Review Article

Javier Carlos Quagliano Amado*, Pablo Germán Ross, Natália Beck Sanches, Juliano Ribeiro Aguiar Pinto, Jorge Carlos Narciso Dutra

Evaluation of elastomeric heat shielding materials as insulators for solid propellant rocket motors: A short review

<https://doi.org/10.1515/chem-2020-0182>

received September 26, 2020; accepted November 3, 2020

Abstract: This review addresses a comparison, based on the literature, among nitrile rubber (NBR), ethylene-propylene-diene-monomer rubber (EPDM), and polyurethane (PU) elastomeric heat shielding materials (EHSM). Currently, these are utilized for the insulation of rocket engines to prevent catastrophic breakdown if combustion gases from propellant reaches the motor case. The objective of this review is to evaluate the performance of PU–EHSM, NBR–EHSM, and EPDM–EHSM as insulators, the latter being the current state of the art in solid rocket motor (SRM) internal insulation. From our review, PU–EHSM emerged as an alternative to EPDM–EHSM because of their easier processability and compatibility with composite propellant. With the appropriate reinforcement and concentration in the rubber, they could replace EPDM in certain applications such as rocket motors filled with composite propellant. A critical assessment and future trends are included. Rubber composites novelties as EHSM employs specialty fillers, such as carbon nanotubes, graphene, polyhedral oligosilsesquioxane (POSS), nanofibers, nanoparticles, and high-performance engineering polymers such as polyetherimide and polyphosphazenes.

* **Corresponding author: Javier Carlos Quagliano Amado**, Applied Chemistry Department, Institute for Scientific and Technical Research for the Defense (CITEDEF), Ave. JB de La Salle 4397 B1603ALO, Buenos Aires, Argentina, e-mail: jquagliano@citedef.gob.ar

Pablo Germán Ross: Applied Chemistry Department, Institute for Scientific and Technical Research for the Defense (CITEDEF), Ave. JB de La Salle 4397 B1603ALO, Buenos Aires, Argentina

Natália Beck Sanches: Coordenação de cursos, Universidade Guarulhos (UNG), R. Eng. Prestes Maia, 88 – Centro, CEP 07023-070, Guarulhos, SP, Brazil

Juliano Ribeiro Aguiar Pinto: Instituto de Aeronáutica e Espaço (IAE), Divisão de Produção de Motores (APM), Estrada municipal LúciaMarcondes, km 4,5, Varadouro, 12315-020, Jacareí, SP, Brazil

Jorge Carlos Narciso Dutra: Departamento de Química, Instituto Tecnológico de Aeronáutica (ITA), Praça Marechal Eduardo Gomes, 50, Vila das Acácias, CEP 12228-900, São José dos Campos, SP, Brazil

Keywords: EHSM, EPDM, NBR, polyurethane, thermal insulation

1 Introduction

Thermal protection systems (TPS) are materials that shield the metallic or the composite casing of rocket engines by undergoing a process called ablation, which is the thermal decomposition under high temperature (pyrolysis) of the organic constituents that form the char layer. The ablated layer acts as a barrier against the high mass and heat transfer during the solid propellant combustion. The high temperatures present during SRM combustion have been found to very easily destroy even the strongest metallic alloys. If not appropriately protected, the case may experience extremely harsh conditions that lead to total destruction through explosion [1,2].

During the ablation process of a TPS, three main zones are formed (Figure 1):

- The charring zone: The first zone that is affected by the high temperature in the solid propellant combustion process giving rise to the char layer.
- The pyrolytic zone: Region between the charring zone and the virgin material, where the TPS decomposition and pyrolysis processes occur.
- The virgin TPS zone: Region that consist on unreacted TPS [3,4].

The char layer is formed in the charring zone and is the mainly responsible for the success of the ablative TPS. The stronger and stable the char layer is, the slower the consumption of TPS will be, which results in a low ablation rate. Microstructure origin of heat shielding of temperatures in the range of 2,000–3,000°C is mainly the formation of a thick layer of char, which insulates the

Figure 1: The three main regions formed during the ablation process [4].

underlying material from the hot gases coming from burning propellant [5,6].

