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DEVELOPMENT OF POLYMER COMPOSITE LINER AS INSULATION MATERIAL: RHEOLOGICAL, MECHANICAL AND THERMAL PROPERTIES

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Abstract: The purpose of this study was to develop and analyze new composite material as a liner insulation material for rocket propulsion charges, hydroxyl-terminated polybutadiene (HTPB) based and reinforced with carbon fibers (CFs) and inorganic filler powders (IFPs). Novel material is an elastomeric adhesive, improving mechanical properties between the insulation/rocket motor chamber and the propellant and preventing heat penetration. Liner formulations were made for each material with a range of weight loadings of CFs and IFPs, and with different NCO/OH ratios of 0.85–1.5. Also, processability was observed by monitoring the change in viscosity during and immediately after mixing, depending on the composition and mixing parameters. Material rheological and mechanical characterization additionally contributed to the selection of a composition suitable for application to various geometric profiles. In order to offer more trustworthy information about the viscoelastic behavior of the liners, a dynamic-mechanical analysis (DMA) was performed and rheological measurements of uncured and cured materials were obtained. Small scale ablation testing was performed using an oxy-acetylene test as a significant factor in the material verification. The ablation results demonstrated that the prepared insulation materials could deliver good thermal ablative and insulative properties, also decrease in erosion rate. Therefore, developed polymer composite liners (PCL) could be an excellent heat-insulation and thermal-protection materials with applications in the field of rocket propulsion.

Keywords: HTPB, carbon fibers, liner, processability, ablation.

1. INTRODUCTION

The composite rocket propellant (CRP) is composed from elastomeric binder, plasticizer, bonding agents, ballistic modifiers and solids, metallic fuel and oxidizer. When ignited, CRP burns giving designed combustion profile, with the required thrust to launch rockets, missiles, and bullets. The elastomeric matrix with its carbon and hydrogen organic rich part binds the solids together and allows for the shaping and maintenance of the integrity of the propellant [1]. A combustion process of propellant is a complex process through which the system is subjected to highly severe conditions of temperature and pressure. A rocket motor is designed for enduring extreme conditions of temperature, pressure and turbulence during propellant combustion, so there is a need for some thermal insulation material between motor case and propellant, either for case bonded or cartridge loaded grains.

Case bonded systems use a thermal insulation lined inside the rocket motor, which protects motor case from high temperature during combustion of propellant. Contrary, cartridge loaded systems use inhibiting materials or inhibitors for case protection and maintaining the designed combustion profile. This helps to achieve the desirable pressure-time profile for a specific application and requirements. So, the performance of the propellant grain depends not only on the propellant but to an inhibition or insulation system [2].

Solid-propellant rocket motors consist of a motor case, igniter, propellant, nozzle, liner and/or insulator. Liner for solid propellants is an elastomeric adhesive, which amortizes difference in coefficinet of linear thermal dilatation between steel or composite motor case and elastomeric propellant. In that way, the liner absorbs generated stress during prolonged storage and exploitation, providing good mechanical integrity of the

propellant. During combustion process the temperature can reach above 2.000 °C, pressure can exceed 10 MPa the velocity of the combustion gases can reach or exceed 0.2 Mach. These extreme conditions lead to eroding thermal insulation, which further can cause a failure of the rocket motor [3]. The selection of material for thermal insulation and liner is crucial to the design of the propellant grain.

Some of the requirements for solid rocket motor insulation are [4]:

- Low density (from 1.05 to 1.5 g cm⁻³);
- Sufficient tensile strength (0.5 MPa);
- Excellent bonding of the insulation material with propellant and motor case over the entire range of the working temperature;
- Low erosion rate (from 0.09 to 0.20 mm s⁻¹);
- Very low outer case temperature (<150 °C) over the entire range of working temperature;
- Low thermal conductivity (from 0.2 to 0.5 W m⁻¹K⁻¹);
- High specific heat (from 1000 to 2100 J kg⁻¹ K⁻¹); and
- Ability to resist mechanical and thermal stresses during storage, handling and curing operations.

