

Viscoelastic properties of hydroxyl-terminated poly(butadiene)-based composite rocket propellants

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Abstract

In the present study, the viscoelastic response of three composite solid propellants based on hydroxyl-terminated poly(butadiene), ammonium perchlorate and aluminum has been investigated. The investigation was surveyed by dynamic mechanical analysis over a wide range of temperatures and frequencies. The mechanical properties of these materials are related to the macromolecular structure of the binder as well as to the content and nature of solid fillers. The storage modulus, loss modulus, loss factor and glass transition temperature for each propellant sample have been evaluated. The master curves of storage ($\log G'$ vs. $\log \omega$) and loss modulus ($\log G''$ vs. $\log \omega$) were generated for each propellant. A comparison of $\log a_T$ vs. temperature curves for all propellants indicate conformance to Williams-Landel-Ferry equation. Choosing the glass transition as the reference temperature, WLF equation constants are determined. Fractional free volume at the glass transition temperature and thermal coefficient of free volume expansion values are in accordance with the consideration that Al is reinforcing filler.

Keywords: composite propellant, hydroxyl-terminated polybutadiene (HTPB), dynamic mechanical analysis, viscoelastic properties.

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Composite rocket propellant formulations based on hydroxyl-terminated poly(butadiene) (HTPB) as a binder, ammonium-perchlorate (AP) and aluminum (Al) as solid ingredients, are at present the state-of-the-art propellants in solid fuel rocket engines. A major component in propellant, by weight and volume, is an oxidizer. AP is currently the most widely employed oxidizer because of its high specific impulse, high density, relatively high availability, low cost, high energy, etc. The function of metal fuel is to increase the flame temperature and generate hot metal particles for improved ignition. By far, the most common metal in use as a solid propellant fuel is fine divided aluminum. The binder, as the name implies, holds the composition together and acts as an auxiliary fuel. Once cured, the binder makes the propellant flexible, which decreases the likelihood that the propellant will fracture under stress and pressure. The binder comprises at least two components. The first one is a liquid or semi-liquid prepolymer and the second one is a curing agent. Hydroxyl-functional prepolymers, such as HTPB, are cured using multifunctional isocyanates. Preferably, the curing agent is an isophorone diisocyanate (IPDI), which is a less reactive isocyanate and, therefore, helpful to pot life. To insure the desired degree of crosslinking, IPDI is added in an amount sufficient to generate a ratio of

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isocyanate to hydroxyl groups (NCO/OH) of about 0.8 to about 1.20, preferably about 0.85 to about 0.90. The selection of both solid ingredients (AP and Al) and the binder is not dictated by the optimization of the mechanical properties. The optimum choice of these ingredients has to enhance the energetic and ballistic performance rather than mechanical properties. Thus, mechanical properties are, on one hand a result of formulation adjustment, and on the other hand are expected to match the structure integrity requirements with very little means of improvement. For the purpose of meeting the energy and ballistic characteristics for practical applications, the oxidizer is about 70 wt.%, while the metal fuel represents about 15 wt.% of the propellant [1]. In addition, considering process-ability aspect of propellant production, this formulation gives acceptable values of viscosity. In other words, there is sufficient "pot life", defined as the time the propellant mixture remains sufficiently fluid to permit processing and casting. One of the most common used methods in order to achieve the required mechanical properties is a variation of AP/Al ratios for a fixed solid loading, without drastic influence on energetic and ballistic properties. 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.

Due to presence of a polymeric binder, as viscoelastic materials, composite propellants show time and temperature dependence of mechanical properties.

The time–temperature superposition principle (tTTS) is still widely applied to the viscoelastic properties of these energetic materials. The best-known relation is that derived by Williams, Landel and Ferry (so-called WLF equation), which defines the shift factor a_T , temperature change as:

$$\log a_T = -C_1(T - T_0) / (C_2 + T - T_0) \quad (1)$$

where: T – test temperature, T_0 – reference temperature, C_1 , C_2 – constants.

If the reference temperature is such that $T_0 - T_g = 50$ °C, where T_g is the glass transition temperature, then C_1 and C_2 are general constants with values of 8.86 and 101.6, respectively [2]. Since 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 type of rocket propellant. Despite the importance of HTPB-based composite propellant for rocket engines and the obvious concern about structure and properties relationships, very few comprehensive investigations appear to be available in the open literature. De la Fuente *et al.* analyzed unfilled elastomeric binder and the effect of the different types of fillers on the viscoelastic behavior of a several HTPB based solid composites by dynamic mechanical measurements [3]. Cogmez *et al.* compared dynamic data of two HTPB based composite propellants with different solid compositions, one with 86 wt.% of solid loading including 16 wt.% Al, and the other with 86 wt.% solid loading without Al. The former was found to be less stiff and more dissipative than the latter at higher temperatures [4]. Borsus *et al.* showed that Al particles (having OH-groups on the surface) make fine dispersion in polyurethane foams through a molecular bonds between the particles and the binder [5].

