bonding agent on the physicochemical, viscoelastic and uniaxial tensile mechanical properties of carboxyl-terminated (butadiene-co-acrylonitrile) cured with the polyglycidyl ether of glycerol and epichlorhydrin was investigated. Cross-link density values were estimated by swelling measurement. Temperature and frequency dependencies of rheological behaviour parameters (storage modulus, loss modulus, loss factor and glass-rubber transition temperature) were also analyzed. Based on the frequency dependencies of storage modulus, put in the range of temperature from -50 to 20 °C by the experiment, master curves ($\log G'$ vs. $\log \omega$) were generated, reaching broader frequency interval in comparison to that used in the measurements. By choosing the glass-rubber transition temperature to be the reference one, Williams-Landel-Ferry equation constants were determined. Further, material constants, fractional free volume at the glass-rubber transition temperature and thermal coefficient of free volume expansion were calculated. Although small quantity of tris(2,3-epoxypropyl) affects the network density, the dynamic mechanical analysis showed that the bonding agent content did not affect the glass-rubber transition temperature of the tested materials.

Keywords: carboxyl-terminated (butadiene-co-acrylonitrile), viscoelastic properties, glass-rubber transition temperature.

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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) poly(butadienes) 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 [1–3]. In order to improve uniaxial tensile 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 [4]. Due to the highly polar carboxyl (-COOH) group, carboxyl-terminated prepolymers (CTPB) do not require the use of bonding agents. If for composite propellant production, carboxyl-terminated (butadi-

ene-co-acrylonitrile) (CTBN) based propellant binder is taken, experiments have shown that tris(2,3-epoxypropyl) isocyanurate (TEIC) as bonding agent significantly improves uniaxial tensile characteristics [5]. The molecular structure of the polymer based composite propellant binder is the largest factor in determining the mechanical properties of the mixed and cured propellant. The mechanical properties of composite propellants depend strongly on the time, temperature, loading procedure and loading history [6]. Since the bonding agent is ingredient that is added to modify the mechanical properties of the propellant, precise knowledge of the dynamic mechanical behaviour 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 binder. 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 binder but also the effect of this type of bonding agent on the CTBN-based composite propellant binder behavior.

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EXPERIMENTAL

Materials

Four CTBN-based composite propellant binder compositions (Table 1) selected for this study consisted of 100 phr of CTBN (1300×15, BF Goodrich, viscosity at 25 °C: 66.2 Pa s, carboxyl functionality: 1.9, number-average molecular weight: 3800 g/mol, specific gravity at 23 °C: 0.931 g/cm³, glass-liquid transition temperature, T_g : -63.3 °C), 1.7 phr of antioxidant (2,2'-methylene-bis(4-methyl-6-tertbutyl phenol), commercially available as a product called AO 2246 and under a lot of other brand names (Fluka AG, Switzerland) and 0.44 phr of cure catalyst (iron(III)-acetylacetonate, (Fe(acac)₃, Merck-Schuchardt, Germany). Mix ratio of propellant binder ingredients is expressed in phr, this means parts per hundred of resin based on 100 parts of CTBN.

Preferred curing agents for carboxyl functional prepolymers are multifunctional epoxides. When epoxy curing agents are used to cure a carboxy functional prepolymer in composite propellant formulation, the E/COOH ratio between the two components is preferably in the range of from 1.05 to about 1.2. Presence of ammonium perchlorate as oxidizer, causes side reactions including the curing agent. As a result, less complete polymer network is formed. 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, Ladd Research Industries, USA).

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

Tris(2,3-epoxypropyl) isocyanurate was prepared by the reaction of cyanuric acid and epichlorhydrin in

accordance with a modified literature method [7]. Investigated composite propellant binder samples differ from each other in bonding agent content. Composition CPB00 is a baseline propellant binder composition containing no bonding agent. TEIC content (ξ) varied from 0.1 to 0.3 wt.% of the total mass of the investigated propellant binder.

Methods

Mixing of propellant binder formulations was conducted in a 1.5 l DRAIS FH planetary mixer at a temperature of 60 °C. CTBN, AO 2246 and TEIC were blended thoroughly for 15 min at ambient pressure and then vacuum mixed for another 15 min. LX 112 was then added to the mixture, mixed for 10 minutes at ambient pressure and then vacuum mixed for another 10 min. Then, Fe(acac)₃ was added to the mixture and the same procedure was repeated. Finally, the prepared mixture was cast and cured in teflon-coated metal plates to form 3 mm thick slabs. The curing was performed for 5 days at 70 °C.

The network density of a cured propellant binder samples was estimated by the degree of swelling by an appropriate solvent at equilibrium [8]. As solvent, toluen was used. The gravimetric technique was applied for measuring the swell ratio of crosslinked propellant binder networks. Swelling test was carried out on rectangular specimens with length of 20 mm, width of 20 mm and thickness of 3 mm at the $T = 25$ °C. In preliminary experiments, the sample was allowed to swell for 4 days, but mass became constant after two days, indicating that equilibrium was reached. Therefore tested binder samples were swelled for two days.

