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DEVELOPMENT OF LINER FOR CASE-BONDED GRAIN WITH END-BURNING CONFIGURATION

TIHOMIR KOVAČEVIĆ
Military Technical Institute, Belgrade, tkovacevic@tmf.bg.ac.rs

SLAVKO MIJATOV
Military Technical Institute, Belgrade, slavko.mijatov@yahoo.com

ALEN CRNALIĆ
Military Technical Institute, Belgrade, alen.crnalic@student.ni.ac.rs

JELENA GRŽETIĆ
Military Technical Institute, Belgrade, jrusmirovic@tmf.bg.ac.rs

DARKO KUPREŠAK
Technical Test Center, Belgrade, darkokvb7@gmail.com

SAŠA BRZIĆ
Military Technical Institute, Belgrade, sasabrzic@gmail.com

Abstract: *This paper deals with the potential to manufacture case-bonded propellant grain with the end-burning configuration. The end-burning configuration is not quite suitable for case-bonded architecture due to problems related to structural integrity. One approach to address this issue is to insert a liner between thermal insulation layer and the composite propellant, which absorbs stress generated during curing process and exploitation conditions. The prepared liner is a highly elastomeric material, based on hydroxyl-terminated polybutadiene (HTPB) and castor oil (CO). The amount of curing agent, isophorone diisocyanate (IPDI), is higher to establish a covalent bonding and thus good adhesion between the liner and the propellant/thermal insulation. CO provides more anchoring sites since it has higher functionality of HTPB and, in other hand, isotropy of the liner making it more able to withstand and reduce accumulated stress within the propellant grain. The molar ratio between prepolymer (HTPB and CO) and IPDI was varied and cured material was subjected to an unaxial tensile test and examination of adhesion with propellant using a peel test.*

Keywords: *burning profile, adhesion, mechanical properties, grain configuration, OH:NCO ratio.*

1. INTRODUCTION

Solid propellant grains appear in the two varieties: free-standing or cartridge-loaded and case-bonded. Case-bonded grain meets the requirements of long ranges and high payload-carrying capacity making it a favorable choice for spatial applications [1,2]. The case-bonded grain consists of a metallic motor case, a rubbery thermal insulator, an elastomeric liner and propellant as the energetic component which gives thrust upon burning. All of the mentioned sub-systems need to be securely fastened to avoid problems when the rocket motor starts. Even when the all integral parts of solid propellant grain appear to be tightly bonded to each other, separation and develop of uncontrolled burning surface may occur after ignition, especially during flight. This phenomenon is a consequence of the forces of acceleration and rotation which surpass established bonding strength between the integral parts within the propellant grain [3]. In addition, the grain configuration has a great impact on the bond strength (adhesion), particularly between the thermal insulator or motor case and the propellant due to problems related to large differences in coefficients of linear thermal expansion. Polyurethane-based propellant is prone to dimensional changes due to external temperature and curing conditions, which create stress within the propellant and cause separation. An example of such a design is an end-burning configuration which is not entirely suitable for case-bonded architecture, particularly when the propellant grain is subjected to extremely low temperature (-40 ºC). The main approach to deal with this issue is to insert a liner between thermal insulation and the composite propellant, which absorbs stress generated during the curing process and the exploitation conditions [4].

In most cases, propellant and thermal insulation are incompatible with each other and inserting a liner between them overcomes this issue, ensuring their good attachment. The liner is placed on the surface of the

Corresponding author: T. Kovačević;
E-mail tkovacevic@tmf.bg.ac.rs
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thermal insulator surface and pre-cured prior to propellant casting, afterwards complete solidification of the prepared system is applied. During the solidification period, the liner is completely cured, establishing good adhesion with the propellant [1]. It is important to accomplish good bonding between the critical surfaces: motor case - thermal insulation, thermal insulation – liner and liner – propellant. Bond failure at the interfaces of integral parts within the propellant grain can form an increased burning surface resulting in improper ballistic properties or motor case cracking.

There are several mechanisms involved in the adhesion process where some of them act together and some of them are mutually exclusive [5]. Mechanisms include physical and chemical interactions (or combination) that are reflected in the following phenomena: adsorption, chemical linkage, electrostatic force attraction, interdiffusion and so on. The latter is most signicant in a polymer/polymer system, such as the liner/propellant interface.

The major issue regarding good adhesion between the propellant and the liner or thermal insulation originates from the dissimilar materials used to prepare these two components of the case-bonded grain. This primary refers to thermal insulation obtained from rubbery-like materials such as ethylene propilene diene monomer (EPDM) or polybutadiene acrylonitrile (PBAN) [2]. Hereupon, the composition of the liner should be compatible with the polymer matrix of the propellant, which ensures good interaction between them, *i.e.* strong adhesion.

