



Influence of Polyglycidyl-type Bonding Agents on the Viscoelastic Properties of a Carboxyl-terminated Poly(butadiene-co-acrylonitrile)-based Composite Rocket Propellant

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Abstract: In the present study, functionally substituted bonding agents (triglycidyl isocyanurate and diglycidyl dimethylhydantoin) were incorporated into a composite propellant formulation based on carboxyl-terminated poly(butadiene-co-acrylonitrile) and ammonium perchlorate. Bonding agents are an important component of a composite propellant, making up to 0.5 wt.% of the formulation. They affect processing, mechanical properties, ballistics, ageing and the characteristics of insensitive munition (IM) propellants. All of the testing has been done using an unmetallized propellant formulation (80 wt.% bimodal ammonium perchlorate and 20 wt.% binder). The focus has been on the mechanical properties of the propellant, as influenced by the presence of these bonding agents. Mechanical uniaxial tensile tests were accompanied by a dynamic mechanical analysis (DMA) over a wide range of temperatures. The storage modulus, loss modulus, loss factor and glass transition temperature for each propellant sample have been evaluated. The network characteristics, such as sol-gel content and crosslink density have been calculated and successfully correlated with the mechanical properties. The dynamic mechanical studies showed that the content of the bonding agent did not influence the glass transition temperature; however, the loss factor was shown to be a function of the crosslink density.

Keywords: composite propellant, carboxyl-terminated poly(butadiene-*co*-acrylonitrile), dynamic mechanical analysis, viscoelastic properties

1 Introduction

One of the major factors which enhances the mechanical properties of composite rocket propellants is adhesion between the filler particles and the polymeric matrix. The binder-filler adhesion and hence the mechanical properties of these propellants may be improved by the use of surface active agents called “bonding agents” [1, 2]. A bonding agent produces an interaction between the oxidizer particles and the polymeric binder by forming either primary or secondary bonds with the oxidizer (by means of adsorption and attraction) and a primary bond with the binder. Several authors have described this feature of bonding agents for different prepolymer types [3-7].

Bonding agents have been developed and they are typically used in hydroxyl-terminated poly(butadiene) (HTPB)-based composite propellants, since these polymers are weakly polar [8]. In the last ten years, functionally substituted isocyanurates and dimethylhydantoins have been found to be suitable bonding agents for HTPB-based composite propellants [9, 10]. Functionally substituted isocyanurates have also been shown to be universal in comparison to the oxidizers used in composite rocket propellant formulations. They can be used with such common oxidizers as ammonium nitrate, potassium perchlorate, ammonium perchlorate (AP), HMX (cyclotetramethylenetetranitramine) or RDX (cyclotrimethylenetrinitramine) [11-14]. These additives are also important since they contribute to a significant reduction in the viscosity of the propellant slurry. In other words, there is sufficient pot “life”, defined as the time the propellant mixture remains sufficiently fluid to permit processing and casting. It should also be noted that the rheological characterization of elastomer-based, concentrated, energetic suspensions emphasizes the importance of the generating parameters, *i.e.* mixing conditions, which significantly affect the dynamic and other properties of such systems [15, 16]. Due to the highly polar carboxyl (–COOH) group, carboxyl-terminated prepolymers (CTPB) do not require the use of bonding agents. Even so, an increase in temperature produces a decrease in the experimental values of the uniaxial tensile strength of composite propellants based on carboxyl-terminated poly(butadiene-*co*-acrylonitrile), known as CTBN, which may confirm the assumption of significant involvement of secondary bonds. In order to enhance the interaction between a CTBN-based propellant binder and AP, two functionally substituted well-known bonding agents,

trisubstituted isocyanurate and disubstituted dimethylhydantoin, are included in the baseline composite propellant composition.