Swell ratio is computed as:

Table 1. Investigated propellant binder compositions, phr (wt.% of the total mass of the tested propellant binder)

Sample	Propellant binder				
	CTBN 1300x15	LX 112	TEIC	AO 2246	Fe(acac) ₃
CPB00	100 (90.22)	8.70 (7.85)	(0)	1.70(1.53)	0.44 (0.40)
CPB01	100 (90.13)	8.70 (7.84)	(0.1)	1.70(1.53)	0.44 (0.40)
CPB02	100 (90.04)	8.70 (7.83)	(0.2)	1.70(1.53)	0.44 (0.40)
CPB03	100 (89.95)	8.70 (7.83)	(0.3)	1.70(1.53)	0.44 (0.40)

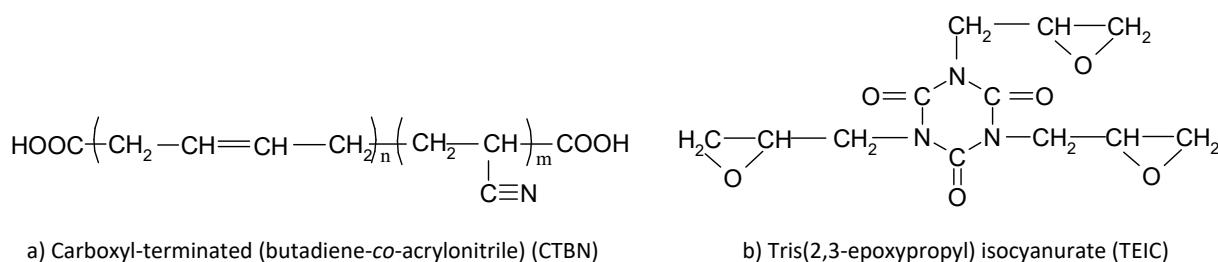


Figure 1. The chemical structures of the ingredients of the investigated propellant binders.

$$q = \frac{W_d + W_g - W_d K}{W_d} \quad (1)$$

where: W_d – sample weight before immersed in toluen, W_g – sample weight after two days in toluen and K – ratio of the densities of the solvent to the polymer.

The density of toluene is 0.86 g/cm^3 , and those of cured propellant binder samples were in the range from 0.953 to 0.956 g/cm^3 , measured following Archimedes principle [9].

The value of network density, N , of the binder samples was estimated by the value of v_r using the Flory–Rehner equation, Eq.(2):

$$\ln(1 - v_r) + v_r + \chi v_r^2 = -N V_1 \left(v_r^{\frac{1}{3}} - \frac{v_r}{2} \right) \quad (2)$$

where: v_r – volume fraction of the binder in the swollen gel, χ – Flory–Huggins polymer–solvent interaction parameter, V_1 – molar volume of the solvent, N – network density of the tested binder sample. The value of Flory–Huggins polymer–solvent interaction parameter (χ) taken for polybutadiene–toluene system and the value of molar volume V_1 of swelling solvent are: 0.35 and $106 \text{ cm}^3 \cdot \text{mol}^{-1}$, respectively [8].

The DMA measurements were carried out in the torsion deformation mode by using a mechanical spectrometer model “RMS-605” manufactured by the former Rheology Business Unit of company Rheometric Scientific Inc., Piscataway, NJ, USA. The temperature range applied was from -90 to $80 \text{ }^\circ\text{C}$, the heating rate was $5 \text{ }^\circ\text{C min}^{-1}$ and the single frequency point of 1 Hz was chosen. Strain amplitude was 0.1% . The samples for DMA tests were of rectangular bar shape ($63 \text{ mm} \times 12 \text{ mm} \times 3\text{--}4 \text{ mm}$). Complex shear modulus was determined, $G^*(\omega) = G'(\omega) + iG''(\omega)$. Extracted data were the shear storage and loss moduli, G' and G'' , respectively, and the loss factor $\tan \delta = G''/G'$. Each binder sample was first tested at a constant frequency and temperature over above mentioned range.

The temperature corresponding to the maximum of the loss factor is taken as the nominal glass transition temperature, correctly named as glass–rubber transition temperature (T_g) [10]. Finally, the viscoelastic properties were measured over three decades of frequency in the temperature range from -50 to $20 \text{ }^\circ\text{C}$, scanned with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$.

Frequency was varied from 0.1 to 100 rad/s , with 16 equidistant values on a logarithmic scale. The measurement reproducibility is very high so only one sample per each testing condition was tested [11].

DSC analyses, in order to investigate the thermally based glass–rubber transition temperature of the samples, were carried out using the DSC Q20 manufactured by TA Instruments with liquid nitrogen cooling for low temperatures. The temperature scale was calibrated

using the melting temperature of high purity indium. The small amount of the sample ($\sim 5 \text{ mg}$) was scanned with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$, starting from $-90 \text{ }^\circ\text{C}$ and ending at $50 \text{ }^\circ\text{C}$. The glass–rubber transition temperature of the sample was determined from the midpoint of the transition.