The ablation rate determines the ablation performance of a TPS and indicates how resistant a TPS is when under the effect of a propellant combustion. The ablation rate expresses the recession or consumption of the TPS material during a given amount of time (Figure 2). According to ASTM E-285-08, this value is measured by the ratio between initial and final thickness and time during the ablation test [5,6].

The oxyacetylene torch test is the most simple and inexpensive ablation test, in which the TPS material is exposed to a flame of a torch provided by a mixture of acetylene and oxygen under controlled conditions (pressure, flow, and temperature) [6].

However, as the TPS materials have improved over the years adjusting to the new space programs, new equipment had to be developed to quantify the ablation rate of the novel TPS materials [3]. Arc-jet torches, electrodeless torches, and small-scale rockets are some examples of the ablation test equipment currently used. Table 1 presents the operating cost estimated for their utilization [3,7].

To minimize the costs measuring the ablation properties of TPS, since the 1950s several computational codes (programs) have been developed to simulate the pyrolysis and the ablation of a TPS material under hyperthermal environment conditions, pressure, mass, and heat flux.

Figure 2: Recession of TPS material under the ablation test [5].

Table 1: Operating cost estimate for some ablation tests [3,7]

Test equipment	Operating cost estimate
Oxyacetylene ablation test	Low cost
Small-scale rocket test	Medium to high cost
Arc-jet torch and electrodeless test	High cost

Table 2 presents some simulation programs used for the design and the analysis of TPS [7].

According to the study by Natali et al. [7], all indicated simulation programs are aimed at the optimization of the studies and developments of TPS, so that the test laboratories can lower the operating costs.

2 Polymeric insulators for solid propellant rocket motors

The development of rocket motors has propelled studies assessing plastics as heat insulators since the 1960's [8]. Since then, the ablation mechanisms of elastomeric rocket motor thermal insulators have been established. Research in this field has increased significantly, and several excellent reviews have been published in recent years [7,9–12] from leading countries such as China, India, Iran, Italy, Russia, and the United States.

South American countries have also contributed to the development of materials in the field of rocket science [4,5,13–16]. By forming an inner lining on the inner surface of rocket motors, insulators prevent their exposure to the extremely high-temperature gases of the propellant during combustion and help the integrity of motor without failure during operation [17].

Table 2: Simulation programs for ablation properties

Program	User	Application
CMA	NASA, SNL	Design
FIAT 3D	NASA, ARC	Analysis
FABL	ISA/ESA/FG E	Analysis
SCMA2	JAXA	Not available

CMA: Aerotherm's Charring Material Thermal Response and Ablation Program. NASA-SNL: NASA's Sandia National Laboratory. FIAT 3D: Fully Implicit Ablation and Thermal Analysis Program. NASA's Ames Research Center. FABL: Fluid Gravity Engineering Ablation code. ISA/ESA/FG E: Israel Space Agency/European Space Agency. SCMA2: Super Charring Material Ablation. JAXA: Japan Aerospace Exploration Agency.

Polymeric ablatives, such as fiber-reinforced polymeric ablatives (both rigid and elastomeric), heat shielding materials (HSM), lightweight ceramic ablators, and nanostructured polymeric ablatives are materials that act as thermal insulators. The most promising materials for manufacturing HSM are elastomers, among them rubbers, foamed rubbers, and rubber-fabric or rubber-fiber composite materials [18]. Rubbers present a limited resistance to high temperatures (around 300–400°C). Therefore, they cannot endure severe environments such as those found in a rocket motor: very high temperature, pressure, and high-speed flow erosion. However, the incorporation of several fillers in the composition could enhance these properties [19].

The most important material properties required for ablative resistance are low density, low thermal conductivity, high temperature resistance, formation of a stable char, and high char shear strength [9,20,21] and also good erosion performance [22]. Thermal insulation must also bond to propellant and casing and inhibit propellant grain surfaces. Internal thermal insulations use elastomeric materials with various powders or fibers that are designed to enhance the material properties. From the thermal point of view, a material should have low thermal conductivity and high specific heat. For finding the best candidate materials and their combinations (elastomer plus mineral fillers and/or fibers), several models and theoretical developments are continuously under way [23,24].

