12th INTERNATIONAL SCIENTIFIC CONFERENCE ON DEFENSIVE TECHNOLOGIES
OTEH 2026
Serbia, Tara, 21 - 24 October 2026

EFFECT OF SIO_2 NANOPARTICLES ON THE MECHANICAL PROPERTIES OF POLYURETHANE THERMAL INSULATION LINERS

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Abstract: *This study investigates the development and characterization of thermal insulation composite liners (L) based on hydroxyl-terminated polybutadiene reinforced with carbon fibers of different lengths and modified with silicon dioxide nanoparticles (nano-SiO_2). The aim of this study was to examine the influence of nano-SiO_2 contents on the physicochemical and mechanical properties of the liners. The prepared composite liners were characterized by Fourier transform infrared (FTIR) spectroscopy, physicochemical analyses, and uniaxial tensile testing. The obtained results showed that the addition of nano-SiO_2 affects the dynamic viscosity of uncured composite liners, density and mechanical properties of the cured composite liners, indicating the importance of proper nano-filler dispersion and compatibility with the polymer matrix. This study provides a foundation for further optimization of liner formulations intended for rocket motor thermal protection systems. The results suggest that improved dispersion of nano-SiO_2 could further enhance the overall properties of the composites.*

Keywords: *composite liner, nano-SiO_2, dispersion, physical and mechanical properties*

1. INTRODUCTION

Thermal protection and structural integrity of solid rocket motors are highly dependent on the materials located between the propellant grain and the motor case. In composite solid rocket motors the propellant is bonded to the motor case through an elastomeric interfacial layer known as a liner. Positioned between the propellant and the motor case wall, the liner provides adhesion, transfers mechanical stresses and contributes to the overall integrity of the motor system [1].

Reliable bonding between the liner, propellant and motor case is essential for the proper operation of a solid rocket motor [2]. The liner acts as a structural interface responsible for stress transfer to the load-bearing components and prevents propellant grain movement. Loss of adhesion may lead to void formation, pressure fluctuations, unstable combustion, motor failure or explosion [3].

Therefore, the liner formulation must be chemically compatible with the propellant constituents while also being capable of establishing a stable chemical bond with them. To ensure such compatibility, the liner binder is typically based on the same polymeric system used as the binder in the propellant formulation [1]. In this study hydroxyl-terminated polybutadiene (HTPB) was used as the polymer matrix. HTPB is one of the most widely used binders in composite solid rocket propellants due to its favorable mechanical, thermal and chemical properties. It is characterized by a low glass transition temperature, pronounced hydrophobicity and a high concentration of terminal hydroxyl groups, which enable effective crosslinking with isocyanate curing agents forming a cross-linked polyurethane network.

Fibrous reinforcements, such as short Kevlar or carbon fibers, and flame retardants or intumescent additives, such as melamine or ammonium polyphosphate, improve the thermal properties of HTPB-based composite liners by forming a thermally protective char layer.

Moreover, liner composite formulations filled with micron-sized particles generally exhibit limited mechanical and functional properties. The development of nanocomposites, based on ultrafine fillers in the nanometer scale, enables significant improvements in mechanical, thermal and dynamic-mechanical performance compared to microfilled systems. The properties of these materials depend on the degree of cross-linking of the polymer matrix, the functional group

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DOI: 10.5937/OTEH26132P

ratio (NCO/OH) and the type and content of fillers. Increased cross-linking density leads to higher stiffness and elastic modulus, while reducing elongation at break and swelling capacity. Therefore, functional fillers are used to optimize performance by simultaneously enhancing mechanical and barrier properties.

In this context, silicon dioxide nanoparticles (nano-SiO_2) is recognized as an effective filler due to its high specific surface area and excellent thermal stability. It contributes to improved mechanical properties and reduced migration of low-molecular-weight components [4]. However, its pronounced hydrophilicity may lead to particle agglomeration, making controlled dispersion within the polymer matrix essential [5].

The aim of this study was to investigate the effect of different nano-SiO_2 contents on the physicochemical and mechanical properties of HTPB-based thermal insulation liners containing carbon fiber reinforcement and flame-retardant additives for solid rocket motor applications. A four liner formulations containing various amounts of nano-SiO_2 were prepared and characterized. The influence of nano-SiO_2 concentration on thermal insulation liner performance was evaluated in order to identify the optimal filler content and to improve the overall material properties.