The uniaxial tensile mechanical properties of the investigated samples were evaluated at $20 \text{ }^\circ\text{C}$ using INSTRON 1122 uniaxial tensile test machine fitted with a 500 N load cell. Small dog bone samples (115 mm length, 25 mm width and 3 mm thickness) were used. Crosshead speed of tensile machine was 50 mm/min , while the effective gauge length of the test samples was 46.5 mm .

RESULTS AND DISCUSSION

Network density of propellant binder samples

Since the swollen binder sample is very touch-sensitive and prone to cracking, the gravimetric technique is used for measuring the swell ratio of cross-linked propellant binder network. Results of the analysis (Table 2) show that with the increase of TEIC content, the cross-link density of the investigated binder samples increase also. The highest N value is observed for CPB02 (0.2 mass\% of TEIC) binder sample. We conclude that the cross-link density of a polymer network cannot be determined definitely using this method alone. Gel fraction, as a result of sol–gel analysis could be important additional molecular parameter when prediction of cross-link density of a polymer network is contemplated. However, the increase in N value suggests that the degree of cross-linking should increase.

Table 2. Values for network density N and volume fraction of binder in swollen gel v_r of propellant binder samples determined by swelling tests.

Parameter	Sample			
	CPB00	CPB01	CPB02	CPB03
$\xi / \text{mass\%}$	0	0.1	0.2	0.3
v_r	0.102	0.108	0.112	0.110
$N \times 10^{-5} / \text{mol} \cdot \text{cm}^{-3}$	4.37	4.90	5.26	5.10

The increase of the network density value points to the fact that the functional epoxy groups of TEIC are involved in the propellant binder network formation.

Dynamic mechanical analysis of composite propellant binder samples

Based on a weakly cross-linked polymeric matrix, composite rocket propellants show very large changes in mechanical properties with temperature [12]. Figure 2 shows the viscoelastic response of baseline composite propellant binder sample CPB00 in terms of G' , G'' and $\tan \delta$ as a function of temperature.

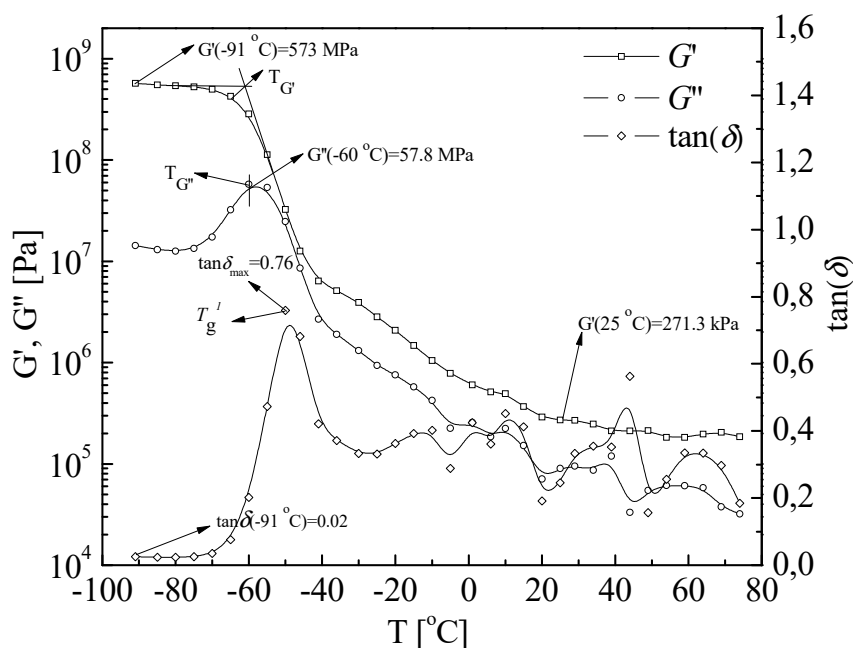


Figure 2. Characteristic values of the CPB00 baseline composition shown by the DMA thermogram of $\omega = 6.28 \text{ rad s}^{-1} = 1 \text{ Hz}$.

It follows from Figure 2 that the G' is almost constant at low temperatures and it reaches the maximum value in the region below the glass transition (-70 to -40 °C). The transition from the glassy to the rubbery state (the onset point on the G' - T curve at $T = -65$ °C) has as consequence a drop in the G' value by a factor of about 90 (from 573 MPa at -91 °C to 6.4 MPa at -40 °C). With increasing temperature (between $T = -40$ °C and $T = 20$ °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 composition having AP [5]. 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 slow decrease of the storage modulus could be crystallinity within a polymer structure of tested propellant binder samples [13].