Gajiwala and Hall [25] have proposed a universal insulation composition, which could be used on different parts of a particular rocket engine or artifact. The insulation material proposed was formulated on the basis of EPDM rubber and filled with silica and magnesium oxide and was able to protect against heat, erosion, and other extreme conditions experienced by the engine or artifact during use and operation. The enhanced composition was able to improve mechanical, physical, rheological, thermal, and ablative properties compared to conventional silica-filled EPDM-based insulations.

Organic elastomers suitable for use in insulators include ethylene propylene-diene monomer (EPDM) rubber, nitrile rubber (NBR), and polyurethane (PU) rubbers. Others are polybutadiene, polyisoprene, butadiene-styrene copolymer, and natural rubber. Although main advances originated in developed countries, South American-specific reports are available in the state of the art, particularly on EPDM [12,13,15,26–29].

This review does not include rigid heat shielding materials, which is a special area of study involving other types of materials particularly suited for low orbit and

space vehicles, such phenolic resin, silicon oxides, and ceramics [30,31].

2.1 Main types of elastomeric heat shielding materials

Main types of elastomeric heat shielding materials (EHSMs) were classified into three different main categories: ethylene propylene diene rubber (EPDM), nitrile rubber based, and silicone based, as reviewed by leading authors in the field [7,9,10]. However, PU EHSM could be included in this classification, emerging as an alternative in the field of EHSM.

2.1.1 EPDM-based and nitrile-based heat shielding materials

Currently, EPDM represents one of the best matrices among elastomers used on solid rocket motor (SRM) liners [17]. Solid rocket motor is a rocket engine that uses solid propellant as fuel. Combustion produces gases that are expanded through a nozzle to generate thrust. EPDM/aramidic ablatives were reported as the state of the art in ablatives [9,12,32]. Sureshkumar *et al.* [33] have pointed out the excellent potential of EPDM as insulator regarding its ageing resistance, low-temperature flexibility, low erosion rate, and low specific gravity. EPDM typically starts to decompose at around 400°C [34]. It is preferred for military applications because of its outstanding ageing resistance characteristics.

As a secondary polymer to EPDM, hydroxy terminated polybutadiene (HTPB) has been successfully used as an adhesion-promoting polymer [35]. Aramid fibers (Kevlar or Twaron brand) or in the form of pulp is the most used fiber in EPDM-based SRM liners and has been successfully employed as a low density reinforcement [36,37]. Figure 3 shows the structural units of polymers cited.

Aramid fibers in the EPDM matrix increase the mechanical properties of rubbers, ensuring higher resistance to erosion and significantly enhanced ablative properties. This reinforcement prevents the virgin material from being exposed to the hot gases of the chamber, thus limiting degradation and allowing the use of the surface carbonized layer as a heat insulator [25]. Zirconium dioxide, a type of mineral oxide, has been tested for EPDM. Introduction of zirconium dioxide increases the coke

Figure 3: EPDM chemical formula and Kevlar fibers used as an example of reinforcement.

residue by 4–30% and when associated with graphite improves the physicochemical parameters relative to the sample containing zirconium dioxide only, ensuring the formation of a looser carbon–mineral coke structure and enhances coking on the surface of dispersed particles [38]. Figure 4 shows EPDM filled with 20% silica after the oxyacetylene test, which have proved to be effective as EHSM in our conditions. At that concentration, clear silica residues can be seen surrounding burn-through orifice.

EHSM based on nitrile rubber (NBR) have also been studied although not as thoroughly as EPDM-based EHSM. NBR is a synthetic copolymer of acrylonitrile and butadiene. Figure 5 shows the structural units of NBR-based EHSM.

Figure 4: EPDM filled with 20% silica after the oxyacetylene torch test (samples shown from ref. 29).

Figure 5: NBR EHSM and exemplary fillers utilized in them.