The aim of this work was to characterize and evaluate changes in the viscoelastic properties of composite propellants which follow propellant formulation adjustment by variation of AP/Al ratios for a fixed solid loading.

EXPERIMENTAL

Three HTPB-based propellant compositions (Table 1) selected for this study consisted of 85 wt.% of solids loading including 70–73.5 wt.% AP (oxidizer, with two particle sizes, 200 and 10 μm), 11.5–13 wt.% Al (fuel, with 30 and 15 μm particle sizes) and 15 wt.% of polymeric binder.

Table 1. Tested propellant compositions

Sample	AP ₂₀₀ /AP ₁₀	Al ₃₀ /Al ₁₅	Al %	AP _{tot} %	Solid loading wt.%
CP1	80/20	50/50	13.0	72.0	85.0
CP2	80/20	50/50	15.0	70.0	85.0
CP3	80/20	50/50	11.5	73.5	85.0

The binder composition consisted of 11.08 wt.% of HTPB (R-45HT, Sartomer, viscosity at 23 °C: 8000 mPa s, OH value: 47.12 mg KOH/g, hydroxyl functionality: 2.4–2.6, average molecular weight: 2800 g/mol, specific gravity at 23 °C: 0.901 g/cm³, glass transition temperature, T_g : –76 °C), 2.77 wt.% of plasticizer (dioctyladipate; Fluka AG, Switzerland), 0.17 wt.% of antioxidant (phenyl- β -naphthylamine; Fluka AG, Switzerland) and 0.06 wt.% of bonding agent (triethylenetetramine, Riedel). Tested propellant samples differed from each other in a solid particle content ratio.

Curing occurs when hydroxyl groups on the prepolymer (HTPB) react with isocyanate groups of the curing agent (IPDI, purity: 98%, Sigma Aldrich, Germany) to form urethane crosslinks (Figure 1).

The NCO/OH ratio between the isocyanate groups of IPDI to the hydroxy groups of the R45HT was 0.87. Mixing of propellant was conducted at a temperature of 60 °C in 1-gallon Baker-Perkins planetary mixer, while the corresponding propellant binder (HTPB) was hand-mixed, degassed, cast and cured in moulds to obtain 4 mm thick slabs. The curing was performed for 5 days at 70 °C.

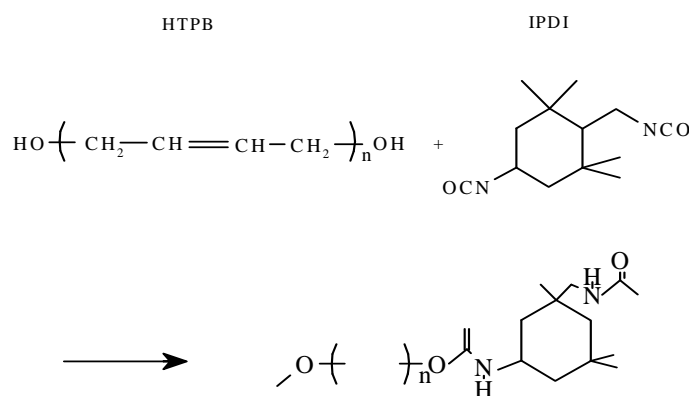


Figure 1. Scheme of urethane reaction.

The DMA tests were carried out by using mechanical spectrometer „Rheometrics“, model RMS-605, in the torsion mode. The temperature range studied was from -90 to 60 °C, the heating rate was 5 °C/min 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 mm \times 12 mm \times 3 to 4 mm). Complex modulus was determined, $G^*(\omega) = G'(\omega) + iG''(\omega)$. Extracted data were the storage modulus (G'), loss modulus (G'') and the loss factor, $\tan \delta = G''/G'$. Each sample was first tested at a constant frequency and temperature over above mentioned range.

The glass transition temperature (T_g) determined by dynamic mechanical measurements was estimated as the temperature at which the loss modulus G'' , maximized. Finally, the viscoelastic properties were measured through three decades of frequency over a range of temperatures from -70 to 20 °C.

DSC analyses were carried out using the DSC Q20 manufactured by TA Instruments with liquid nitrogen for low temperatures. The temperature scale was calibrated using the melting temperature of high purity indium. These measurements were made with the purpose to investigate the thermal based glass transition temperature of the tested samples. The small amount

of the samples (~ 5 mg) was scanned with a heating rate of 10 °C min^{-1} , starting from -90 °C and ending at 50 °C. The glass transition temperature, T_g , of the samples were determined from the midpoints of the transitions.

RESULTS AND DISCUSSION

The propellant specimens were analyzed in the dynamic torsion mode. This mode enables determining the binder characteristics without distortions due to the particle–particle contact as it can happen in tensile-compression or in bending mode [6].