The glass–rubber transition temperature (T_g) of elastomer bonded composite propellant is one of the most important property determining their in-service application [14]. This means that the T_g value of the composite propellant binder must be lower than the minimum service temperature (usually -40 to -54 °C depending on application).

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. Poly(butadiene)-based elastomers contain soft and rigid segments [6]. The soft segments consist of large flexible non-crystalline polymer chains, in this case, poly(butadiene), while rigid (hard) segments consist of cross-linking units.

The peak of $\tan \delta$ positioned between $T = -50$ °C and $T = -45$ °C (its temperature location is designated as T_g), is attributed to the glass–rubber transition temperature (Table 3). This relaxation process involves reorientational motions of prepolymer (CTBN) main chains between the crosslinks within the soft segment regions. These polymer network segments have very low density of ester groups and are the polybutadiene

Table 3. $\tan \delta_{(\max)1}$ values and T_g (°C) values determined by G'' , G' , $\tan \delta$ and from DSC curves

Sample	T_g / °C				Maximum value of $\tan \delta_{(\max)1}$
	T in max of G''	Tangens method with G'	T in max. of $\tan \delta$	DSC at 10 °C/min	
CPB00	-57.9	-64.3	-48.7	-62.4	0.76
CPB01	-59.8	-66.3	-47.5	-62.0	0.57
CPB02	-57.9	-64.2	-48.5	-60.5	0.83
CPB03	-56.5	-62.2	-47.9	-62.8	0.85

part of binder which reorient at very low temperatures. The T_g value for the baseline composition, CPB00, is -48.7°C .

The peaks, that appear at higher temperatures, between -30 and 60°C , correspond to the relaxation process related to the motions within hard segment units. Hard segments could also contain polymeric chains formed by the reaction of secondary hydroxyl groups and epoxy groups [15] (Figure 3). However, the parts of $\tan \delta$ above seem somewhat scattered in data, so interpretation is difficult to give.

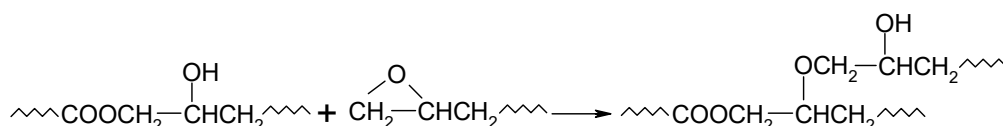


Figure 3. The reaction of the epoxy group of bonding agent TEIC and the secondary hydroxyl group of the binder system formed by the curing reaction between CTBN and the epoxy-based curing agent.

The Figure 4 shows temperature dependencies of the storage modulus, G' , loss modulus, G'' and the loss factor, $\tan \delta$ of the composite propellant binder samples. CPB01 binder sample (0.1% TEIC) has the low-

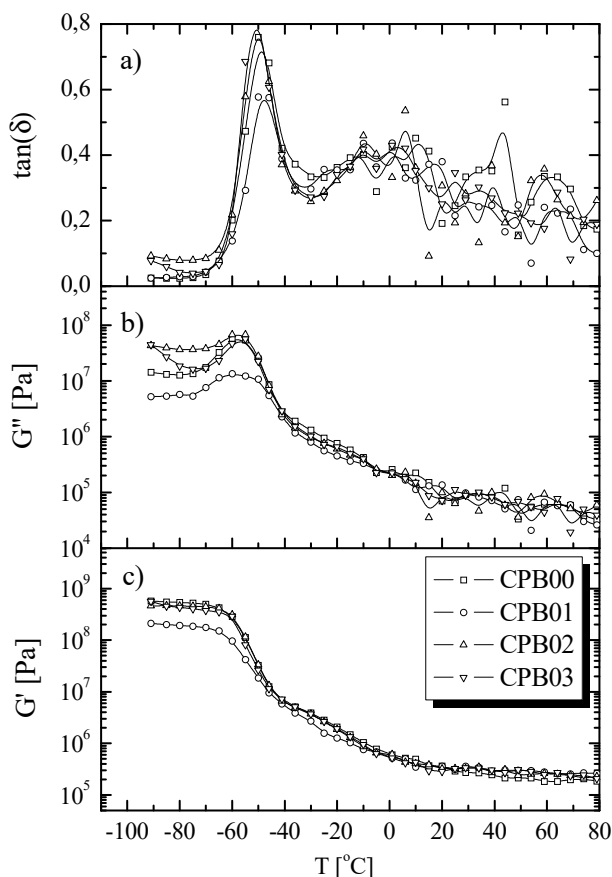


Figure 4. Temperature dependencies of: a) loss factor ($\tan \delta$), b) loss modulus (G'') and c) storage modulus (G') for the investigated propellant binder samples.

est 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 [16]. The increase in storage modulus values with increasing TEIC content suggests that a tougher, more rigid network is obtained at higher TEIC concentrations. The results are consistent with swelling measurements which indicate an increase in the crosslink density with introduction TEIC in binder samples.