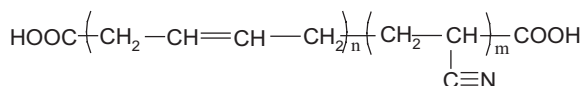
The main goal of this study was to analyze the influence of the applied bonding agents on the viscoelastic behaviour of a composite propellant based on CTBN by dynamic mechanical measurements. As far as we are aware, there is no publication in the extensive literature that has surveyed the viscoelastic properties of composite propellants based on CTBN and the effect of this type of bonding agent on the composite propellant behaviour.

2 Experimental

2.1 Materials and methods

1,3,5-Triglycidyl isocyanurate was prepared by the reaction of cyanuric acid and epichlorhydrin in accordance with a literature method [17]. N,N'-Diglycidyl-5,5-dimethylhydantoin was synthesized by the reaction of hydantoin, epichlorhydrin and benzyltrimethylammonium chloride in accordance with a modified literature procedure [18]. Five 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). The binder composition consisted of 100 phr of CTBN (1300 \times 15, BF Goodrich, viscosity at 25 $^{\circ}\text{C}$: 66.2 Pa·s, carboxyl functionality: 1.9, number-average molecular weight: 3800 g/mol, specific gravity at 23 $^{\circ}\text{C}$: 0.931 g/cm 3 , glass transition temperature, T_g : -63.3 $^{\circ}\text{C}$), 30 phr of plasticizer (dioctyl adipate DOA; Fluka AG, Switzerland), 1.7 phr of antioxidant (2,2'-bis(4-methyl-6-tertbutyl)phenol, commercially available as a product called AO 2246; Fluka AG, Switzerland) and 0.44 phr of cure catalyst [iron(III) acetylacetonate] ($\text{Fe}(\text{acac})_3$, Merck-Schuchardt, Germany).

The E/COOH ratio between the epoxy groups of EPON 812 (triglycidyl ether of glycerol and epichlorhydrin, Shell Chemical Company, USA, epoxide equivalent: 150, refractive index: 1.48) to the carboxyl groups of the CTBN was 1.20. The chemical structures of the propellant ingredients are shown in Figure 1.



a) carboxyl-terminated poly(butadiene-*co*-acrylonitrile)

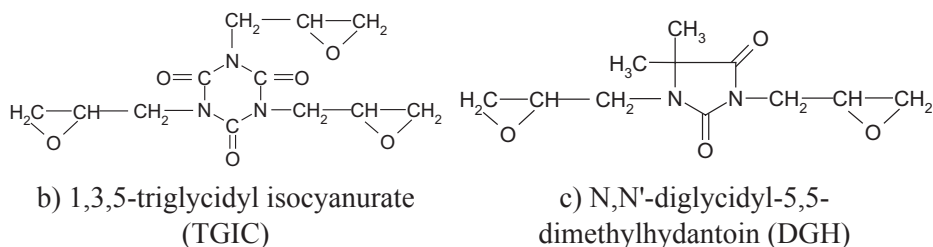


Figure 1. The chemical structures of the propellant ingredients.

The compositions of the composite propellants tested differ from each other in the bonding agent type (TGIC and DGH) and its content. The composition CP1 is a baseline propellant composition containing no bonding agent.

Table 1. Composite propellant formulations tested

Sample	phr (wt.% of the total mass of the tested propellant sample)						
	CTBN 1300×15 prepolymer	EPON – 812 curing agent	DOA plasticizer	Fe(acac) ₃ cure catalyst	AO 2246 antioxidant	TGIC bonding agent	DGH bonding agent
CP1	100 (13.77)	11.24 (1.55)	30 (4.13)	0.44 (0.06)	1.7 (0.23)	(0)	(0)
CP2	100 (13.60)	11.24 (1.53)	30 (4.08)	0.44 (0.06)	1.7 (0.23)	(0.25)	(0)
CP3	100 (13.43)	11.24 (1.51)	30 (4.03)	0.44 (0.06)	1.7 (0.23)	(0.50)	(0)
CP4	100 (13.60)	11.24 (1.53)	30 (4.08)	0.44 (0.06)	1.7 (0.23)	(0)	(0.25)
CP5	100 (13.43)	11.24 (1.51)	30 (4.03)	0.44 (0.06)	1.7 (0.23)	(0)	(0.50)

The carboxyl groups of the prepolymer react with the epoxy groups of the curing agent to form a β -hydroxypropyl ester (Figure 2).