Temperature dependence

Based on a weakly cross-linked polymeric matrix, composite rocket propellants show very large changes in mechanical properties with changing temperature. Figure 2 shows the viscoelastic response of tested propellant samples in terms of storage modulus, loss modulus and loss factor at 1 Hz as a function of temperature.

DMA measurements have shown that tested propellants exhibited viscoelastic behavior by passing through glassy transition and rubbery region.

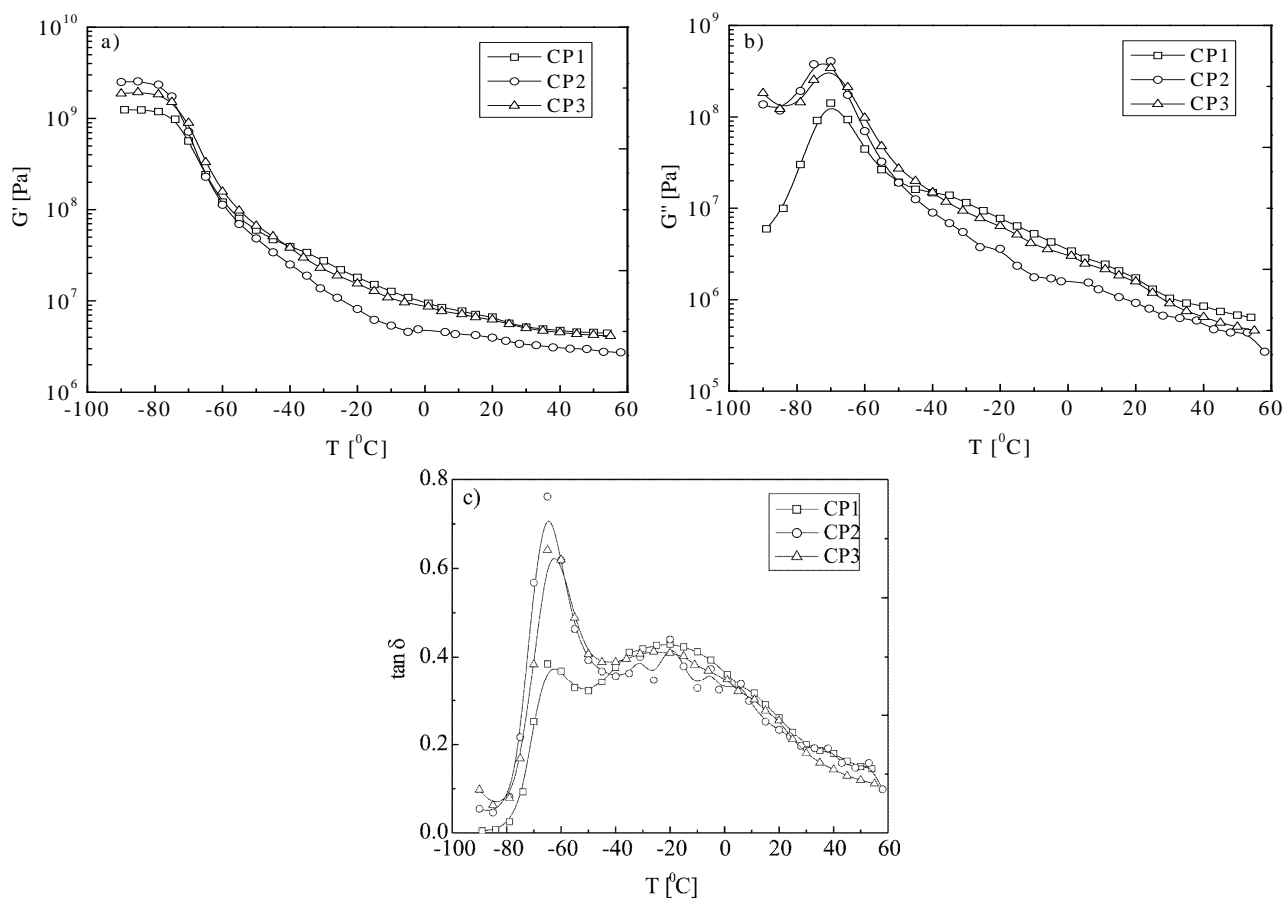


Figure 2. Temperature dependences of a) storage modulus (G'), b) loss modulus (G'') and c) loss factor ($\tan \delta$) for tested propellant samples.

Table 2 shows T_g values of the tested samples determined through DMA *via* G'' , G' , $\tan \delta$ and through DSC. Also, values of peak widths at half-height (w) of $\tan \delta$ –temperature dependence are shown.