Various inhibitor, insulation and liner compositions are developed with different polymers like epoxy, polyurethane, siloxanes and butadienes with incorporation of different fillers like silica, antimony trioxide, kaolin etc. for various applications [5], [6]. Out of these, a butadiene and Sb₂O₃ based composition is selected with the aim to enhance the integrated performance of elastomeric insulation material. These materials stand out on enhanced mechanical strength, thermal stability and barrier properties with ablation resistance [7]. For elastomers filled with carbon black, the ablation resistance is inadequate to withstand the high stresses and erosion rates resulting from the combustion gases [4]. Zirconium dioxide, a type of mineral oxide, has been tested as a filler for thermal insulation materials and it was found that it ensures the formation of a looser carbon-mineral coke structure in polyurethane materials during the ablation tests [5].

Commonly used insulators consist of either phenolic or some type of rubber and carbon black, asbestos, carbon fibers or aramid (Kevlar®) fibers as reinforcements [4]. It is desirable that liner and propellant have similar polymer basis to provide good compatibility *i.e.* adhesion between them. Appropriate modifiers or fillers form a protective layer in-situ at elevated temperatures to withstanding very high temperatures.

In this paper these characteristics were taken into account during the selection of three formulations based on polybutadiene resin with about 40-50% fillers. When fillers are added to polymeric matrices, they increase thermal stability and mechanical properties. Also, filled polyurethanes show pseudoplastic behavior, *i.e.* the shear rate has significant effect on viscosity [8]. In this contribution, we studied the effect of different reinforcements, *i.e.* chopped carbon fibers and inorganic powders onto the processability, mechanical, rheological and thermal properties of HTPB-based liners, with the ultimate and practical objective of determining its

application in solid rocket motors.

2. EXPERIMENTAL PART

2.1. Materials

Hydroxyl-terminated polybutadiene (HTPB) prepolymer resin in commercial grade (mean molar mass of 2900 g mol⁻¹, functionality 2.4) was obtained from Evonik, Germany.

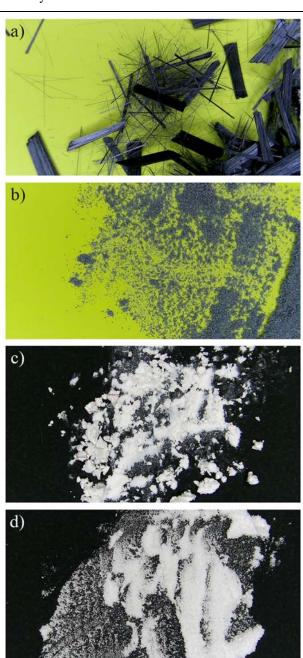


Figure 1. Carbon fibers (a) and inorganic filler powders: SiC (b), SiO₂ (c) and ZrO₂ (d)

Castor oil (CO), made by Interhem, Serbia, with mean molar mass 933 g mol⁻¹ and functionality 3.0, was used as reactive (cross-linkable) plasticizer and bonding agent. The curing agent for the described materials was isophorone diisocyanate (IPDI, Evonik, Germany), while

AO 2246, with N,N'-di-2-butyl-1,4-phenylenediamine as active component, was used as antioxidant. Materials, used for the preparation of thermally stable liner, were as follows: carbon roving (Tenax HTS40), which was cut in millimeter size before use, (Figure 1 (a)), aluminium trihydroxide (ATH, Technipur, Germany), catalyst ferric acetyl acetonate (FeAA)₃ (Merck, Germany), SiC (97.5% 200 mech, Schnelldorf, Germany), SiO₂ (99.9% 325 mech, Cerac, UK) and ZrO₂ (99% 325 mech, Sigma Aldrich, USA) (Figure 1(b), (c) and (d), respectively). All solids were dried at 60 °C for three days to remove moisture before use.