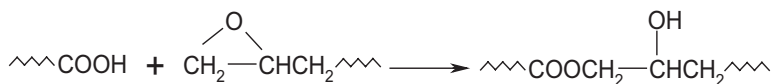


Figure 2. The reaction of the prepolymer carboxyl group and the curing agent epoxy group.

2.1.1 Mixing conditions for the propellant slurry

The tested propellant formulations were mixed in a 1-gallon Baker-Perkins planetary mixer at a temperature of 60 °C. All of the binder ingredients, except the curing agent and the cure catalyst, were blended thoroughly for 15 min at 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 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. The mixture thus prepared was cured for 5 days at 77 ± 2 °C.

2.1.2 Sol-gel measurements

The sol content of the propellant binder is the weight of the soluble fraction of the propellant, obtained by extraction with a solvent, as described in STANAG 4581 [19]. The extraction was carried out in three Soxhlet extraction units (with refluxing solvent) for 16 hours using approximately 150 mL of dichloromethane (CH_2Cl_2) in each. The formula for the sol fraction evaluation was modified [20, 21] and, in accordance with Equation (1), the polymeric part S_{poly} of the total soluble part E_{total} of the propellant sample was determined with respect to the polymeric part of the formulation $A_{\text{k-p}}$.

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

where:

S_{poly} – the polymeric part of the soluble (extractable) part of the propellant composition,

E_{total} – the total amount of the extract [g], obtained by the method,

E_{poly} – the polymeric part of the total extract [g], corrected for the nominal parts of DOA, AO 2246 and $\text{Fe}(\text{acac})_3$,

A – amount of the propellant sample weighed-in for the extraction [g],

$A_{\text{k-p}}$ – amount of the propellant sample weighed-in for the extraction [g], corrected for the nominal parts of AP, DOA, AO 2246 and $\text{Fe}(\text{acac})_3$,

P_{AP} – nominal part of AP in the propellant composition (e.g. 80 wt.% mean 0.80) [-],

P_{DOA} – nominal part of DOA in the propellant composition [-],

$P_{\text{AO 2246}}$ – nominal part of AO 2246 in the propellant composition [-],

$P_{\text{Fe(acac)}_3}$ – nominal part of $\text{Fe}(\text{acac})_3$ in the propellant composition [-].

2.1.3 Uniaxial tensile properties of the composite propellant samples

The mechanical (uniaxial tensile) properties of the cured propellant samples were evaluated at 20 °C using a uniaxial tensile test machine INSTRON 1122, fitted with a 500 N load cell. "JANNAF C" dog-bone samples (length 120.65 mm, width 25 mm, thickness 8 mm) were used in the test. The crosshead speed of the uniaxial tensile test machine was 50 mm/min, while the effective gauge length of the "JANNAF C" samples was 68.6 mm.

2.1.4 Dynamic mechanical measurements of the composite propellant samples

The DMA tests were carried out using a 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 a single frequency point of 1 Hz was chosen. The strain amplitude was 0.1%. The samples for the DMA tests were of a rectangular bar shape (63×12×3-4 mm). The complex shear modulus was determined, $G^*(\omega) = G'(\omega) + iG''(\omega)$. The extracted data were the storage shear modulus (G'), the loss shear modulus (G'') and the loss factor $\tan(\delta) = G''/G'$. The glass transition temperature (T_g), determined by the dynamic mechanical measurements, was estimated as the temperature at which the loss modulus G'' reached its maximum value.