$\tan(\delta)$ is a composed distribution function describing the distributions of the glass transitions of the structural elements of the polymer network in propellant formulations. Polymer network in composite

Table 2. T_g values determined through G'' , G' , $\tan \delta$ and DSC; $\tan \delta_{\max}$ and widths (w) of $\tan \delta$ peaks

Sample	$T_g / ^\circ\text{C}$				$T_g^{\text{hard}} / ^\circ\text{C}$	$\tan \delta_{\max}$	$w / ^\circ\text{C}$
	G''	G'	$\tan \delta$	DSC			
CP1	–69.9	–77.2	–63.1	–78.9	–20.1	0.385	13.2
CP2	–72.0	–79.3	–64.5	–78.3	–19.1	0.762	14.6
CP3	–70.6	–77.6	–62.7	–78.3	–24.1	0.641	14.8
HTPB	–	–	–	–72.7	–	–	–

The differences between T_g values of tested samples determined through DMA *via* G'' , G' and $\tan \delta$, respectively, are within experimental error. The T_g is easily identified as a peak in the $\tan \delta$ or the G'' trace. These maxima do not coincide exactly. The maximum in the $\tan \delta$ is at a higher temperature than that in G'' , because the $\tan \delta$ is the ratio of G'' and G' and both these moduli are changing in the transition region. T_g values based on G'' show that it cannot be observed any regularity of its change with increasing Al content in the tested propellant formulations. However, the lowest T_g is observed for CP2 sample. The T_g of the tested propellants based on the DSC is nearly as same as reported by Cerri *et al.* [6]. The T_g of HPTB cured with IPDI determined by DSC is higher than that of IPDI cured HTPB reported as -83°C by Bhagawan *et al.* [7]. Although incorporation of fillers significantly modifies the molecular mobility, it is found that T_g of HPTB binder is higher than that of corresponding propellants. The position of T_g depends on the experimental techniques and conditions of the experiment (*e.g.*, heating rate of the sample). Phase transitions are time-dependent relaxation processes, so the most reliable values for the phase transition temperatures could be obtained at the lowest cooling rate.

Comparing G' values of tested propellant samples, sample CP2 (AP/Al = 70/15) has the lowest G' values in the rubbery plateau region. Based on the assumed presence of non-homogeneously distributed OH groups on the Al particle surface, that interferes with the curing agent, incorporation more Al particles in propellant formulation with fix solid loading gives less cured propellant [6]. The decrease of G' value is connected with the increase of the macromolecular mobility.

Beside T_g , a molecular interpretation of the viscoelastic behavior can be given considering the $\tan \delta$, which is extremely sensitive to all kinds of relaxation processes, structural heterogeneity and the morphology of multiphase systems such as filled or composite materials.

propellant formulations is made of polyurethane elastomer, which contain soft and rigid segments. The soft segments consist of the flexible non-crystalline polymer chains, in this case poly(butadiene), and the rigid or hard segments consist of diisocyanate residues, chain extenders and urethane groups.

Two maxima in the $\tan \delta$ curves of all tested propellant samples were observed. The first peak positioned between -80 and -60°C could be attributed to the main glass transition temperature (α -relaxation peak) in the soft segment regions (HTPB main chain elements). These segments are formed by the reaction of the diisocyanate and the long-chain diol. They have low polarity as they have a very low density of urethane groups, and therefore, they are flexible at room temperature. At this temperature range the molecular rearrangements reach a maximum extend and it is defined as the temperature at which the polymeric material changes from the entropy-elastic rubber behavior to the energy-elastic behaviour or *vice versa*. This temperature is called T_g^{soft} . The intensity of T_g^{soft} for CP2 sample (15 wt.% Al) is the highest, although its temperature location is quite equal to that in the other tested propellants. The highest Al proportion within the solid loadings causes the highest value of T_g^{soft} intensity for the sample CP2. Although Al particles are considered as reinforcing fillers, less AP content means less content of ionic bonds between the bonding agent (triethylenetetramine) and AP particles, which cause increased mobility of the macromolecule chains. Comparing intensity of T_g^{soft} values for CP1 and CP3, although CP1 has a higher proportion of AP, since the Al particles are smaller, they make a stronger adhesion to the polymer matrix, which results in a higher T_g^{soft} value of CP3.

The second peak of the $\tan \delta$ curves is broader than the first one. It appears at higher temperatures (between -40 and 20°C) and it can be related to the motions within the polymer short-hard segment units. These segments have a high density of high polarity urethane groups, and for this reason, they are rigid at

room temperature. Temperature range, which corresponds to relaxation related to short-hard segment units is called T_g^{hard} . T_g^{hard} exhibits a small difference in intensity, but its broadness is enlarged in sample CP1, compare to those for samples CP2 and CP3. This can be explained by the free extended HTPB chains (found with GPC) intermixed in the short-hard segment regions and in this way creating more free volume [6]. The fraction of these free chains should be higher in CP1, because of consumption of IPDI by Al particles.

Frequency dependence

An example of the small deformation response properties measured for each of the propellants is presented in Figure 3. The figure shows the effect of temperature and frequency on the storage modulus of the propellant CP3. The response of tested propellants was measured during a frequency sweep for different isothermal temperatures. Frequency was varied from 0.1 to 100 rad s^{-1} , through 16 equidistant values on a logarithmic scale.