For the propellant binder samples only quite small variations in T_g were observed, despite the changes in effective crosslink density as evident in the storage modulus values. The reason is the concentration of cross-link points apart from the polybutadiene parts, which are responsible for the main glass-rubber transition at low temperatures.

For all binder samples, regardless the TEIC content, T_g values are located in the narrow temperature range ($T_g \approx -50^\circ\text{C}$).

Numerous studies indicate that the restricted mobility and the heterogeneity of the polymer system arise from the presence of cross-link within the polymer network [17]. Crosslinks are leading towards the decrease in number of possible conformational motions, *i.e.*, conformational freedom of polymer chain segments, resulting in limited mobility regions around the crosslink points. It is also significant to consider the influence of crosslink density on the glass-rubber transition temperature position.

Extremely high crosslink density values shift the glass-rubber transition toward higher temperatures. Glass-rubber transition temperatures, determined by DSC (Figure 5 and Table 3), are 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 [18].

The invariance in T_g values, regardless of the method of determining, indicates that distances between the crosslink points within the polymer network of 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 reorientational motions of polymer network segments, related to main

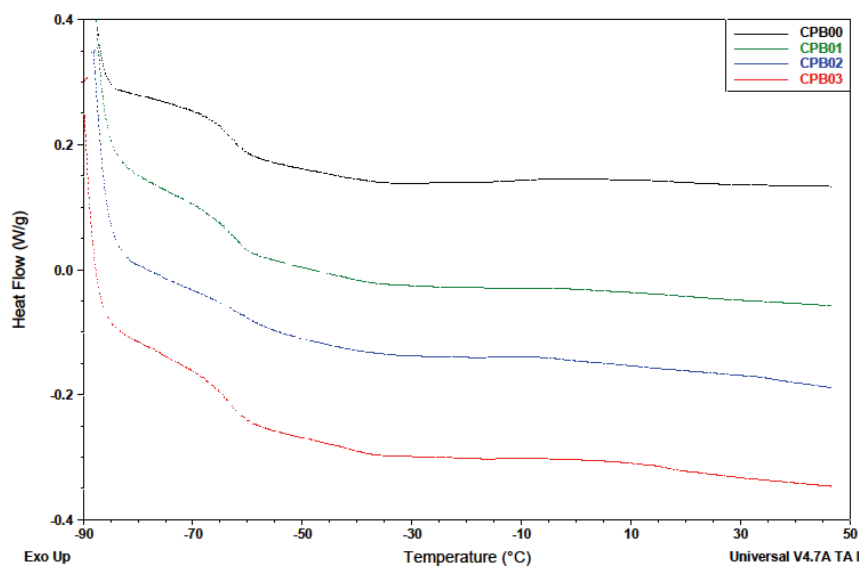


Figure 5. DSC curves of tested binder samples.

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.

In Table 3 are shown the intensity of T_g , $\tan \delta_{(\max)1}$, values on the loss factor curve for the tested propellant binders. The $\tan \delta_{(\max)1}$ value is influenced by the segmental motion of the polymer chains. The lower the mobility restrictions on the polymer chains are, the higher the $\tan \delta_{(\max)1}$ values. Although the $\tan \delta_{(\max)1}$ decrease with addition of 0.1 wt.% of TEIC, further increase bonding agent content significantly increase this value. The maximum was recorded for the CPB03 propellant binder sample. This can be explained by inhibition of the chain segment relaxation processes or by an increase in the rigidity of the chain segments, increasing the propellant polymer network heterogeneity.

Frequency dependence of composite propellant binder samples

Figure 6 shows the frequency dependences of G' of propellant binder samples. Storage modulus increases in a regular fashion with increasing frequency or decreasing temperature, suggesting that time-temperature superposition of the data is possible. Similar results were obtained for each of the four propellant binder samples.

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 [19]. The amount of shifting along the horizontal (x -axis) of each curve to align with the reference temperature curve is generally described by the Wil-

liams-Landel-Ferry (WLF) equation [20], which defines the shift factor a_T , in dependence of the temperature change:

$$\log(a_T(T)) = \frac{-C_1(T-T_0)}{C_2 + T - T_0} \quad (3)$$

The symbols are: 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. The authors of the WLF equation found that for many amorphous polymers, independent of chemical structure and with the glass transition temperature as reference temperature, the two constants C_1 and C_2 have universal values of 17.44 and 51.6 °C, respectively. 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.