2. MATERIALS AND METHODS

2.1. Materials

For the preparation of thermally insulating liner formulations, several components were used. Hydroxy-terminated polybutadiene (HTPB) (average molecular weight, Mn: 2900 g·mol^{-1} and hydroxyl functionality: 2.4, glass transition temperature, T_g: -80 ºC) supplied by Evonik, Germany, was used as the polymer binder. Carbon fibers of different geometries were used as reinforcing fillers, including milled carbon fibers (0.2 mm) and chopped carbon fibers (3 mm), purchased from R&G Faserverbundwerkstoffe GmbH, Waldenbuch, Germany (Figure 1) and carbon nanofibers (CNFs) (purity ≥ 99.9%, 1-15 µm). Additional carbon fillers were used to improve the thermal stability and mechanical performance of the liner systems.

Ammonium polyphosphate (APP) and melamine (purity ≥ 99.8%) both procured by Thermo Scientific Chemicals, Germany, were incorporated as additives to enhance the thermal resistance and flame-retardant properties of the formulations.

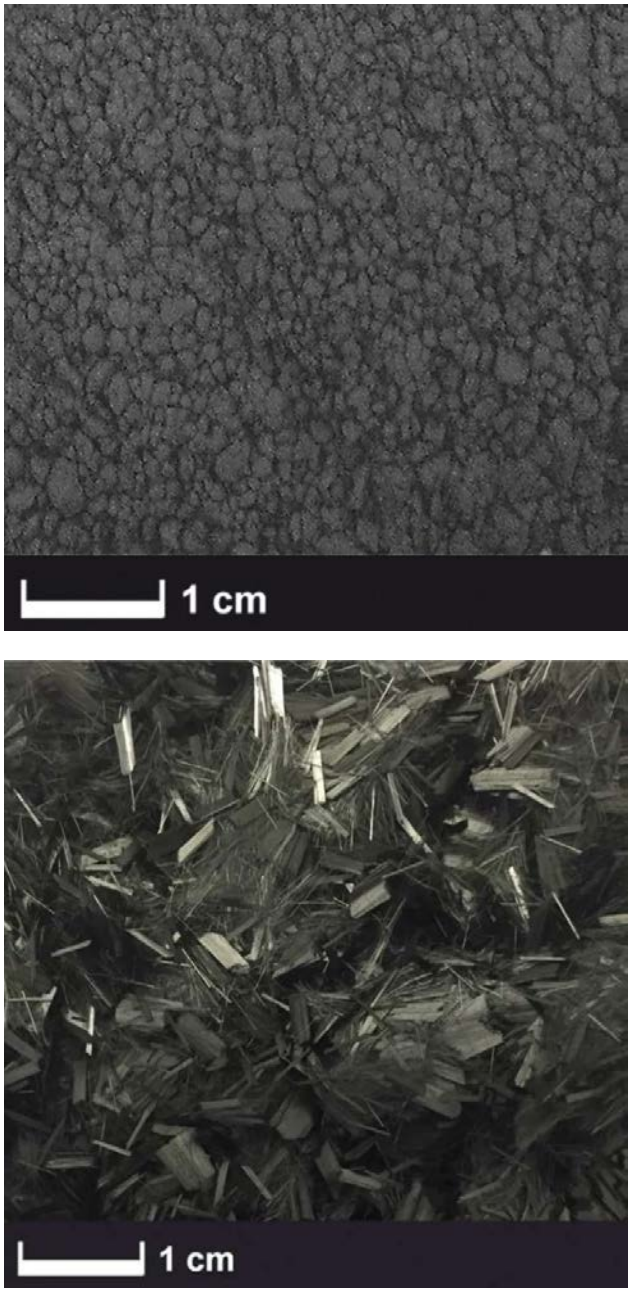


Figure 1. a) Milled carbon fiber 0.2 mm b) Chopped carbon fiber strands 3 mm (retaken from the R&G Faserverbundwerkstoffe GmbH)

Castor oil (*Ricinus communis seed oil,* functionality: 3, average molecular weight, Mn: 933 g·mol^{-1}) was used as a reactive plasticizer. The NCO/OH ratio in the formulations was adjusted to 0.33 to control the crosslinking density. The antioxidant AO 2246 (2,2'-bis(4-methyl-6-tertbutyl) phenol) supplied by Sigma Aldrich, Germany, was used to prevent oxidative degradation of the polymer matrix. Isophorone diisocyanate (IPDI) supplied by Evonik, Germany, while dibutyltin dilaurate (DBTDL) was used as a catalyst for the curing reaction. Nano-SiO_2 (purity ≥ 99.5%, particle size in the range of 20-30 mm), purchased by Speed UP (US Research), was used as a nano-filler to improve mechanical reinforcement and thermal stability of the liner systems.