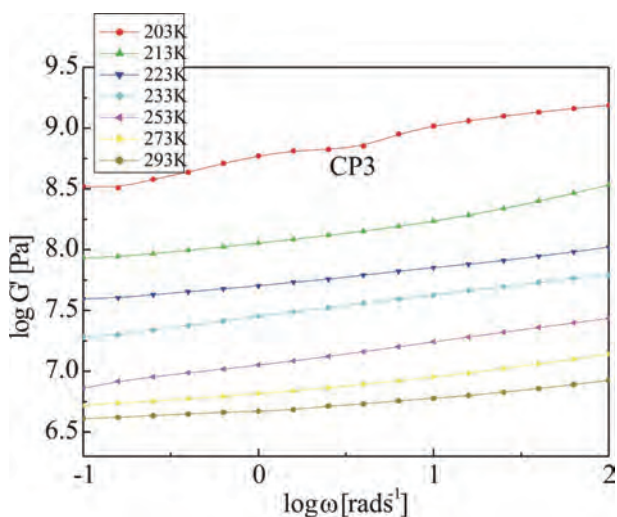


Figure 3. Storage modulus (G') as a function of frequency for CP3 propellant sample.

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 tested propellants.

Figure 4 shows the $\tan \delta$ –frequency dependences for sample CP1.

For sample CP1 the frequency dependence at -60°C is not observed below 1 rad s^{-1} . Above this value, the $\tan \delta$ increases with increasing frequency. The frequency dependence at -50°C is scarcely detected in the frequency range from 0.1 – 10 rad s^{-1} . The frequency dependence at -40 and -20°C is observed in the whole range of frequencies: $\tan \delta$ decreases with increasing frequency. Above -20°C , frequency dependence is not

observed below 1 rad s^{-1} . Above 1 rad s^{-1} , the value of $\tan \delta$ increases with increasing frequency.

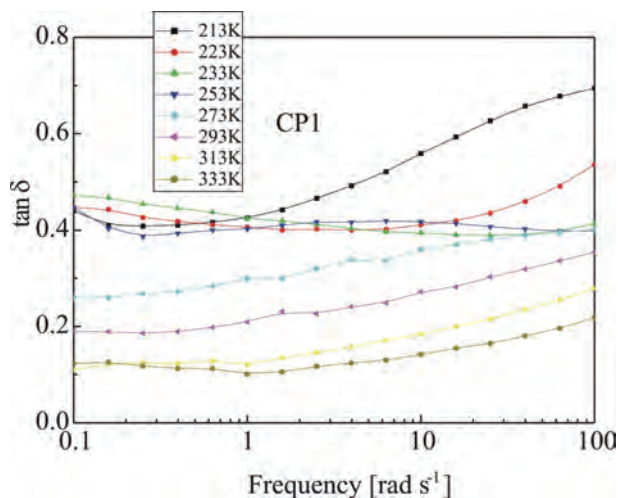


Figure 4. Loss factor $\tan \delta$ as a function of frequency for sample CP1.

Application of Williams–Landel–Ferry equation

Temperature range for testing was selected so that the lowest testing temperature propellant is in glassy state and that the highest testing temperature is the temperature of use. Temperature step was 10°C . The master curves represent essential inputs for evaluating the margin of propellant safety usage. The most critical stage during rocket motor operation is the ignition stage. During such conditions, the propellants are exposed to high-speed deformation of the order of 1 to 6 m/s , which corresponds to periodic deformations of 628 – 3140 rad s^{-1} . Such a high-speed deformation is very difficult to achieve in real life tests.

By dynamic mechanical measurements at small deformation, it is possible to obtain information about the behavior of materials at such high strain rates, because the proper analysis of the measurement results in three decades of frequency can determine the values of these parameters and up to 20 decades for the selected reference temperature. In this way, we can make conclusions about the tested material behavior under conditions of very large or very small strain rates. The master curve reference temperature was $T_0 = 20^\circ\text{C}$. In addition, it is very important to emphasize that WLF equation is valid in T_g to $(T_g+100^\circ\text{C})$ region.

Figure 5 shows master curves of storage and loss shear modulus comparison for the tested propellant samples.

Figure 5 shows several important features concerning the viscoelastic response of the tested propellants. For all tested propellants, at low temperatures (high frequencies), G' and G'' slopes maximize.