The master curve reference temperature was $T_0 = -20$ °C. In practice, it is best to choose a reference temperature at the midpoint of the data and superpose the data to this temperature [13]. Figure 5 shows several important features concerning the viscoelastic response of the propellant binder samples. G' reaches the maximum at low temperatures (high frequencies). At higher temperatures (lower frequencies) G' curves enter the rubbery plateau. Master curves of the binder samples show a gradual slope in transition region. Storage modulus change along with the strain rate change is small, indicating these materials are almost insensitive to the strain rate, *i.e.*, temperature. The influence of

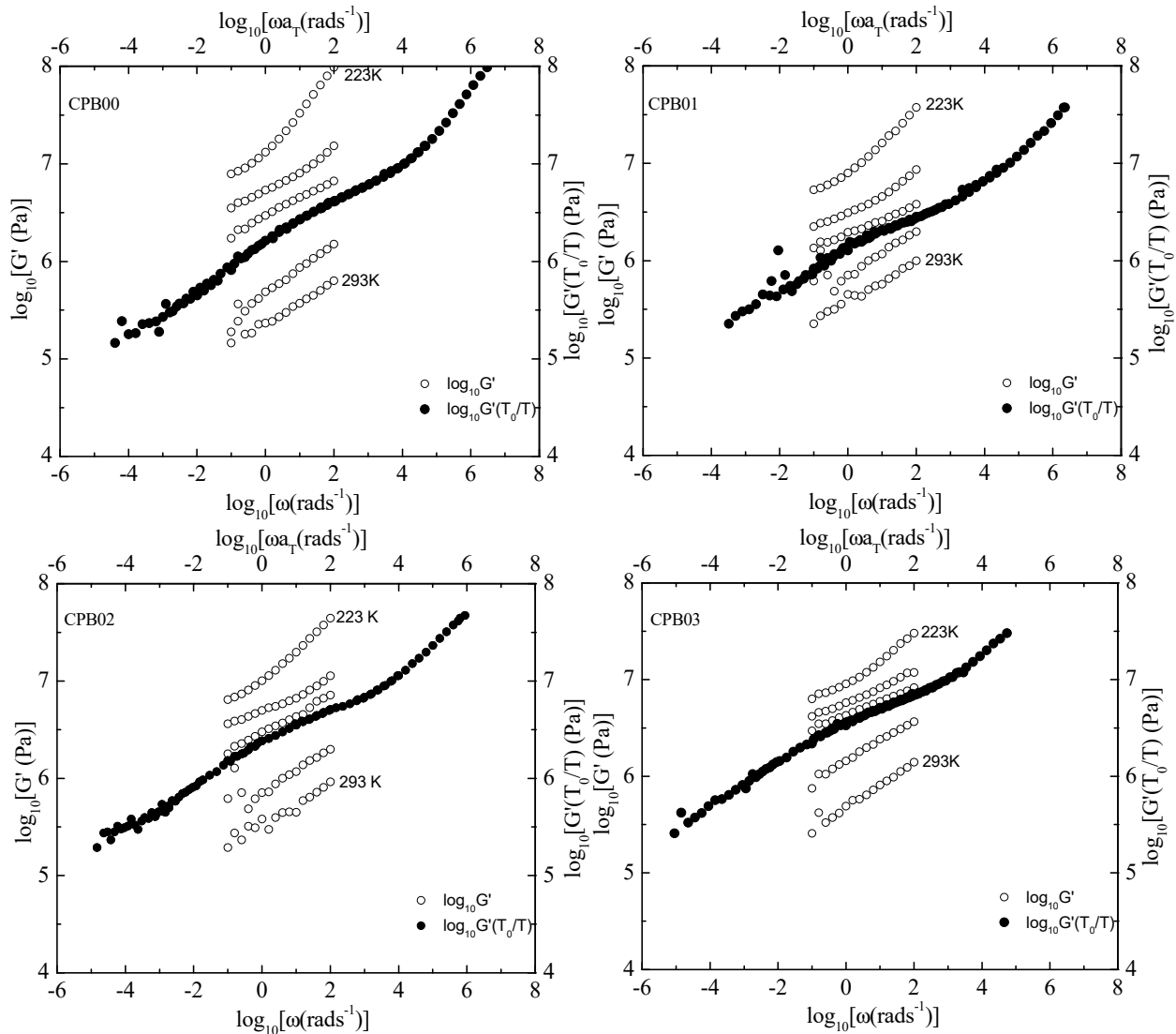


Figure 6. Storage modulus (G') as a function of frequency for tested binder samples and corresponding master curves established with the reference curve obtained at $T_o = -20$ °C.

reference temperature's choice on master curve's position and shape of storage modulus frequency dependence for a binder sample CPB00 is shown in Figure 7.

It is notified that, regardless of the reference temperature, master curves are of the same shape, but the curve representing higher reference temperature is shifted to the higher frequency. The temperature dependency of shift factor a_T values for all binder samples is shown in Table 4.