2.2. Preparing of liner insulation materials

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 Fe(AA)₃ and IPDI (Table 1), was made by mixing HTPB, CO, AO2246, chopped carbon fibers and inorganic powders for 20 min under atmospheric pressure and 30 min under the vacuum. Afterwards, catalyst and curing agent were added in the obtained mixture and homogenization was continued for 5 min under atmospheric pressure and 10 min under the vacuum

Table 1. Compositions of prepared insulation materials

Component	L4	L6	L10	
	parts per hundred ratio (phr)			
HTPB	100	100	100	
CO	16.09	8.05	8.05	
AO 22	0.5	0.5	0.5	
Fe(AA) ₃	0.0075	0.0075	0.0100	
IPDI	9.69	8.74	8.74	
	mas.%			
CFs	1.2	1.2	1.54	
$Al(OH)_3$	50	50	-	
SiC	-	-	1.92	
SiO ₂	-	-	23.04	
ZrO_2	-	-	13.44	

Such obtained material was poured into the standard polytetrafluoroethylene (PTFE) molds and cured in the vacuum oven for the next four days at 60 °C. The specimens for the mechanical, rheological and thermal measurements were cut out from the cured material. The liner insulation materials are designed as follows: L4 and L6 contain chopped carbon fibers and aluminium trihydroxide, while L10 contains chopped carbon fibers, SiC, SiO₂ and ZrO₂ inorganic reinforcements. All these formulations were evaluated for their physical, mechanical, thermal and ablative properties.

2.3. Physical, rheological, mechanical and thermal analysis of materials

Shore A hardness (Sh A) of inhibitor samples was estimated by durometer (Zorn Stendal DDR testing device) according to the standard ASTM D2240 [9]. The five measurements were performed to determine mean values of Sh A hardness.

Density of prepared materials were obtained by a Mettler density kit at 25 °C, whereas isopropyl alcohol was used as a solvent [10]. The density, D, was determined according to the following Eq. 1:

$$D = \frac{m_0}{m_s} D_s \tag{1}$$

where D is the sample density (g cm⁻³), m_0 is weight of the sample (g), m_s is weight of the sample in solvent (g) and D_s is the specific gravity of the solvent (g cm⁻³). The five measurements were performed to determine mean values of liners density. Distribution of the filler particles within the polymer matrix after curing was determined using optical microscope (SMTV Visor Inspection System, Michael Bruch, Germany).

Dynamic mechanical analysis (DMA) study for cured materials was performed in torsion deformation mode using the Modular Compact Rheometer MCR–302 (Anton Paar GmbH), equipped with standard fixtures (SRF12) for rectangular bars, temperature chamber (CTD–620) with high temperature stability (±0.1 °C), and automated cooling accessories using liquid nitrogen. The samples for the DMA tests were of a rectangular bar shape (44 mm × 10 mm × 4 mm). Dynamical–mechanical measurements were performed by using "temperature ramp test" and the following conditions: the temperature range from -80 °C to 40 °C, the heating rate was 5 °C·min⁻¹ and the single angular frequency of 1 Hz. Strain amplitude was 0.1% (0.001), within linear viscoelastic region.

Viscosity is an easily measurable parameter to monitor curing and chemo-rheological properties of liners and propellants. As the cure proceeds, the molecular size increases, and so does the cross-linking density, which decreases the mobility of the molecules. Viscosity studies are worth to be continued to make compositions more process friendly, considering the technical difficulties involved in mixing during manufacturing. The rheological behaviors of the uncured liner formulations, before and 15 min after IPDI addition, were also investigated at shear rates ranging from 0.1 to 500 rad s⁻¹ at 25 °C. A series of measurements are performed in a cone-and-plate geometry with a diameter of 35 mm and a gap of 0.5 mm.