3 Results and Discussion

3.1 Results of the sol-gel analysis

When the soluble fraction content (S_{poly}) is known, the crosslink density (C) of the propellant binder (Table 2) can be estimated following the modified version of the Charlesby-Pinner equation [22], see Equation (2):

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

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

Sample	CP1	CP2	CP3	CP4	CP5
S_{poly} [-]	0.1182	0.1000	0.0907	0.1018	0.0889
C [-]	2.93	3.42	3.73	3.37	3.80

With an increase in bonding agent content, a reduction in the soluble fraction is evident, as well as an increase in the crosslink density value. This indicates that, during the curing process, the functional carboxyl groups of the prepolymer do not react completely with the functional groups of the epoxy curing agent. Finally, the propellant compositions containing a higher content of bonding agent have a higher ratio of the functional groups (E/COOH), compared to the baseline propellant composition CP1. This reduces the content of the propellant binder remaining in the uncrosslinked state, so a smaller amount of unreacted and

linear polymer chains may be removed by the solvent. The highest percentage reduction in the soluble fraction was 23.3% in CP3 (0.5 wt.% TGIC). For an equivalent content of DGH, only approximate soluble fraction values were obtained. An increase in the crosslink density value points to the fact that the functional epoxy groups of the bonding agents are involved in propellant polymeric network formation.

The parameters obtained by the sol-gel analysis are very useful and will be used for a correlation with the responses obtained by the mechanical characterization of the tested propellants.

3.2 Results of the dynamic mechanical analysis

In order to quantify the changes of the DMA properties as influenced by adding the bonding agent, several characteristics of the baseline composition (CP1), viz. G' -T, G'' -T and $\tan(\delta)$ -T traces, were followed, as shown in Figure 3.

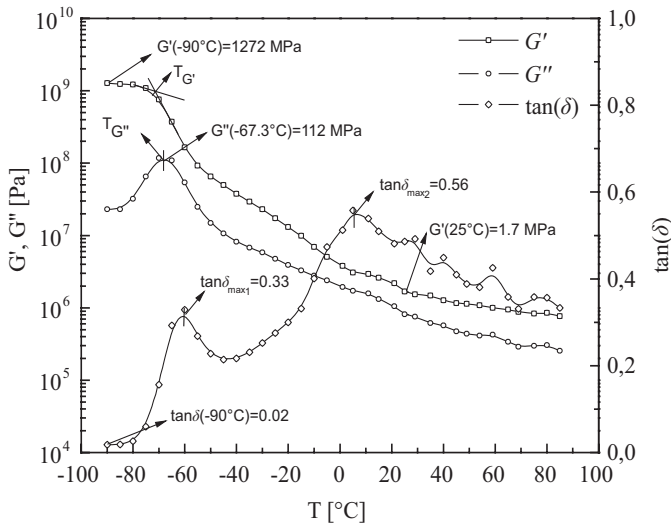


Figure 3. Characteristic values for the CP1 baseline composition DMA thermogram at $\omega = 6.28 \text{ rads}^{-1}$.

It follows from Figure 3 that the G' is almost constant, and reaches its maximum value in the region below the glass transition temperature (-85°C to -50°C). The transition from the glassy to the rubbery state (with an onset point on the G' -T curve at $T = -74.9^\circ\text{C}$) exhibits, as a consequence, a drop in the G' value by a factor of about 730 (from 1240 MPa at -85°C to 1.7 MPa at 25°C). The G'' has its maximum value in the glass transition region. The maximum on the

G'' - T curve, at $T_g = -67.3$ °C, is taken as the nominal glass transition temperature for the baseline composition, CP1. A molecular interpretation of the viscoelastic behaviour can also be given, by considering the $\tan(\delta)$ values, which are extremely sensitive to all kinds of relaxation processes, structural heterogeneity, and the morphology of multiphase systems such as filled or composite materials. $\tan(\delta)$ describes the molecular rearrangement regions, corresponding to the binder fractions with different mobility. The peaks in the $\tan(\delta)$ curve are related to the relaxation processes of individual kinetic units in the polymeric material. In composites, the $\tan(\delta)$ value is also influenced by the incorporation, type and distribution of fillers, as well as by the filler/matrix interactions [23, 24].