2.2. Homogenization of the liners

Mixing and homogenization of the components (Table 1.) were carried out in a laboratory DRAIS mixer (1.5 L capacity) at room temperature and a stirring speed of 40 rpm. In the first stage, HTPB, RU and DBTDL were added into the mixing vessel. Subsequently, AO2246, APP, melamine, chopped and milled carbon fibers and nano-SiO_2 were gradually added in small portions under continuous mixing. Finally, the IPDI curing agent was added into the mixture and homogenization was continued at room temperature for an additional 15 minutes to ensure a uniform dispersion of all components. The liquid mixture was then cast into a PTFE mold (200 mm × 200 mm × 3 mm) and cured in an oven for four days at 60 ºC.

Table 1. Composition of liners

Component	Mass content (wt. %) of liner formulations			
	L1	**L2**	**L3**	**L4**
HTPB	36.57	36.77	36.89	36.97
Castor oil	5.85	5.88	5.90	5.91
AO 2246	0.18	0.18	0.18	0.18
Melamine	25.00	25.00	25.00	25.00
APP	25.00	25.00	25.00	25.00
CNFs	0.50	0.50	0.50	0.50
Carbon fibers; 0.2 mm	2.40	2.40	2.40	2.40
Carbon fibers; 3.0 mm	0.50	0.50	0.50	0.50
Nano-SiO_2	**0.50**	**0.25**	**0.10**	**-/-**
DBTDL	0.06	0.06	0.06	0.06
IPDI	3.44	3.45	3.47	3.47

2.3. Characterization of Materials

The remaining amount of the uncured liner was used for the determination of dynamic viscosity using Brookfield HBT viscometer at 25 ºC. Measurements were performed during the first 75 minutes after completion of the mixing procedure and incorporation of all components.

The Fourier transform infrared spectroscopy (FT-IR) spectrum of the cured liners was recorded in absorbance mode using a Nicolet™ iS™ 10 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA), within a range of 400-4000 cm^{-1} at a resolution of 4 cm^{-1}.

The density of the cured liner formulations was determined using a KERN YDB-03 analytical balance (Version 1.4; 2021-003) at 23 ºC.

For the evaluation of mechanical properties, test specimens were prepared with dimensions of 115 x 25 x (3 ±1) mm and a gauge length of 46.5 mm. Mechanical testing was performed on an Instron 1122 Universal Testing Instrument (Instron, Nortwood, MA, USA) at 20 ºC with a loading rate of 50 $mm \cdot min^{-1}$.

The following mechanical properties were determined:

- tensile strength (σ_m),
- elongation at maximum force (ε_m), and
- elongation at break (ε_p)

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis

FTIR analysis was used to evaluate the chemical structure of the prepared liner formulations and to confirm the formation of the polyurethane network during the curing process. The FTIR spectra of samples L1 – L4 are shown in Figure 2. The absorption bands at 3463 and 3516 cm^{-1} are assigned to N-H stretching vibrations characteristic of polyurethane structures, while the weak band at 3322 cm^{-1} indicates the presence of residual hydroxyl groups that did not fully react during network formation. The absorption bands at 2916 and 2845 cm^{-1} correspond to aliphatic (-CH_2-) stretching vibrations of the HTPB backbone. The characteristic band at 1706 cm^{-1} corresponds to the stretching vibration of the urethane carbonyl group (C=O), confirming the formation of the polyurethane structure. The band at 1640 cm^{-1} is assigned to C=C stretching vibrations of residual unsaturated bonds within the polybutadiene chains.

Bands at 1516 and 1435 cm^{-1} are attributed to N-H bending and C-H bending vibrations, respectively, while the peak at 1238 cm^{-1} corresponds to C-N stretching vibrations within the urethane structure. In the lower wavenumber region, absorption bands at 964 cm^{-1} and 910 cm^{-1} confirm the presence of Si-O-Si and Si-O vibrations, confirming the presence of nano-SiO_2 particles within the polyurethane matrix.