Uniaxial tensile measurements of samples cured for four days were performed using an Instron 1122 tester according to standard procedure [11]. All tests were performed at 20 °C adjusted at crosshead speed of 50 mm min⁻¹. Dumbbell-shaped specimens (100 mm \times 6 mm \times 3 mm) were used. The effective gauge length of the test samples was 46.5 mm. The tensile strength is calculated as $\sigma_m = F/S$ where F is the force, S is the transect area of sample at direction. Each value is an average of the five measurements with a relative standard deviation of $\pm 3\%$.

Flame resistance was evaluated using ASTM E285, Standard Test Method for Oxyacetylene Ablation Testing of Thermal Insulation [12]. The test equipment consists of an oxygen—acetylene control unit, gadget for data measuring (time, temperature) and a specimen-fixing unit (Figure 2).



Figure 2. Specimen-fixing unit for oxy-acetylene torch test

The size of the liner insulation material specimens was $100 \text{ mm} \times 100 \text{ mm}$ and 3-4 mm thickness. The flame of $3000 \,^{\circ}\text{C}$ was generated with a 1:1 oxygen-acetylene ratio and the distance between the specimen and torch was set at 60 mm. The erosion test lasted until the flame penetrated through the material. Additionally, the back surface temperature was measured using a mobile infrared thermometer (TFI 550, Xylem Analytics Germany, Ebro).

Samples were subjected to a flame torch of oxygen and acetylene and time to bore a hole in samples was recorded. The calculated parameter was erosion rate, Eq.2,

$$E = \frac{d}{t_b} \tag{2}$$

where E is the erosion rate (m s⁻¹), d is the thickness of panel (m) and t_b is the burn-through time (s).

3. RESULTS AND DISCUSSION

3.1. Physical and mechanical properties

Table 2 shows the mean Sh A and density, where a slight differences in resulting values is remarked.

Table 2. Hardness and dencity values for prepared insulation materials

Material	L4	L6	L10
Hardness (Sh A)	38	42	40
Density, D (g cm ⁻³)	1.3517	1.3486	1.2853

Figure 3 shows the distribution of filler particles and carbon fibers in cured polymer matrix. Presence of copped carbon fibers is visible in the case of all samples, while in the case of the L10 material the presence of different powdered fillers is especially emphasized.

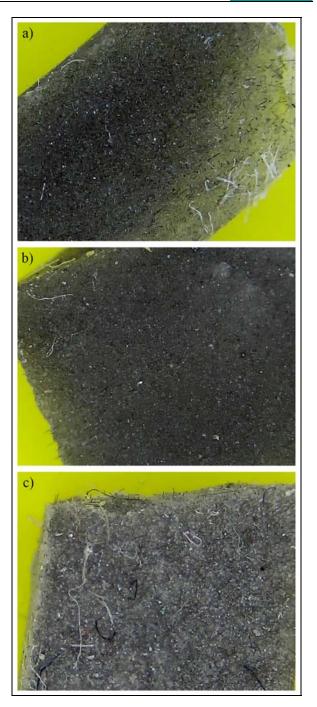


Figure 3. Distribution of reinforcements within the L4 (a), L6 (b) and L10 (c) by optical microscopy

Figure 4 shows the viscosity as a function of shear rate for the uncured liner insulation materials. It is obvious that viscosity increases with the decrease of CO content, in the case of L6. In addition, viscosity values less than 100.000 mPa·s are suitable in terms of composition processability, which means that L4 and L10 formulations could be suitable in liner insulation manufacturing process.

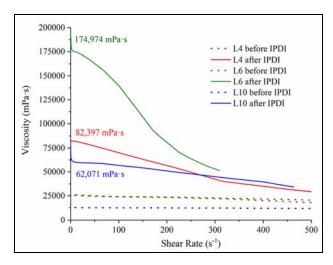


Figure 4. Viscosity versus shear rate of uncured material formulations

In the case of L10 material, due to carbon fibers lower content compared to other formulations, viscosity is lower, but requires a longer processing time.