Since conventional composite propellants contain hydroxyl terminated polybutadiene (HTPB) as the polymer matrix, there are myriad studies which consider use of this material for liner preparation [6–9]. Liner as well as propellant contain a plasticizer which makes them easy to process and adjust the required mechanical properties. Conversely, the plasticizer can easily migrate and accumulate at the propellant/liner interface and affect the adhesion between them, resulting in debonding [10]. In addition, the plasticizer softens the propellant, leading the cohesive failure near the interface liner/propellant when good adhesion is established between them [4]. One of the approaches to address this issue is employing the reactive plasticizer that participates in the creation of polymer network, *i.e.* it is anchored to the main polymer backbone and cannot migrate [10].

In this study, several liner samples are prepared using HTPB as a polymer matrix and castor oil (CO) as a reactive plasticizer. CO, in addition to softening the propellant, has a multiple role as follows: it takes part in the curing reaction by including itself in the polymer network, acts as a chain extender and a cross-linking agent. The reference sample is prepared using a deficient amount of the curing agent, isophorone diisocyanate (IPDI), which produces a hydroxyl terminated product. Other samples possess an excess of IPDI giving the isocyante terminated material capable to establish a covalent bonds with the propellant (NCO:OH ratio within the propellant is less than 1).

2. EXPERIMENTAL SECTION

2.1. Materials

HTPB, R-45M (USA, viscosity at 30 °C: 5500 mPa·s, OH value: 44-51 mg KOH·g^{-1}, hydroxyl functionality: 2.4, average molecular weight, Mn: 2900 g·mol^{-1}, glass transition temperature, T_g: 80 °C) was used as a binder while Castor oil (CO-Interhem Ltd, Republic of Serbia, hydroxyl functionality: 3.0, Mn: 933 g·mol^{-1}) was used as a reactive plasticizer. Curing agent, isophorone diisocyanate (IPDI) and antioxidant (2,2'- bis(4-methyl-6-tertbutyl) phenol (AO 2246) were supplied from Acros Organics, Belgium and Sigma Aldrich, Germany, respectively. Catalysts, ferric acetyl acetonoate $(FeAA)_3$ was procured from Merck, Germany.

2.2. Sample preparation

The homogenization of liner compositions was performed using laboratory mixer (LR 1000 B S099, Ika, Germany) at a temperature of 30 °C in two-step procedure. Firstly, the premix excluding catalyst and curing aegnt was prepared by mixing HTPB, CO and AO22 for 1 hour under the reduced pressure (vacuum). After that, catalyst and curing agent were added in the obtained mixture and homogenization was carried on for 5 min under atmospheric pressure and 10 min under the vacuum. The obtained slurry was poured into two standard polytetrafluoroethylene (PTFE) molds and cured in the oven for the next 2 h (first mold) and 24 h (second mold) at 60 ºC. In addition, liquid liner was applied on propellant surface and cured for 24 h at 60 °C to obtain sample for peeling test, *i.e.* determination of adhesion. Composition of the prepared liners is shown in Table 1.

Table 1. Composition of prepared liners in [%]

No.	HTPB	CO	AO22	$(FeAA)_3$	IPDI	NCO/OH
L1	72.89	18.22	1.09	0.0255	7.760	0.59
L2	70.92	17.73	1.06	0.0248	10.26	0.80
L3	68.29	17.07	1.02	0.0239	13.59	1.10
L4	67.87	16.97	1.02	0.0238	14.12	1.15
L5	67.46	16.86	1.01	0.0236	14.64	1.20
L6	66.64	16.66	1.00	0.0233	15.67	1.30
L7	65.85	16.46	0.99	0.0230	16.68	1.40
L8	65.07	16.27	0.98	0.0228	17.66	1.50

L1 and L2 has NCO:OH ratio less than 1, *i.e.* these liners are hydroxyl terminated, while L3 – L8 are isocyanate terminated. The first group forms hydrogen bonding with the same terminated polymer matrix within the propellant. Second group is designed to enforce interaction between liner and propellant, *i.e.* to achieve good adhesion. Adhesion and mechanical properties of the prepared liners are determined using peeling and unaxial tensile tests.

2.3. Characterization methods

The viscosity of the liquid liners was measured at the 60 °C by HBT type Brookfield viscometer with a T-C spindle at a rotation speed of 5 rpm.

The mechanical properties of the cured liner samples at

+20 °C were determined employing an Instron 1122 uniaxial tensile test machine. Dimension of the samples was is as follows: initial length: 46.5 mm, width: 6 mm and thickness: 4.0 mm). The crosshead speed of the uniaxial tensile test machine jaws was 50 mm·min^{-1}. Three samples were tested for each liner composition and the average value was calculated.