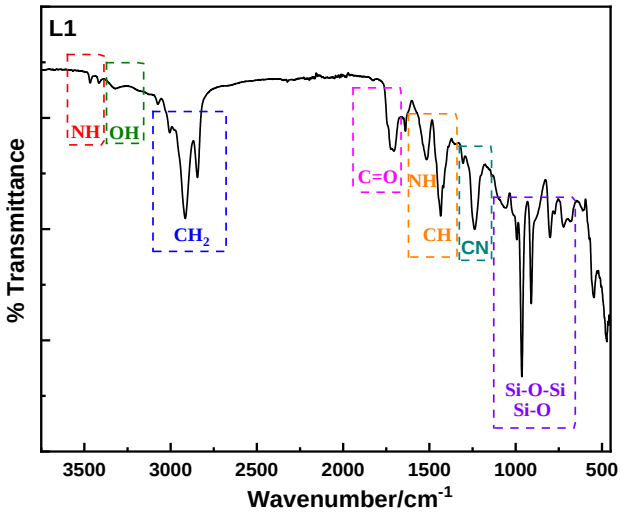


Figure 2. FTIR analysis of the liner L1

3.2. Viscosity measurements of uncured composite liners

After the homogenization process, the liner must exhibit an appropriate viscosity to ensure proper casting and application onto the inner wall of the rocket motor chamber. The time during which the material retains suitable rheological properties for processing is defined as the gelation time – *pot life*. This parameter depends on the resin-curing agent system, as well as on the type and content of fillers and other additives.

The viscosity of uncured liner formulations changes over

time and represents a key parameter for *pot life* determination. Therefore, dynamic viscosity was measured at 15-minute intervals after homogenization, over a total period of 75 minutes, which was considered sufficient for the planned application procedure.

The results are presented in Table 2, while the corresponding graphical representation is shown in Figure 3.

Table 2. Dynamic viscosity of uncured liner formulations.

Time (min)	Dynamic viscosity (Pa·s)			
	L1	L2	L3	L4
15	592	624	736	800
30	736	816	752	1072
45	/	/	800	1312
60	912	1088	896	/
75	/	1184	992	/

Note: L1-L4 represent different liner formulations with different contents of nano-SiO_2

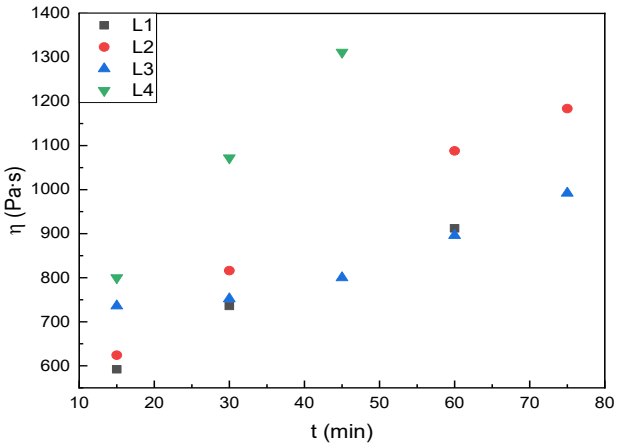


Figure 3. Comparison of the initial viscosity of experimental liner formulations

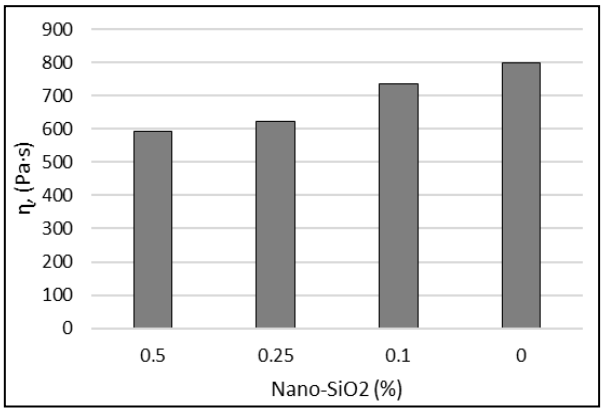


Figure 4. Dynamic viscosity 15 minutes after IPDI addition

Based in the time-dependent viscosity profiles, an increase in viscosity over time is observed, confirming the progress of crosslinking reactions. The results show that sample L4, without nano-SiO_2, exhibits the fastest and most pronounced viscosity increase (Figure 4). With increasing nano-SiO_2 content, the initial viscosity is partially reduced. However, sample L1, containing the highest nano-SiO_2 content (0.5 wt.%), shows the lowest viscosity after 15 minutes from the addition of the curing agent.