NBR often presents problematic processability, limited shelf life, high density ($1\text{--}1.3\text{ g/cm}^3$), and poor high temperature properties. Nevertheless, the nitrile rubber is still used as an insulation liner for solid rocket motors (SRMs) [9], although not to the extent of the EPDM-based EHSM, according to the number of studies published. In some cases, NBR have displayed better than EPDM insulators: vulcanizates based on nitrile rubber with melamine fiber resulted in 15–20% lower thermal erosion rates than EPDM ones [39].

NBR-based EHSMS have good adhesion to solid rocket propellant. They have achieved ablation rates as low as 0.06 mm/s [40] although EPDM based can be as low as 0.015 mm/s . The incorporation of 15 phr of silica aerogel into NBR rubber has decreased the mass of insulator and its linear ablation rate by 15% and 29%, respectively. Silica aerogel has played an effective role in reduction of the back-face temperature of insulators [41]. Thermal stability of NBR-nanoclay composites and the char content at 500°C were calculated from TGA thermograms. The thermal stability of the composites has been enhanced with the addition of nanoclay. The char content of the nanocomposites at 500°C has increased with nanoclay content [42]. Moreover, the use of the coupling agent 3-(mercaptopropyl) trimethoxy silane for incorporating montmorillonite nanoclay (MMT) in a MMT/NBR nanocomposite enhanced thermal resistance [43]. Linear ablation rates as low as 0.012 mm/s have been reported for organoclay/NBR nanocomposite HSM. Modeling of these ablative nanocomposites has been performed to determine the exact required thickness of the insulator and the temperature distribution across it at specific thermal conditions [44]. Figure 6 depicts NBR thermal protection of front and aft section of SRM after test on test bench.

Figure 6: NBR thermal protection: (a) front section and (b) aft section: after test on test bench. Source: Dr. Dutra's laboratory.

2.1.2 Silicone-based heat shielding materials

Silicone-based EHSM are found in the state of the art of insulator formulations [9,11,45] specially for specific spacecraft applications, many times using costly additives such as the polyhedraloligosilsesquioxane (POSS) and carbon fibers. Silicones release an inorganic silica residue after exposure to elevated temperatures under oxygen atmosphere, which serves as an insulating layer to the polymer surface underneath, protecting it from the exposure to the external heat flux. However, the poor mechanical properties associated with silicones severely restrict their utility [46]. Regarding ablation performance, Wu *et al.* [47] have concluded that with a 1:1 blending ratio of silicone/EPDM, the linear ablation rate was 0.06 mm/s after 20 s of the oxy-acetylene ablation test compared to the much lower result of the EPDM insulation (0.215 mm/s). This result highlights the usefulness of silicone as additive in EHSM formulations. Gao and Liu [48] have proved the capability of silicone/benzoxazine resin as ablative material, with an ablation rate as low as 0.065 mm/s with a 20% resin formulation compared to 0.114 mm/s of the control sample.

To achieve an efficient silicone-based EHSM, fillers, fibers, vulcanizing agents, and flame retardant additives are to be incorporated to silicone rubbers.

2.1.3 Polyurethane-based heat shielding materials

Regarding polyurethane elastomeric heat shielding materials (PU-EHSMs), contributions in this specific area

are scarce although the thermal stability of PU composites could be very high, as recently reviewed [12,49]. Figure 7 shows PU-EHSM and most common reinforcements utilized in them.

Among the few published reports, Benli [50] has determined the erosion rate and thermal conductivity of a HTPB-based PU elastomer with silica, alumina, zirconia, and carbon black as mineral fillers. The lowest ablation rate (0.324 mm/s) was achieved with 10% carbon black. As mentioned in his thesis dissertation, Lee [51] has utilized Desmopan[®] DP 6065A, a soft aromatic polyether-based thermoplastic polyurethane elastomer (TPU) from Bayer to prepare a PU-EHSM. Three different nanomaterials (carbon nanofibers, multiwall carbon nanotubes, and nanoclays) behavior were studied in environments simulating motor firing conditions. Results have showed that of these three nanomaterials, nanoclay enhances the TPU ablative performance the most.