Poly(butadiene)-based elastomers contain soft and rigid segments [25]. The soft segments consist of large, flexible, non-crystalline, polymer chains, in this case, poly(butadiene), whilst the rigid (hard) segments consist of epoxy residues and the generated ester groups. Two maxima in the $\tan(\delta)$ curves of all of the propellant samples tested were observed. These two transition regions were already known for HTPB-based composite propellants [26]. The first peak (its temperature location is designated as T_g^1), positioned between $T = -70$ and -55 °C, is attributed to the main glass transition temperature. This relaxation process involves the release of the cooperative motions of the prepolymer (CTBN) main chains, between the crosslinks within the soft segment regions. These polymer network segments have low polarity as they have a very low density of ester groups and are therefore flexible at room temperature. Consequently the T_g^1 value for the baseline composition, CP1, is -60.6 °C.

The second peak of the $\tan(\delta)$ curve (its temperature location is designated as T_g^2) is broader than the first one. It appears at higher temperatures, between $T = -15$ °C and 80 °C. This relaxation process is related to the motions within the hard segment units or the mobility-restricted, soft segment regions. The hard segments could also contain polymeric chains formed by the reaction of the secondary hydroxyl groups and the epoxy groups (Figure 4) [27].

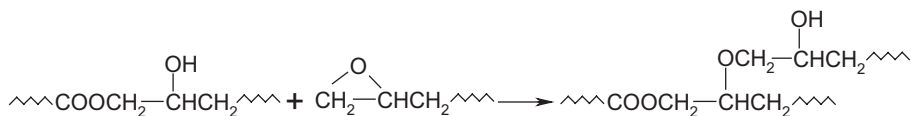


Figure 4. The reaction of the epoxy group and the secondary hydroxyl group.

In a composite propellant, particle-polymer interactions as well as physical confinement effects, have a significant influence on the polymer chain mobility. Although the molecular segments are almost free to move in the rubbery region, the incorporation of highly active fillers such as aluminum and AP, significantly modifies

the molecular mobility. Such systems indicate the emergence of a second, higher T_g , reflecting a constrained population of polymer chain segments in the vicinity of the filler particle surface [28, 29]. The hard segments have high density and high polarity and, for this reason, they are rigid at room temperature. The observed relaxation processes correspond to the maximum values of $\tan\delta_{(\max)1} = 0.33$ and $\tan\delta_{(\max)2} = 0.56$, respectively. Figure 5 shows the viscoelastic response of the propellant samples tested in terms of G' , G'' and $\tan(\delta)$ at 1 Hz, as a function of temperature.

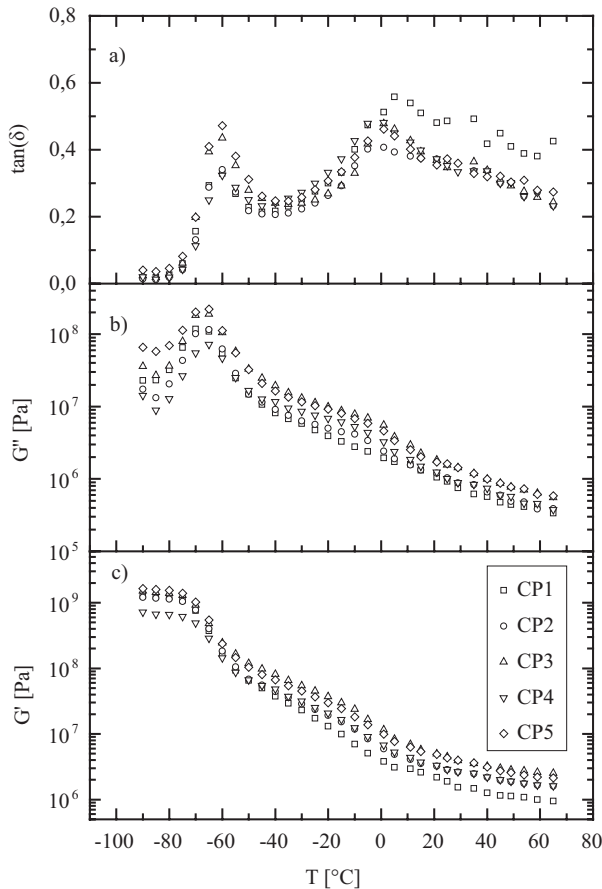


Figure 5. Temperature dependences of a) loss factor $\tan(\delta)$, b) loss modulus (G'') and c) storage modulus (G') for the tested propellant samples.