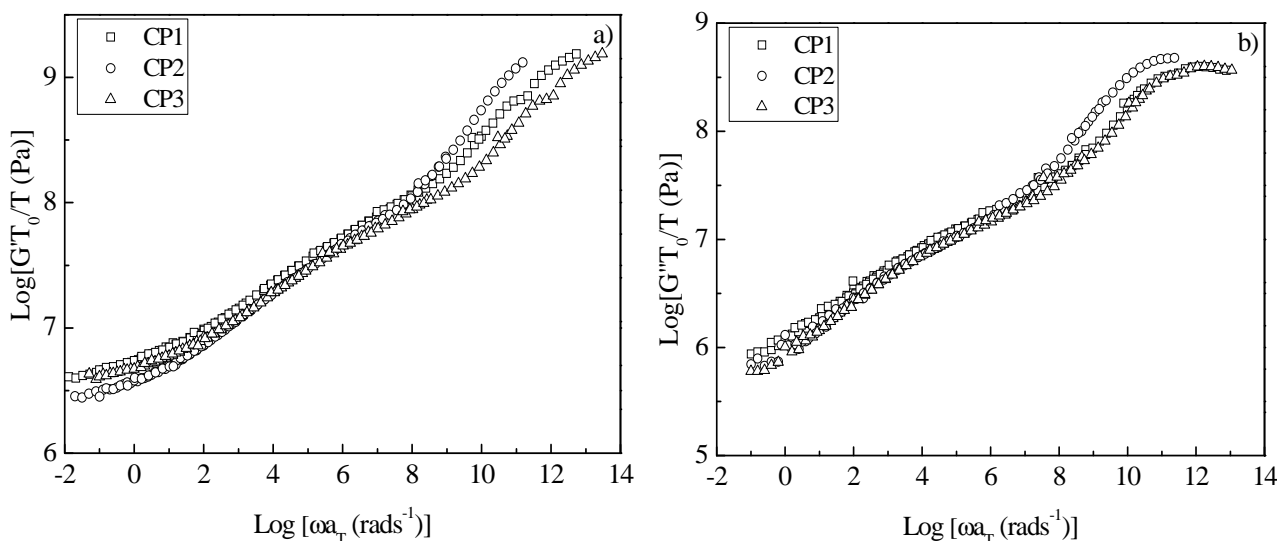


Figure 5. Master curves of a) storage modulus (G') and b) loss modulus (G'') for tested propellant samples.

At higher temperatures, or lower frequencies, G'' becomes progressively smaller than G' , with both curves entering the rubbery plateau. For both moduli change curves, the differences are observed at high and low frequencies for sample CP2. It is observed that the decay of modulus with the reduced frequency (time) is pronounced in CP2 than in other propellant. 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_τ , used to superpose the G' and G'' experimental data into a master curve for tested propellants are shown in Table 3.

Table 3. Shift factor, $\log a_\tau$, temperature dependences determined through G' and G'' superposition

$T / ^\circ\text{C}$	CP1		CP2		CP3	
	G'	G''	G'	G''	G'	G''
-69.75	-10.73	-10.88	-9.18	-9.36	-11.47	-11.04
-60.06	-7.99	-8.38	-6.95	-7.25	-8.74	-8.54
-50.37	-6.17	-6.77	-5.21	-5.61	-6.42	-6.66
-40.06	-4.74	-5.25	-3.96	-4.29	-4.94	-5.23
-21.37	-2.72	-2.97	-2.12	-2.28	-2.84	-2.93
-0.06	-1.21	-1.28	-0.81	-0.89	-1.30	-1.33
19.93	0	0	0	0	0	0

Some evidence of thermo-rheological complex behavior was observed as indicated by slightly different shift factors for G' and G'' . This difference is identical to that previously reported by Stacer and Husband [8]. Figure 6 provides a comparative view of the temperature dependences of a shift factor, a_τ , the values determined through G' and G'' superposed to a temperature $T_0 = 20^\circ\text{C}$ for sample CP3.

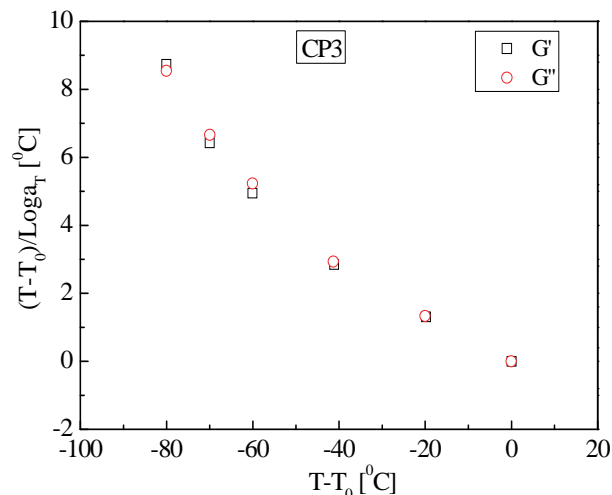


Figure 6. Comparison of the horizontal shift factor values used to superpose G' and G'' data for sample CP3

Temperature dependences of shift factor, a_τ , of all tested propellants show that for each of them could be made satisfactory linearization of experimental data, in order to determine WLF constants C_1 and C_2 , using transformed WLF equation [9]. Obtained WLF constants C_1 and C_2 , are given in Table 4.