Mechanical properties of HTPB-based liners mainly depend on the curing agent, NCO/OH ratio, chain extender nature, microstructure and crosslinkers [13]. Elasticity and high thermal resistance are required for the insulation layer of an propellant grain system. Tensile strength and elongation at break for prepared materials after curing at 60 °C for 96 hours were measured through maximum tensile strength ($\sigma_{\rm m}$) until failure. Figure 5 shows comparison of tensile strength and elongation at break values (a) and the typical tensile stress-strain curves of the cured materials (b). L4 material has the highest elongation (759%) and correspondingly small tensile strength (0.358 MPa). In the case of L6 material, elongation was significantly reduced due to lowering of CO content, but conversely, tensile strength increased because of the higher NCO/OH ratio, which mostly affects mechanical characteristics [8], [13]. L10 shows high elongation value and the highest tensile strength among the tested materials, which is attributed to the greater carbon fibers content givingstiffness to the final material. In addition, it is well-known that the tensile strength of polymer composites strongly depends to the shape and content of the fillers, so L10 tensile strength value may arise due to diversity of inorganic particles in material formulation [14]. Also, it can be assumed that during combustion and high temperature pyrolysis it forms mostly ceramic layers which stick together and do not ablate in the current flow [15].

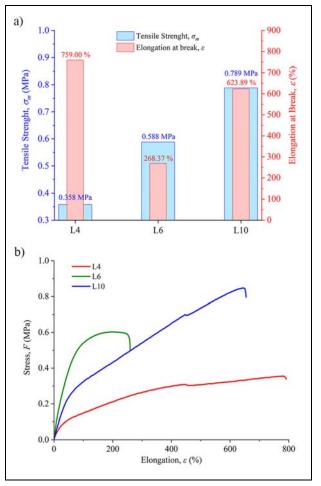


Figure 5. Comparison of tensile strength and elongation at break of samples (a) and tensile stress-elongation curves of the samples (b)

3.2. Rheological properties

Figure 6 shows the DMA curves of prepared liners as a function of different binder formulation and filler loading. The DMA curves provide specific information on the storage modulus, G' (elastic response), loss modulus, G'' (viscous component) and $\tan\delta$, within the applied temperature range. The G' reflects the elastic modulus of materials, G'' is related to the energy dissipation associated with the motion of polymer chains whereas $\tan\delta$ represents the phase delay between the applied force and the response of the material.

The resulting DMA curves are typical for elastomeric HTPB-based composites. Storage modulus decreases with temperature, from 1392, 2110 and 1726 MPa at -80 °C to 0.63, 0.81 and 0.62 MPa at 40 °C, for L4, L6 and L10, respectively. The maximum values are reached below the glass transition temperature zone (-80 °C to -60 °C). The L6 containing half as much CO in binder structure shows higher values of storage modulus in low temperature region due to the conspicuous chemical linkage in polymer network, but similar trend after glass transition zone, compared to L4 and L10.

Table 3. Glass transition temperatures of prepared insulation materials

Material	L4	L6	L10
$T_{\rm g}$ (°C)	-63.53	-60.61	-63.15

In all cases it is noticeable a double peak in the $\tan\delta$ curve, corresponding to alpha and beta transition of the polymeric matrix. The second peak is wide and has a lower intensity than the first peak. This behavior is related to the presence of hard and soft segments in polyurethane material.

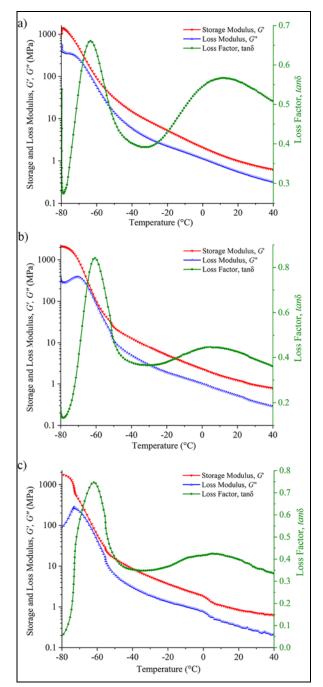


Figure 6. DMA curves of liner insulation material based on HTPB and CO: L4 (a), L6 (b) and L10 (c)