It can be seen that the G' values increase with an increase in the content of the bonding agent for all temperature values above T_g , indicating an increase of an elastic portion within the propellant binder. The increase of the G' value

is connected with a reduction of polymer chain mobility [30]. The differences between the T_g values of the tested samples determined by DMA via G'' , G' and $\tan(\delta)$, respectively, are within experimental error. Considering the $\tan(\delta)$ curves, no change in the main glass transition temperature is observed on varying the content of the bonding agent ($T_g^1 \sim -61$ °C), despite changes in the crosslink density values. In general, higher levels of crosslinking lead to broader relaxations, evidence of greater intermolecular cooperativity, and, at the highest crosslink densities, a positive offset in the glass transition temperature [31]. The invariance observed in the T_g^1 values, indicates that segmental motions associated with the main glass transition occur over such a length scale that the relaxation time is minimally influenced by the underlying structural changes in the network, caused by the increasing content of the bonding agent. This may indicate that for the propellant polymer networks tested, the distance between the crosslink points is such that any reduction in local constraint caused by the presence of the bonding agent during crosslinking is not manifested as a variation in the T_g .

The $\tan(\delta)$ curves are spread over a wider distribution and show a higher first peak for a higher contents of bonding agent. 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. Table 3 gives the $\tan\delta_{(\max)1}$ and $\tan\delta_{(\max)2}$ values on the loss factor curve for the tested propellants. The intensity of T_g^1 , $\tan\delta_{(\max)1}$, 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 $\tan\delta_{(\max)1}$ values remain almost constant on addition of 0.25 wt.% of the bonding agent, both bonding agents at 0.5 wt.% content significantly increase this value (the maximum was recorded for the CP5 propellant), so one can interpret that a higher content of bonding agent leads to a decreased crosslink density in the propellant binder network. This could also indicate that a significant number of chain segments of these propellant samples (CP3 and CP5) do not participate in this glass transition.

Table 3. $\tan\delta_{(\max)1}$ and $\tan\delta_{(\max)2}$ values for the tested propellant compositions

Sample	$\tan\delta_{(\max)1}$	$\tan\delta_{(\max)2}$
CP1	0.33	0.56
CP2	0.34	0.41
CP3	0.44	0.48
CP4	0.32	0.48
CP5	0.47	0.46

The relaxation process related to the second peak of the $\tan(\delta)$ curve represents the transition region of the mobility-hindered propellant binder chains. When compared to the baseline propellant composition, the second transition peak intensity, $\tan\delta_{(\max)2}$, decreases with the addition of a bonding agent as a consequence of a more surface-constrained polymer chain fraction. This is more pronounced in the CP2 propellant composition. In the case of an attractive and strong interaction between the rigid network segments and the AP particles (Figure 6), the polymer chains closest to the surface are more constrained. In other words, the higher concentration of crosslink points is close to the particle surface. Thus, the formation of hydrogen bonds between the bonding agent and AP leads to a stronger and more homogeneous structure.

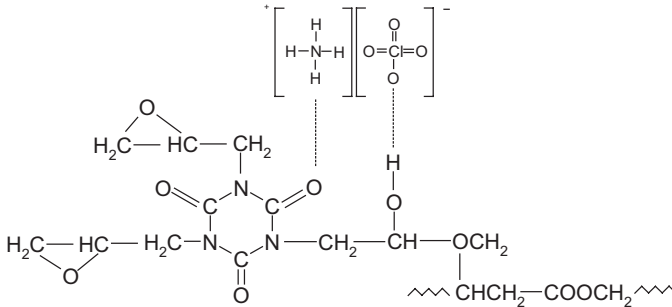


Figure 6. Hydrogen bonds between TGIC as a part of a polymer network and ammonium perchlorate.