Table 4. WLF constants C_1 and C_2 estimated for tested propellants

Sample	G'		G''	
	C_1	C_2	C_1	C_2
CP1	8.49	164.84	9.31	167.37
CP2	4.79	134.50	5.36	138.43
CP2	9.11	165.98	9.74	171.38

Although these values are in agreement with those reported in literature, WLF constants C_1 and C_2 obtained

via G'' data were slightly different but not significant to affect any of the earlier conclusions. The values are almost comparable for the propellants CP1 and CP3, while propellant CP2 shows the lowest values for both the constants.

All, until now discussed, related to the selected reference temperature $T_0 = 20$ °C. Ferry proposed an alternative way of representing the temperature dependence of the shift factors, a_T . It consists of choosing the T_g of the sample as the reference temperature and a_T calculation based on the following WLF equations [9]:

$$C_{1,g} = \frac{C_1 C_2}{C_2 + T_g - T_0} \quad (2)$$

$$C_{2,g} = C_2 + T_g - T_0 \quad (3)$$

$C_{1,g}$ and $C_{2,g}$ constants, calculated using Eqs. (2) and (3), and determined experimentally from the shift factors used to superpose the G' data to T_g as a reference temperature, are compared in Table 5.

Table 5. WLF constants $C_{1,g}$ and $C_{2,g}$ estimated for tested propellants

Sample	$C_{1,g}$		$C_{2,g}$	
	Calcd.	Exp.	Calcd.	Exp.
Universal ^a	–	17.4	–	51.6
CP1	18.68	17.98	74.90	58.31
CP2	14.40	15.08	44.75	55.97
CP3	19.89	17.95	75.98	52.23

^aDetermined by averaging the values of a wide variety of polymers

The deviation of the WLF equation constants $C_{1,g}$ and $C_{2,g}$ for tested propellants is in agreement with literature data. Unlike the constants $C_{1,g}$, which are approximate, values of $C_{2,g}$ significantly deviate from the "universal" values. Regardless of the determining method, $C_{1,g}$ and $C_{2,g}$ values for sample CP2 deviate from the constant values for the other two propellants.

The influence of a reference temperature on the shape and position of storage modulus frequency dependence master curve for propellant CP1 is shown in Figure 7.

Despite the T_{ref} , master curves have the same shape, but the master curve for higher T_{ref} is shifted to a higher frequency. As illustrated in Figure 7, the strain rate of the propellant during rocket motor storage conditions ($\omega \approx 10^{-6}$ rad s⁻¹) is not covered by the master curve superposed to a temperature $T_{ref} = 20$ °C.

The importance of the WLF constants $C_{1,g}$ and $C_{2,g}$ can be seen through the relationship:

$$C_{1,g} = \frac{B}{2.303 f_g} \quad (4)$$

and

$$C_{2,g} = \frac{f_g}{\alpha_f} \quad (5)$$

where B is a constant in the Doolittle equation assumed equal to unity, f_g is the fractional free volume at the glass transition temperature and α_f is the thermal coefficient of free volume expansion. As the values of the fractional free volume at the glass transition temperature, f_g/B , and thermal coefficient of free volume expansion, α_f/B , are directly associated with known WLF constants $C_{1,g}$ and $C_{2,g}$, these are calculated and the values are given in Table 6.

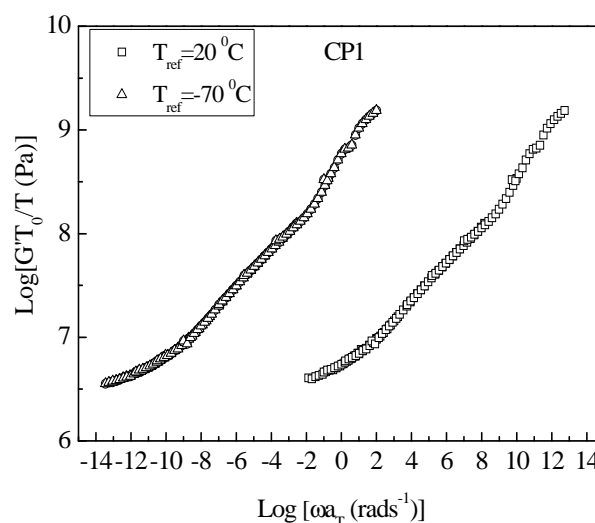


Figure 7. The influence of a reference temperature on the shape and position of G' master curve for sample CP1

Table 6. The values of f_g/B and α_f/B

Sample	$(f_g/B) \times 10^{-2}$		$(\alpha_f/B) \times 10^{-4}$	
	Calcd.	Exp.	Calcd.	Exp.
CP1	2.155	2.40	2.05	4.14
CP2	2.918	2.88	5.28	5.14
CP3	2.374	2.42	3.53	4.63

f_g/B and α_f/B values are round about the limits given in the literature for the largest number of polymer systems ($f_g/B = 2.5 \times 10^{-2}$ and $\alpha_f/B = 4.80 \times 10^{-4}$) [8]. Although they do not match, the trend of these values change is identical.