The first peak is a glass transition temperature of the soft segments (T_g), which determines the beginning or the end of the movement of the segments of the polymer backbone. Determined glass transition temperatures of L4, L6 and L10 cured materials are similar because of the

same binder bases, as presented in Table 3. The second peak is related to a complex process involving two mechanisms: the interactions of the polymer itself and the interactions of the matrix and solid phase. The mobility of macromolecule segmnets are significantly reduced due to solid content and interactions between the binding agent and the solids. Peak height in case of L4 is higher compared to L6 and L10 due to the higher amount of CO in material formulation, which segments remain unattached to polymer network and, thus are more movable.

3.3. Ablation testing

The oxyacetylene torch test results are summarized in Table 4. Exposing the liners to extreme temperatures leads to pyrolysis, which produces char on the material surface, acting as an insulating layer [16].

Table 4. Ablation test parameters and results

Material	L4	L6	L10
Length (mm)	100	100	100
Width (mm)	100	100	100
Thickness, d (mm)	3.90	3.82	2.93
Burning out time, t_b (s)	38	6	5
Burning out back-face temperature, T_b	102	44.0	56.9
E (m s ⁻¹)	1.0263×10 ⁻⁴	6.3667×10 ⁻⁴	5.8600×10 ⁻⁴

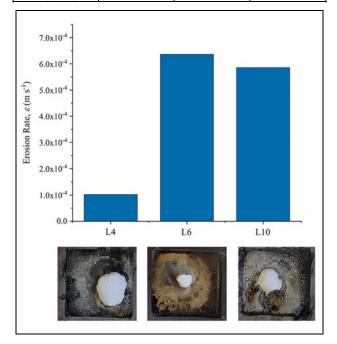


Figure 7. Comparison of erosion rates and appearance of liner insulation material samples after ablation testing

Back-face temperature for L4 reaches 102 °C when the surface temperature exceeds 3000 °C and linear erosion rate is 0.10263 mm s⁻¹, which is considerably lower than those observed for the other two samples (500% and 600%), as shown in Table 4 and Figure 7. These results

are mainly attributed to the higher char yield that can take away more heat to successfully insulate the material beneath the ablated surface.

Considering that the L4 material proved to be good in sense of casting viscosity (after IDPI addition in formulations), satisfactory mechanical characteristics and ablation resistance with small erosion rate, it can be concluded that this material completely meets the requirements of insulating material compared to other two.

5. CONCLUSION

In this work were developed three newly composite materials as a liners based on HTPB and reinforced with carbon fibers and inorganic filler powders, such as ATH, SiC, SiO₂ and ZrO₂. Prepared liner materials with a range of weight loadings of CFs and IFPs, with different NCO/OH ratios, were monitored for their processability and required rheological, mechanical and thermal properties. Prepared L4 material has the most desirable required properties for the majority of applied CRPs, i.e. adaptable mechanical properties, sufficient glass transition temperature and low erosion rate. Casting viscosity ensures good processability of the material while the density value corresponds to the general requirements. According to the same properties of studied L6 material, it is concluded that material formulation is adaptable in correlation to propellant properties and liner/insulation requirements. In addition, a special advantage of studied materials is that the binder has been based on the same polymer system as the composite solid propellant, thus it is considered reasonable to assume that the liner has the same mechanical properties as the propellant.

On the basis of such a composition, research should be continued and test methods should be expanded to application. In a specific optimize its complementary tests should be carried out with a proper rocket motor which should be stored at different temperatures and also test fired to secure no breakage at the long-duration stresses and strains that will occur during prolonged storage and firing. Some of the indispensable tests are the adhesion tests and examination of migration of individual components, depending on the correctly selected materials and construction of the rocket Such studies of ablative and adhesive compositions of HTPB with novel additives, including different nanomaterials and particularly graphene oxide, emerge as novel and evolutionary SRM alternative research path.

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