3.3 Results of the uniaxial tensile test

The uniaxial tensile properties of a composite propellant depend on the uniaxial tensile properties of the propellant binder, its concentration, the particle size and the particle size distribution of the solids, as well as the quality of the interface between the solid particles and the propellant binder [32]. Table 4 shows the uniaxial tensile mechanical properties, *i.e.* the tensile strength (σ_m), the strain at maximum load (ε_m), the strain at break (ε_b) and Young's modulus (E) for the propellant samples containing varying bonding agent content.

Table 4. Tensile test data for the tested propellants at 20 °C

Sample	σ_m , [MPa]	ε_m , [%]	ε_b , [%]	E , [MPa]
CP1	0.49	53.53	69.83	2.24
CP2	0.73	44.64	57.93	3.76
CP3	0.96	44.87	52.33	4.19
CP4	0.72	48.98	62.24	2.74
CP5	0.79	46.59	51.02	3.49

As expected, partly due to a rather weak interaction between the AP particles and the polymeric matrix, the propellant without a bonding agent (baseline formulation CP1) showed lower values of the tensile strength and Young's modulus. The uniaxial tensile test data indicated that the tensile strength and Young's modulus of the propellant samples tested increase as the content of the bonding agent increases. This is caused by an increase of the crosslinking density values. The higher the bonding agent content is, the more polyesters groups are formed. Furthermore, more hydrogen bonds are produced by reducing the flexibility of the polymer network segments. The most pronounced improvement in the uniaxial tensile strength is shown by propellant sample CP3 (an increase of 97.7% compared to the baseline composition).

On the other hand, the incorporation of TGIC and DGH as bonding agents into the propellant formulation reduces the strain at maximum load values as a consequence of the reduced molecular weight of the polymer chains between the crosslink points. The same tendency can be seen in the strain at break values as a function of the effective polymer chains between the crosslink points. Effective polymer chains represent the chains that contribute to the effective deformation, which means that both of the chain ends are involved in the polymer network formation. The reduction of both strain values is not desirable, although the values of the strain at maximum load and the strain at break of the baseline composition are 55% and 70%, respectively. These values are primarily caused by the prepolymer molecular weight. DGH at 0.25 and 0.5 wt.% causes an increase in tensile strength of 48.3% and 62.1%, with a simultaneous reduction in the strain at maximum load values of 14.8% and 14.2%, respectively. In comparison with a bonding agent content of 0.5 wt.% (CP3 and CP5), it can be seen that TGIC is more effective than DGH by 22.0%, when considering the tensile strength value.

4 Conclusions

The uniaxial tensile and viscoelastic properties of a composite propellant based on carboxyl-terminated poly(butadiene-co-acrylonitrile) and AP containing functionally substituted bonding agents (triglycidyl isocyanurate and diglycidyl dimethylhydantoin) have been determined. The results of sol-gel analysis indicated that the crosslinking process is dependent on the content of the bonding agent. Dynamic mechanical analysis revealed that the glass transition temperature of the propellants does not change with either the type or content of the bonding agent. The glass transition temperature, T_g , of all of the tested propellants was

around $-66\text{ }^{\circ}\text{C}$. For all of the tested propellants, the presence of two maxima can be seen in the $\tan(\delta)$ curve. Both of the maximum values, $\tan\delta_{(\max)}$, are shown to be influenced by the propellant crosslink density.

The bonding agent type and its content were found to alter the uniaxial tensile properties of the composite propellants tested. Both Young's modulus and the tensile strength increased, whilst the strain at maximum load and the strain at break slightly decreased. The results presented in this paper indicate that there is a significant influence of the type and the amount of the applied bonding agent on the composite propellant behaviour. The highest effectiveness is observed with TGIC at 0.5 wt.%. Although there is no support in the literature, it can be stated that, based on the analysis of the test results, the use of these types of bonding agents during the homogenization of CTBN-based composite propellants is quite justified.

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