Li [52] has published a comparative research on thermal insulation of HTPB-based PU composites, filled with different types of silica aerogel (SA) and hollow silica microsphere particles. Due to the characteristics of the opened SA pores, mixed interfaces of SA and polymer composites were formed, which decreased the thermal insulation performance. Conversely, this phenomenon has not been observed in the PU composites filled with an undisclosed heat shielding material of closed-cell structure [53].

A HTPB-based PU reinforced with POSS and its ablation behavior has been studied [54]. Results demonstrated that POSS molecules present significant influence on the ablative resistance because they act as protective

Figure 7: (a) PU-EHSM and most common reinforcements utilized in them. (b) PU-EHSM with titanium dioxide as reinforcement after the oxyacetylene test (ref. 57).

silica forming precursors under oxyacetylene condition. However, as stated earlier, currently, these additives are very costly.

HTPB-based PU insulators filled with polycarbodiimide and polysiloxane, which are reactive-type fillers, have been reported to protect the rocket motor from the high-temperature ablation. These modified PUs are a kind of organic–inorganic hybrid with higher modulus and thermal stability than original PU [55]. Lee [56], using matrix as a commercial soft PU, has reached the conclusion that Cloisite® 30B nanoclay displayed a better performance than multiwalled carbon nanotubes (MWCNTs) and carbon nanofibers by preventing the specimen from dripping like the neat material. PU-EHSM based on HTPB/IPDI filled with 5% Cloisite® 30B nanoclay showed a 40% reduction in the ablation rate compared to the unfilled material [57].

Thermoplastic polyurethane elastomer nanocomposites (TPUNs) were studied for ablative applications as alternatives to the other elastomeric matrix in EHSM. Mass loss, recession, and char thickness values were measured for PU formulations with 5 and 7.5% montmorillonite nanoclay (Cloisite® 30B) content. TPUN has shown the best results compared to the reference EPDM–Kevlar filled EHSM in recession and peak temperature measured, but not in mass loss in the oxyacetylene torch test [58].

Ho [59] proposed employing TPUN as EHSM to replace Kevlar-filled EPDM, the current state-of-the-art solid rocket motor internal insulation. Results have demonstrated that TPUNs developed primary polymer as internal insulation materials for solid rocket motor can be used as flame retardant materials for commercial usage as well. On another study, HTPB-based polyurethane was indicated as secondary polymer to enhance EPDM-based

EHSM performance, decreasing compound viscosity and achieving high resilience with low compression set with a blend containing 2 phr of HTPB [35].

The thermal behavior of PU films based on polyoxyethyleneglycol and isophorone diisocyanate (IPDI) as heat insulating material has been evaluated by the thermogravimetric analysis (TGA). Results have showed that the incorporation of tin oxide doped with antimony into the waterborne PU could improve thermal stability dramatically. The maximal decomposition temperature for filled PU increased from 278 to around 300–310°C [60]. These results showed that special oxides could significantly improve heat insulation in PU.

A novel phosphorus and nitrogen-containing flame-retardant polyurethane prepolymer (FRPUP) has been successfully synthesized and characterized. It was found that FRPUP can greatly enhance the char residues of PU sealants. Indeed, a char residue of 7.2% was found compared to the 1.5% residue of the control [61]. A PU obtained from HTPB and 4,4'-methylene bis cyclohexyl isocyanate (H_{12} MDI) and its nanocomposites with Cloisite 30B were tested as inhibitor material in composite propellants. The ablation rate and the density of the compositions containing Cloisite 30B were around 23% and 5% lower, respectively, compared to the base composition [62]. Schiariti and Bellomi [63] have registered a recent patent for an ablative inner coating layer for solid propulsion rocket engines made from a polymeric base, silica, vulcanizing agents, and plasticizers. This layer contains also aramid fiber and microspheres made of glass, quartz, and nanoclay. It is interesting that the author pointed out that the polymer basis of the composition could not only be traditional EPDM, NBR, or even SBR but also HTPB-based PU.

Considering the information available about PU–EHSM, it is possible that they could replace Kevlar®-filled EPDM for a number of reasons, primarily because PU–EHSM exhibit high ablation resistance and insulation characteristics with the appropriate reinforcement, combined with easy fabrication.