The decrease in viscosity with increasing nano-SiO_2 content is attributed to nano-particle dispersion within the HTPB/IPDI matrix. Such insertion of nano-SiO_2 between HTPB polymer chains and IPDI cross-linker partially interrupts the crosslinking reaction. The gradual viscosity decrease at higher nano-SiO_2 contents extends the gelation time and improves control of the liner application process.

3.3. Density determination

A key requirement for thermal insulation liners is low density (1.05-1.10 g·cm^{-3}) to reduce the overall mass of the propellant grain. The addition of fillers requires a balance between improved thermal stability and ablation resistance and the resulting increase in density. High-density fillers such as silicon dioxide contribute to the formation of a more stable char layer. However, their content must be optimized to maintain low liner density. The average density values of the prepared formulations are presented in Figure 5. A slight increase in density with increasing nano-SiO_2 content was also confirmed.

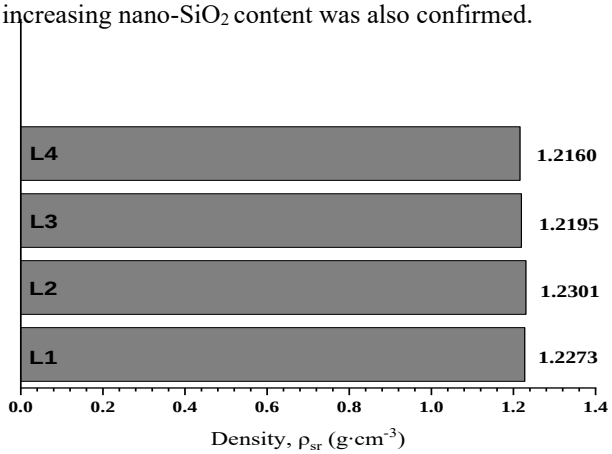


Figure 5. Density values of liner formulations L1-L4.

Note: The reported values are the average of four measurements.

3.4. Mechanical characterization

Mechanical testing was performed to evaluate the effect of nano-SiO_2 content on the tensile properties of the developed liner formulations (Figure 6). The obtained values of tensile strength, elongation at maximum force, elongation at break and Young's modulus (Table 3) indicate that the incorporation of different amounts of nano-SiO_2 significantly affects the mechanical behavior of the liners.

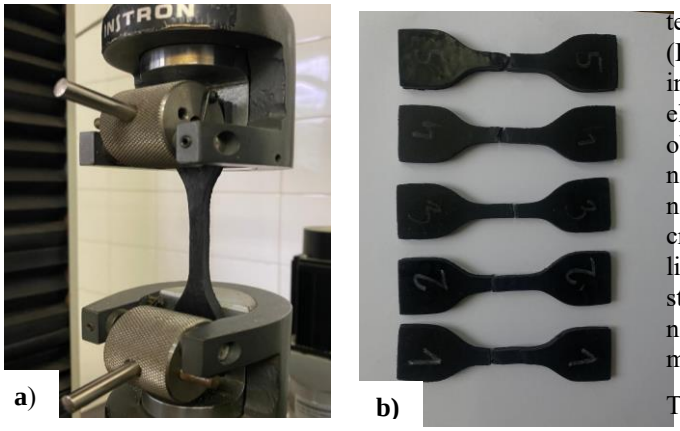


Figure 6. Appearance of L2 specimens before (a) and after (b) tensile strength testing

The polymer structure and mechanical performance of polyurethane-based liners are directly related to the degree of cross-linking achieved during the curing process. Highly cross-linked networks generally exhibit increased stiffness and tensile strength, while lower cross-linking densities promote greater flexibility and elongation. The tested formulations demonstrated typical elastomeric behavior characterized by large reversible deformations under tensile loading.