From the relation between WLF equation constants obtained with two reference temperatures the relation given in Eqs. (4) and (5) can be obtained. In one case, the glass–rubber transition temperature T_g is reference, and in the other case the reference temperature is named T_o .

$$C_{1,g} = \frac{C_1 C_2}{C_2 + T_g - T_o} \quad (4)$$

$$C_{2,g} = C_2 + T_g - T_o \quad (5)$$

Further on, between the two sets of constants the Eq.(6) is valid and Eq.(7) results from above:

$$C_1 C_2 = C_{1,g} C_{2,g} \quad (6)$$

$$T_g - C_{2,g} = T_o - C_2 = T_{inf} \quad (7)$$

T_{inf} is the temperature at which, regardless the way T_o is selected, the $\log(a_T(T))$ value becomes infinite according to WLF equation, see Eq. (8). Physically, it is the temperature at which cooperative motions of polymer network segments appear at infinitely small deformation frequencies, being previously restricted at glass–rubber transition temperature. The WLF equation formulated with T_g as reference is given in Eq.(8):

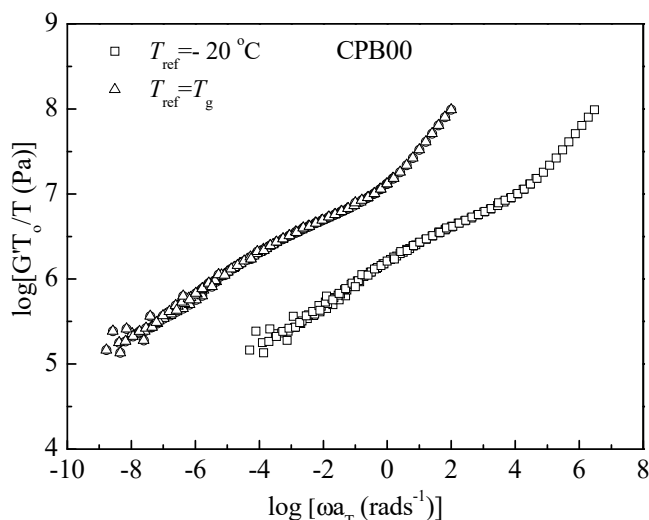


Figure 7. Master curves of storage modulus (G') for the sample CPB00 shown for two referent temperatures, $T_{ref} = T_g$ and $T_{ref} = T_0 = -20$ °C.

$$\log(a_T(T)) = \frac{-C_{1,g}(T - T_g)}{C_{2,g} + T - T_g} \quad (8)$$

Since the WLF equation is based on the free volume concept, the following relations can be derived [21]:

$$C_{1,g} = \frac{B}{2.303f_g} \quad (9)$$

$$C_{2,g} = \frac{f_g}{\alpha_f} \quad (10)$$

where: B is a constant in the Doolittle equation, which is assumed equal to unity, f_g is the fractional free volume of the elastomer at the T_g and α_f is the thermal coefficient of expansion of the free volume above T_g .

Table 5 presents the WLF and free volume constants for the investigated binder samples.

Obtained results confirm that WLF equation constants $C_{1,g}$ and $C_{2,g}$ are not “universal”, but roughly approximated by the universal values. If “universal” constants are used, significant mistakes would be made for estimating how composite propellant behaves at different temperatures and strain rates. According to literature data, there are moderate deviations from the given $C_{1,g}$ value depending on the polymer type, while

with constant $C_{2,g}$ deviations are larger [22]. This also applies to our binder samples. α_f/B values are lower than the one derived from WLF equation. Obtained f_g/B values are within the boundaries found in literature for most of polymer systems.

Uniaxial tensile properties of propellant binder samples

The average and standard deviation (SD) values of uniaxial tensile mechanical properties, *i.e.*, the tensile strength (σ_m), the strain at maximum load (ϵ_m) and Young's modulus (E) for the investigated binder samples are listed in Table 6.

All of the values listed in Table 6 were obtained as an average of five specimens. The uniaxial tensile properties of composite propellant depend on tensile properties of propellant binder, which in turn determines the strain capability of the propellant. High strain capability of binder network is favourable considering long shelf life of propellant system [23]. The value of the strain at maximum load of the baseline composition, primarily caused by the prepolymer (CTBN) molecular weight, is 464.34%, which is quite acceptable value compare to that of other materials used for composite propellant manufacture. CTBN-based composite propellant binder gives much higher value of the strain at

Table 5. Experimental values of WLF equation and free volume constants

Sample	C_1	$C_2 / ^\circ\text{C}$	$C_{1,g}$	$C_{2,g} / ^\circ\text{C}$	$T_{inf} / ^\circ\text{C}$	$(f_g/B) \times 10^{-2}$	$(\alpha_f/B) \times 10^{-4} / \text{K}^{-1}$
Universal ^a	–	–	17.40	51.60	–	2.5	4.80
CPB00	13.37	120.29	17.62	91.29	–141.3	2.46	2.70
CPB01	16.23	133.45	20.74	104.45	–154.5	2.09	2.00
CPB02	14.97	120.36	19.88	90.61	–140.6	2.18	2.41
CPB03	10.64	88.71	15.92	59.27	–109.3	2.73	4.60

^aThese values were determined by averaging the values of a wide variety of polymers [20]