2.2 Bonding of EHSM to composite propellant

Proper bonding of EHSM to composite propellant is critical for solid rocket motor performance. Composite propellant is usually prepared with HTPB as a binder for oxidizer ammonium perchlorate particles and other ingredients. From this point of view, PU–EHSM is better as insulation materials because insulator and propellant are of the same chemical nature. Interfacial bonding of NBR and EPDM to HTPB/IPDI composite propellant revealed that both types of insulation layers considerably decreased bonding [64]. This can be expected, considering the different chemical nature of EPDM and NBR compared to the PU-cured propellant. However, these authors found that drying the insulation layer before spraying or brushing the liner can reduce the negative influence of the heat insulation layer on the bonding property at the interface. Also, to overcome the incompatibility issues, the use of an epoxy–polysulfide copolymer as adhesion promoter caused a significant improvement in the adhesion of EPDM terpolymer to polyurethane [65].

2.3 Fibers and fillers in EHSM

Proper mixing of fibers and fillers with rubber to deliver a good performance of thermal insulation composite is a key factor if nanofillers are to be used as EHSM. Proper wettability of filler and bond strength with rubber is a requisite for such diverse filler additives as a carbon fiber, aramid fiber, and a silica powder. It is also necessary that such additives be homogeneously dispersed throughout the insulation composite as it is being produced. Reinforcement to matrix fraction usually does not exceed 20%, as heat shielding property commence to be compromised. Proper wettability of filler with rubber matrix is a limit to increase the reinforcement fraction in composite.

Several simultaneous factors are involved, such as the mixing method, filler/fiber–matrix interaction, filler–filler

interaction, fiber–fiber interaction, particle surface area, and its activity [66]. Since surface-to-volume ratio of nanoparticles is very high, the resulting interphase fills a large part of the volume of the composite and can become the principal factor in developing the properties of nanocomposite. Excellent properties of nanocomposites can be reached only through new processing techniques that are able to produce a complete and homogeneous dispersion of the fillers [67].

Milhomem [68] have tested several unfilled matrices (epoxy, polyester, polyurethane, and silicone) and verified that the ablation rate was in all cases too high for them to be used as EHSM alone. Ablation rates were in the same extent as those of some solid fuels used in hybrid propulsion. Hence, fillers have to be added to the matrices to obtain good ablative results. Microspheres as density reducer fillers have been used in EPDM-based EHSMs. The material containing 20 phr of microspheres evidenced the best tradeoff among all properties. Perlite has also been tested, but did not survive the manufacturing process used [69].

Fillers generally employed in EHSM are conventional mineral oxides (as powders) and carbon black [50]. However, in recent years, materials such as wollastonite [11], silicate microspheres [40,69], POSS [54], nanofibers [58], nanoclays [70], nanosilica, nanoalumina, and carbon nanotubes [71,72] have been utilized.

Closed structures such as hollow glass microspheres in PU have been found to be advantageous on increasing thermal insulation compared to PU/silica aerogel composites [73].

Regarding fibers, reinforcing elastomeric matrix systems with synthetic fibers have been proved to result in better ablation properties and enhancement in thermal insulation behavior [74]. Historically, asbestos was the fiber of choice for reinforcing many materials and elastomers in particular although it is currently banned for health and safety reasons. Therefore, other alternatives have been emerged such as Kevlar [75], novel polymers such as polyimides [76], polybenzoxazol, or polysulfonamide [77,78]. Melamine fiber has caused a significant reduction in the thermal erosion rate of the EHSM vulcanizates [39].

High levels of fibrous reinforcing (up to 50 wt% on the matrix) have been added to the neat EPDM matrix to properly adjust the mechanical properties of the elastomeric liner [37]. Fibers usually have a higher thermal conductivity compared to the neat matrix, but generally if fibers are oriented parallel to the matrix, thermal conductivity is less affected [79].