The specimen for determining the adhesive strength were obtained from samples of propellants and liners. The equipment for performing the peel test is shown in Figure 1.

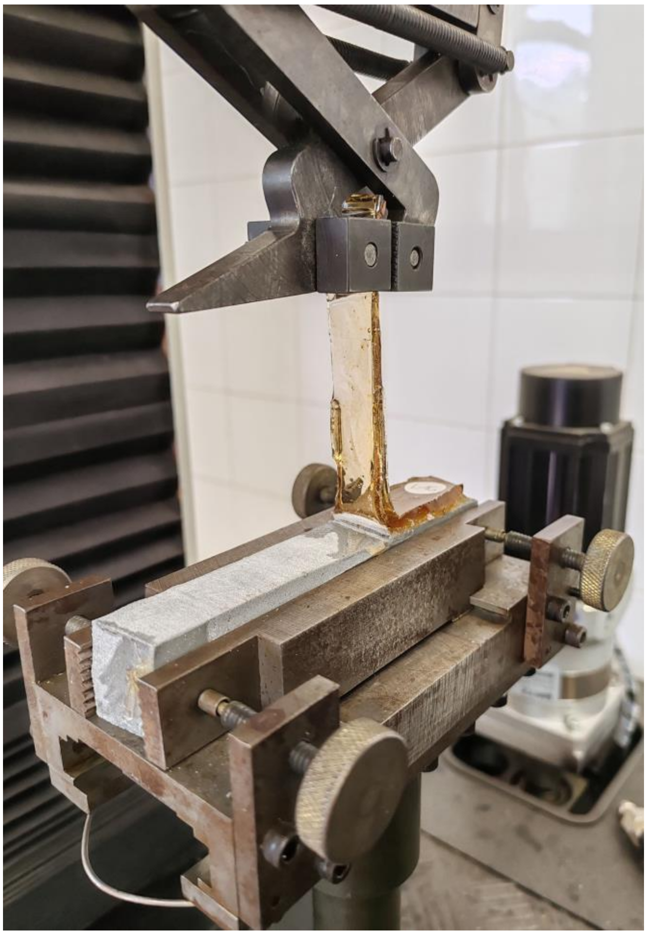

Figure 1. Equipment for peel test

3. RESULTS AND DISCUSSION

3.1. Viscosity measurements

It is important to obtain a fast-curing liner since the ultimate goal is to apply it to the inner surface of the cylindrical motor case. It is essential that the liner is quickly converted into a relatively solid form to avoid dripping and flowing (to achieve gel time). To achieve such curing kinetics, a catalyst is introduced composition of the liner, while amount of curing agent is varied. Table 2 shows the viscosity values for the prepared liner compositions.

Table 2. Viscosity of the tested liners

Sample	η/(Pa·s)					
	15	**30**	**45**	**60**	**75**	**90**
L1	19.2	56.0	176.0	664.0	cured	
L2	9.6	136.0	cured			
L3	16.0	78.4	160.0	cured		
L4	28.8	217.6	cured			
L5	22.4	401.6	cured			
L6	22.4	75.2	1600	cured		
L7	14.4	32.0	41.6	54.4	118.4	600.0
L8	40.0	46.4	41.6	52.2	73.6	94.4

L2 exhibits a higher reactivity compared to composition L1 due to greater presence of curing agent. The main disadvantage of L2 is the short pot life, which disables easy manipulation and application. L1 has an optimal pot life making it suitable for casting and distributing on the inner wall of the motor case. L4 and L5 liners behave similarly to the L2 regarding the pot life. The limit value for the NCO:OH ratio is 1.4 (L7) above which the amount of curing agent is too high, making the final product pasty and sticky (L8).

Most of the samples exhibit low a initial viscosity which increases rapidly. A slower curing rate is obtained when the amount of curing agent is too low (L1) whereas a significant number of macromolecule chains originating from HTPB and CO remain unbound. Another case is when the amount of curing agent is too high (L4 and L5) where remained IPDI makes particular liner too stretchy. Analysis of viscosity shows that the most prominent liner compositions are L1 and L7.

3.2. Mechanical properties

The tensile characteristics of the analyzed liners, expressed as tensile strength (σ_t), strain at maximum load (ε_m), strain at break (ε_b) as well as Young's modulus (E), at +20 °C are shown in Table 3. The mechanical characteristics of the polymeric materials directly depend on the density of chemical bonds, *i.e.* on the content of hard segments of the resulting polymer network, which can be increased by adding diols/triols (CO), thus providing more sites for cross-linking [11]. CO provides more anchoring sites since it has higher functionality of HTPB and, in other hand, isotropy of the liner making it more able to withstand and reduce accumulated stress within the propellant grain.