Comparing the experimentally determined WLF and free volume constants in Table 6 with the "universal" constants (determined by averaging the values of a wide variety of polymers), one may conclude that all tested propellants have a temperature dependent viscoelastic response which is very close to "universal". Data in Table 6 indicate that Al lowering the glass transition temperature while increasing the thermal

coefficient of free volume expansion. All the tested propellants have values that are less than or equal to the "universal".

Dependence of f_g/B and α_f/B as a function of Al content for tested propellant samples is as follows: the values of f_g/B and α_f/B decrease slightly or remain the same with increasing of Al content from 11.5 to 13 wt.%, while over 13 wt.% of Al content these value significantly increases. In conclusion, with the change in the aluminum content there is no linear decrease of α_f/B value confirming that aluminum in composite propellant formulation should be considered as active (reinforcing) filler.

CONCLUSION

The dynamic mechanical analysis in the torsion mode was employed to evaluate the effects of AP/Al content ratio on viscoelastic properties of HTPB-based composite rocket propellants. Temperature and frequency dependences of rheological parameters are determined. Glass transition temperature, T_g , of all tested propellants was nearly -70 °C. DSC measurements could not reveal differences in the tested propellants T_g value. Propellant sample with the lowest content of AP (CP2) has the lowest value of storage modulus in transition and the rubbery plateau region. Storage modulus values in transition region range from 10^6 to 10^9 Pa.

The same trend behavior exhibits loss modulus curve. For all tested propellant the presence of two maxima can be seen on $\tan \delta$ curve. Master curves have been generated for temperature range from -70 to 20 °C considering the curve at 20 °C, as reference.

The temperature dependence of the shift factors, a_T , obtained by generating master curves of storage energy modulus point out that for each of tested propellant satisfactory linearization of experimental data was achieved.

By introducing glass transition as a reference temperature in the WLF equation, values of "universal" constants, $C_{1,g}$ and $C_{2,g}$, are calculated.

The different AP/Al particle ratio change the temperature dependence of the dominant viscoelastic

mechanism as indicated by the change in the free volume constant values, fractional free volume at the glass transition temperature f_g/B , and thermal coefficient of free volume expansion α_f/B .

Values obtained both for fractional free volume at the glass transition temperature f_g/B , and thermal coefficient of free volume expansion α_f/B from 11.5 to 15 wt.% of Al, are in accordance with the consideration that Al is reinforcing filler.

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ИЗВОД**ВИСКОЕЛАСТИЧНА СВОЈСТВА КОМПОЗИТНИХ РАКЕТНИХ ГОРИВА НА БАЗИ ХИДРОКСИ-ТЕРМИНИРАНОГ ПОЛИ(БУТАДИЕНА)**

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У раду је испитан утицај односа удела амонијум-перхлората као оксидатора и алуминијума као металног горива у оквиру дефинисаног садржаја чврсте фазе, на вискоеластична својства композитних ракетних горива на бази хидрокси-терминираног поли(бутадиена), умрежених изофорондиизоцијанатом. Анализиране су и поређене вредности динамичко механичких својстава: температуре остакљивања T_g , модула сачуване (G') и изгубљене енергије (G'') и тангенса угла губитака $\tan \delta$. На основу реолошких параметара, експериментално одређених на температурама од -70 до 20 °C, конструисане су збирне (мастер) криве, које прекривају знатно шири интервал фреквенција (14 логаритамских декада) у односу на онај у коме је вршено мерење. Формирањем мастер кривих поступком "редукције" модула сачуване и модула изгубљене енергије, за референтну температуру $T_0 = 20$ °C, добијене су вредности фактора помераја, a_T , за све температуре на којима је експериментално одређивана фреквенциона зависност овог параметра. Поређене су овако добијене вредности фактора помераја, a_T . Одабиром температуре остакљивања као референтне температуре, одређене су "универзалне" константе WLF једначине, на основу којих су израчунате вредности парцијалне слободне запремине на температури остакљивања, f_g/B , и коефицијент топлотног ширења слободне запремине, α_f/B . Резултати показују да повећањем удела алуминијума до одређене границе, која за дати удео чврсте фазе износи 13 мас.%, долази до незнатног смањења вредности слободне запремине и коефицијента топлотног ширења слободне запремине. Изнад ове границе, повећање удела алуминијума до 15 мас.% доводи до повећања испитаних вредности. Закључак да променом удела алуминијума не долази до линеарног смањења вредности коефицијента топлотног ширења слободне запремине наводи да се алуминијум у саставу композитног ракетног горива треба посматрати као активни пунилац.

Кључне речи: Композитно ракетно гориво • Хидрокси-терминирани поли(бутадиен) • Динамичка механичка анализа • Вискоеластична својства