Relative to metrics for evaluating performance of EHSM, ablation rates should range from 0.09 to 0.20 mm/seg;

Table 3: Comparison of main parameters for ablation performance of EPDM, NBR, and PU-based elastomeric heat shielding materials (EHSs)

Sample	Ablation rate (mm/s)	Thermal conductivity (W/m K)	Tensile strength (MPa)	Elongation (%)	Thermal properties TGA*	Ref.
EPDM matrix						
0–50% phr KF/EPDM	0.13–0.18	0.013–0.018 (calculated)	2–13	175–300	464–474°C	[9]
Control – MWCNT/EPDM	0.078–0.092	—	6.28–7.84	385–483	$T_{10\%}$ 29% higher than control	[83]
Aramid fiber-silica-ZnO/EPDM	0.11/0.12	—	—	—	TGA: 465°C	[84]
15 phr Kevlar/EPDM	0.03	—	—	—	—	[85]
Virgin EPDM, no additives or compounding	0.29 to 0.72 (different erosion conditions)	—	—	—	—	[86]
20% phr KP + 5% alumina + 5% silica + 40% dechlorane + 20% Sb ₂ O ₃ /EPDM	0.10	0.21	8.5	16	500°C maximal weight loss	[87]
Aramid fiber-PR-mineral oxide/EPDM	—	—	4.15	45	Max. loss 350°C	[88]
20% Wollastonite/EPDM	Max. T OAT test 202°C/5 mm	—	3.8	195	Max. weight loss 480–500°C	[11]
Sepiolite/EPDM – silica/NR EPDM	0.177/0.40 (control)	—	1.2–1.5	15	First transition 360–450°C	[89]
30 phr KP/EPDM	0.015	0.171	9.35	11.7	—	[90]
Kevlar/EPDM, composition not disclosed	0.151	—	1	700	53.45% loss at 670 K	[91]
25 phr CF/25 phr KP/EPDM	—	0.198	11	7.4	27% original mass*	[91]
SiO ₂ /EPDM	—	0.202	5.2	350	—	[25]
Polyurethane matrix						
20–50 phr KF/EPDM	—	0.363	—	—	—	[92]
5% nanoclay/HTPB-PU	0.42–0.69	n.d.	1.07//1.47	700//650	—	[57]
5% phr perlite/HTPB	0.70	—	1.22	130	—	[16]
POSS-PU	0.22–0.39	—	—	—	$T_{5\%}$ 260–285	[93]
HTPB-based PU	0.346	—	—	—	PHHR 1,037 kW/m ²	[94]
23% POSS/HTPB-based PU	0.298	—	—	—	PHHR 632 kW/m ²	[94]
10% Cloisite 30B/TPUN	Data not disclosed, but as 13.5% more mass loss than Kevlar/EPDM	0.2 (PU matrix)	—	—	80% weight loss at 400°C	[51]
5% Cloisite® 30B/TPU	—	0.40	—	—	450°C main loss (10°C/min); mass remaining 2–5%*	[59]
16% Al ₂ O ₃ /HTPB-based PU	0.13	0.30	1.877	411	—	[50]
5–15% nanoclay/Sb ₂ O ₃ /70–78% weight loss	0.169–0.199	0.25–0.4	—	—	382–488°C	[64]
Nitrile rubber matrix						
0% MMT/NBR//10% MMT/NBR	0.087//0.075	0.156//0.151	2.58//2.54	157//151	TGA: max. weight loss between 411–474°C	[95]
0% PR/NBR-50%/NBR	0.235/0.095	—	—	—	First loss 264.7/263.8°C	[96]
Silica and carbon phenolic/HNBR	<0.852	1.036 to 1.039	3.7 to 5.2	300 to 450	Max. weight loss 425 to 600°C	[97]
Carbon + SiC/NBR	—	0.52–1.61	85–125	0.4–0.47	474°C	[98]
Fumed silica-nanoclay-EG/HNBR	0.063/0.047/0.067	—	—	—	—	[99]