Table 6: Values of tensile strength (σ_m), strain at maximum load (ε_m) and Young's modulus (E) on uniaxial tensile test of CTBN based propellant binder samples at $T = 20$ °C. SD: standard deviation, ξ : TEIC content of the total mass of the investigated propellant binder

Sample	ξ / wt.%	σ_m (SD) / MPa	ε_m (SD) / %	E (SD) / MPa
CPB00	0	0.275 (0.33)	464.34 (38.40)	0.179 (0.43)
CPB01	0.1	0.287 (0.19)	529.42 (56.41)	0.188 (0.23)
CPB02	0.2	0.250 (0.37)	473.03 (40.94)	0.165 (0.21)
CPB03	0.3	0.219 (0.10)	369.98 (25.36)	0.182 (0.14)

maximum load compare to the HTPB-based one, which can have the value which does not exceed 275%. Addition of 0.1 wt.% TEIC in CTBN based propellant binder increases all uniaxial tensile properties. On one hand, increasing the tensile strength and Young's modulus is caused by larger amount of hard segments. On the other hand, the incorporation of TEIC into the propellant binder formulation increases the value of strain at maximum load as a consequence of the increased molecular weight of the polymer chains between the crosslink points. TEIC at 0.1 wt.% causes an increase in tensile strength of 4.62% with a simultaneous increase in the strain at maximum load value of 14.02%. Further increase of TEIC content resulted in a slight decrease of values of all uniaxial tensile characteristics.

CONCLUSIONS

Samples of composite propellant binder 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 DSC, DMA and uniaxial tensile testing. Although the network density increased with addition of TEIC, the temperature dependences of rheological parameters reveal that the glass-rubber transition temperature of the investigated propellant binders does not change by the addition of tris(2,3-epoxypropyl) isocyanurate. The glass-rubber transition temperature, T_g , of all propellant binders was about -48 °C determined as maximum temperature of $\tan \delta$ with DMA at 1 Hz deformation frequency. Considering the temperature dependencies of $\tan \delta$ the fluctuation behavior around a storage temperature is observed.

Time-temperature superposition was used to construct modulus-frequency master curves that have been generated for the temperature range from -50 to 20 °C considering the curve at -20 °C as reference. The experimental frequency range of three logarithmic decades measured between -50 to 20 °C, is extended to ten logarithmic decades. By choosing the glass-rubber transition temperature of tested binder samples to be the reference temperature in WLF equation and 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. Due to the requirements during in-service applications, composite propellant binders with low glass-rubber transition and certain stress-strain capabilities are desired. Of the various composite propellant binder properties, none has been more difficult to achieve than the low temperature requirements. It has been so difficult to find composite propellant binder that meet the -54 °C goal. Based on shown test results, considering the fact that this type of prepolymer is commercially available, it can be stated that CTBN could be successfully used as composite propellant prepolymer. More specific, T_g values (about -48 °C), considered together with favorable values of the strain at maximum load, quite justify the use of the CTBN as prepolymer for case-bonded composite propellant grain production.

In order to achieve higher values of uniaxial tensile characteristics, it is acceptable to introduce TEIC as bonding agent within the binder composition in amounts not higher than 0.1%.

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IZVOD

VISKOELASTIČNO PONAŠANJE VEZIVA KOMPOZITNOG RAKETNOG GORIVA NA BAZI KARBOKSI-TERMINIRANOG (BUTADIEN-CO-AKRILONITRIL) KOPOLIMERA SA VEZUJUĆIM AGENSOM POLIGLICIDILNOG TIPA

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U radu je ispitan uticaj tris(2,3-epoksiopropil)-izocijanurata kao vezujućeg agensa na fizičko-hemijske, viskoelastične i jednoosne mehaničke karakteristike karboksi-terminiranog kopolimera (butadien-co-akrilonitril) umreženog sa poliglicidil etrom glicerola i epihlorhidrina. Vrednosti gustine umreženosti određene su metodom bubrenja. Analizirane su temperaturne i frekvencione zavisnosti parametara reološkog ponašanja (modula sačuvane (G') i izgubljene energije (G''), tangensa ugla gubitaka, $\tan \delta$, kao i temperature ostakljivanja, T_g). Na osnovu vrednosti frekvencionih zavisnosti modula sačuvane energije, eksperimentalno određenih u temperaturnom opsegu od -50 do 20 °C, konstruisane su zbirne (master) krive, koje prekrivaju znatno širi interval frekvencija (11 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 parcijalne slobodne zapremine na temperaturi ostakljivanja, f_g/B , i koeficijent toplotnog širenja slobodne zapremine, α_f/B . Iako male količine tris(2,3-epoksiopropil)-izocijanurata utiču na gustinu umreženosti, rezultati dinamičke mehaničke analize pokazuju da sadržaj ovog vezujućeg agensa ne utiče na temperaturu ostakljivanja ispitivanih sastava veziva.

Ključne reči: Karboksi-terminirani kopolimer (butadien-co-akrilonitril) • Viskoelastična svojstva • Temperatura ostakljivanja