Table 3. Average values of tensile properties of corresponding liners

No.	σ_t/MPa	ε_m/%	ε_b/%	E/MPa
L2	0.64	114.5	114.7	0.98
L3	0.57	130.0	130.1	0.73
L4	0.58	81.4	81.5	1.10
L5	0.99	75.4	75.5	1.92
L6	1.02	98.4	98.5	1.74
L7	0.29	247.2	247.6	2.47

Tensile test results for liner L1 is not shown because it has an elongation of more than 1000% and is beyond the measuring range of a uniaxial tensile test machine. In contrast, L2 is quite stiff compared to L1 and does not possess sufficient strain at maximum load to be a good candidate for liner application. L1 is deposited on the inner wall of the motor case and after that the propellant is cast, but separation occurs when the resulting grain is subjected to a temperature of -40 °C. That is the reason to prepare an isocyanate terminated liner that can form a covalent bond with the polymer matrix from the propellant (L1 exhibits hydrogen bond interactions instead of covalent). The energy of the C-O covalent bond (allophanate linkage) is 351 kJ·mol^{-1} compared to hydrogen bonds whose strength is 18.8 - 31.8 kJ·mol^{-1} (O-H···O bond).

All liners behave as a highly cross-linked elastomeric material since there is no area of plastic deformation, which is reflected in a very close value of strain at maximum load and strain at break. Isocyanate terminated liners (L3 - L6) are very rigid materials, especially those containing a higher amount of IPDI. These characteristics exclude them as candidate for liner application where the strain at maximum load has to be at least 200%. The situation changes drastically when NCO:OH ratio is 1.4 (L7). Mentioned composition has sufficient elasticity to be applied as a liner in the case-bonded propellant grain. The analyzed liners have an effective polymer network where total amount of macromolecule chains are bound without the rest of the loose segments. The reason for the results obtained in the case of L7 may be the insertion of an increased amount of polar and relatively small IPDI molecules between non-polar polymer chains, which reduces their mutual interactions, *i.e.* the threshold for such a drastic change is reached. Results for the liner L8 are not shown because it is not completely cured and therefore not tested.

3.3. Peel test

The peel test is performed to quantify the adhesion strength between the prepared liners and the composite propellant. It is important to note that obtained results do not give a realistic picture of the bonding strength, which is a consequence of the nature of the resulting liners. Namely, most liners are stiff and tear during the test, *i.e.* adhesion between the liner and the propellant is much higher than the cohesion of the liner itself (Figure 2).

Figure 2. Collapse of the liner during the peel test

Each isocyanate terminated liner splits near the interface liner/propellant except L7 which breaks in a similar manner to the tensile test. The recorded value of the adhesion strength until breaking is 5.55 N·cm^{-1} for L7 liner. Others has lower values, but the samples are stiffer and break easily, while, on the other hand, they are firmly attached to the propellant. Even L1 liner, which is hydroxyl terminated, exhibits good adhesion with the propellant, but the bond strength is not recorded due to great elasticity of such material which absorbs the stress generated during the test. These results are consistent with those obtained for tensile properties, where most of the analyzed liners break relatively quickly.

4. CONCLUSION

This research is performed to find a way to prepare a case-bonded propellant grain with the end-burning configuration. Such a motor has to contain thermal insulation, liner and propellant. The essential aspect to be fulfilled is to achieve good adhesion between the mentioned sub-systems. First attempt is focused on obtaining a highly elastic material capable to overcome the physical and chemical differences between those layers, *i.e.* receiving the generated stress and relaxing entire system. Consistency with this, a hydroxyl terminated liner with a loose polymer network (L1), which enables great flexibility, is prepared and analyzed. Since the L1 liner has great elasticity, it is applied to the inner wall of the motor case and after that propellant is cast, but separation occurs when the resulting grain is subjected to a temperature of -40 °C. This is the reason for the change of course toward preparation of isocyanate terminated liners. To achieve the given goal, several liner compositions are homogenized, cured and analyzed using viscosity, tensile and peel tests. All of the resulting liners are castable but solidify too fast, except composition L7.

Prepared liners are very tough materials, especially those containing a higher amount of IPDI. These characteristics exclude them as candidate for liner application where the strain at maximum load has to be at least 200%. The only one which is suitable for liner application is composition L7, since it has a strain of 247% at maximum load.

The peel test shows that all analyzed liners have good adhesion with the propellant, but break easily during the test. Again, L7 exhibits the best behavior, which, combined with viscosity values and tensile properties, makes it the best candidate for liner application in case-bonded propellant grain.

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