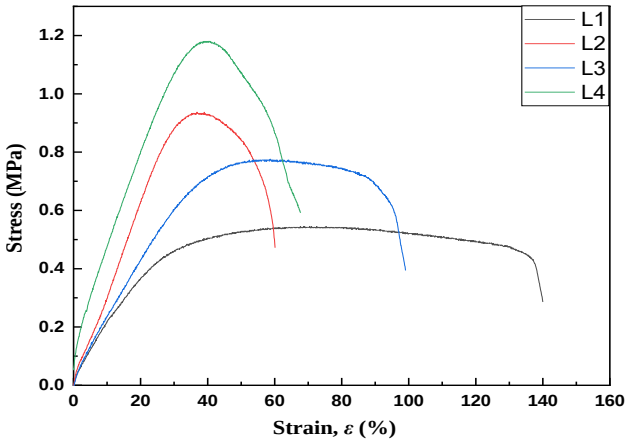


Figure 7. Stress-strain curves of the tested materials L1-L4

Table 3. Tensile strength, deformation at maximum force and at break and Young's modulus of the tested materials at T=20 ºC.

	σ_m, [daN/cm^2]	ε_m, [%]	ε_p, [%]	E [MPa]
L1	5.66 ± 1.30	51.97 ± 14.77	116.23 ± 23.68	1.08 ± 0.02
L2	9.34 ± 1.14	39.59 ± 8.25	66.85 ± 15.98	3.98 ± 0.02
L3	8.30 ± 1.34	52.54 ± 11.98	90.50 ± 29.54	3.98 ± 0.01
L4	10.75 ± 1.51	49.75 ± 10.78	79.22 ± 27.72	3.98 ± 0.01

Note: The reported values are the average of five measurements.

Among the investigated samples, L1 containing the highest nano-SiO_2 content (0.5 wt.%) exhibited the lowest tensile strength and the highest elongation at break (Figure 7). As the nano-SiO_2 content decreased, a gradual increase in tensile strength accompanied by a decrease in elongation at maximum force and elongation at break was observed. This behavior suggests that higher amounts of nano-SiO_2 contribute to the more pronounced insertion of nano-SiO_2 between HTPB polymer chains and IPDI cross-linker which significantly interrupts the cross-linking reaction. Moreover, the reduction in tensile strength may be attributed to the tendency of silica nanoparticles to form agglomerates within the HTPB matrix.

The observed decrease in tensile strength with increasing nano-SiO_2 content is consistent with literature data and can be primarily associated with nanoparticle agglomeration [7]. At lower concentrations, nano-SiO_2 particles are more uniformly distributed within the polymer matrix, whereas increasing particle content promotes particle-particle interactions and the formations of larger agglomerates. These agglomerates act as stress concentration sites and facilitate crack initiation during tensile loading, leading to a reduction in tensile strength Furthermore, the optimal values of tensile strength and elongation at break and maximal force were obtained for sample L3 indicating an optimal homogenization condition and nano-SiO_2 distribution.

Overall, the obtained results indicate that the mechanical performances of the developed liners are strongly dependent on the dispersion state of nano-SiO_2 and the resulting structure of the polyurethane network. Surface modification of nano-SiO_2 with reactive organosilane coupling agents, such as amino-, epoxy-, or isocyanate-functionalized silanes, represents a promising strategy for improving nanoparticle dispersion and overcoming compatibility limitations.

4. CONCLUSION

The influence of nano-SiO_2 and carbon nanofibers on the properties of HTPB-based thermal protection liners was investigated. FTIR analysis confirmed the formation of polyurethane bonds and successful curing of all developed formulations. Rheological measurements showed that the incorporation of nano-SiO_2 affected the viscosity evolution and *pot life* of the liner mixtures, indicating its influence on the curing process and network formation.

Mechanical testing revealed that increasing the nano-SiO_2 contend led to a decrease in tensile strength and an increase in elongation at break. The highest tensile strength was obtained for the formulation without nano-SiO_2 content exhibited the greatest elongation. These results were attributed to the tendency of nano-SiO_2 particles to agglomerate within the polymer matrix, affecting the degree of crosslinking and the homogeneity of the polyurethane network.

The obtained results demonstrate that the content and dispersion of nano-SiO_2 play a crucial role in determining the processing characteristics and mechanical performance of HTPB-based liners. Further optimization

of nanoparticle dispersion and surface modification of nano-SiO_2 may provide additional improvements in liner properties and contribute to the development of advanced thermal protections materials for rocket motor applications.

Acknowledgments

This work was supported by the Ministry of Science, Technological development and Innovations (Serbia), (Contract No. 451-03-34/2026-03/200325).

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