Table 3: continued

Sample	Ablation rate (mm/s)	Thermal conductivity (W/m K)	Tensile strength (MPa)	Elongation (%)	Thermal properties TGA*	Ref.
6 phr Kevlar fiber/NBR	0.137	—	15.4	666.6	—	[100]
5% SCF/NBR	0.06	0.08	4.75	22	6.15% loss at 300°C; 68.83% at 900°C	[40]
SiO ₂ /NBR	—	0.224	7.7–10	300–450	—	[18]

CF: carbon fiber. EPDM: ethylene propylene diene monomer. EG: expanded graphite. KP: Kevlar pulp. MWCNT: multiwalled carbon nanotubes. NR: natural rubber. SCF: short carbon fiber. TPU: thermoplastic polyurethane. (—): not analyzed. *: remaining weight in percentage, phr: parts per hundred resin. OAT: oxy-acetylene torch test.

densities should be low (1.05 to 1.10 mm/seg) to minimize the inert mass of the propulsion unit; low thermal conductivity should range from 4 to 5.10^{-4} cal/cm/°C and specific heat from 0.4 to 0.5 cal/g/°C. In addition, excellent bonding of the insulator with propellant and motor case over the entire range of working temperature is a requisite [80]. Singh and Sekhar [81] also state that the acceptable ablation rate should be less than 0.2 mm/seg.

In general, the performance of an EHSM is evaluated on the basis of several parameters: linear ablation rate, thermal conductivity, mass loss as a function of temperature (TGA analysis), char formation, and the microscopic analysis of burned samples. According to De et al. [82], the use of the TGA technique is very important for the development of a rubber-based thermal insulation for rocket engines.

Table 3 summarizes thermal and mechanical parameters for insulators based on NBR rubber, EPDM rubber, and PU, based on the main thermal parameters indicated in recent studies, as metrics for EHSM. Reports that disclosed the ablation rate were considered in the first place. In addition, Table 3 shows (when available) mechanical properties as an evaluation parameter. These are of equal importance as thermal resistance: when it comes to the overall performance of insulators for SRM, it is also necessary that EHSM resist vibration, physical stress to avoid brittleness, and cracking, especially during aging. Among the reviewed information, it was found that ablation rate ranged from 0.015 to 0.72 mm/s for EPDM insulators; from 0.13 to 0.69 mm/s for PU-based insulators; and from 0.06 to 0.23 mm/s for NBR-based insulators. Although these values result from different materials and testing conditions, they have indicated that the performance of NBR and PU-based EHSM is within the same range of EPDM-based EHSM, which are regarded as the state-of-the-art insulators, as pointed earlier.

In his thesis dissertation, Lee [51] has reported that in polymer nanocomposites (PNCs) based on Desmopan and nanoclay Cloisite® 30B the gaseous barrier property of the nanoclay PNCs helped the PNC to enhance its ablative performance. In addition, he stated that thermal measurements showed that the thermal protection of the PNCs is comparable to that provided by the Kevlar/EPDM composite. Table 4 summarizes main advantages and disadvantages of EHSM.

EPDM-EHSM has flexibility at low temperatures, a low density, good ageing resistance, and the lowest range of ablation rates for EHSM studied. Conversely, they may present compatibility issues with propellant. Anyway, as said, EPDM can be formulated with particulate mineral filler such as silica, or even with finely divided silica plus

Table 4: Main advantages and disadvantages of EHSM

Elastomeric heat shielding materials	Matrix or binder of EHSM			
	EPDM based	Nitrile rubber based	Polyurethane based	Silicone based
Advantages	Flexibility at low temperatures, low density, lowest ablation rates, good ageing resistance	Low ablation rates	Low ablation rates, with appropriate filler-better bonding/compatibility to composite propellant-easy fabrication	Suitable for spacecraft applications, with appropriate filler
Disadvantages	Mixing problems, premature vulcanization	Diminished resistance at high temperatures, higher density, limited shelf life	Short range polyols and isocyanate combinations not always useful	Poor mechanical properties

a reinforcing fiber to render a very efficient EHSM. NBR–EHSM display ablation rates similar to EPDM–EHSM and produce high char during pyrolysis. However, diminished resistance at high temperatures, high density, and limited shelf life put them as a second choice. PU–EHSM can have ablation rates similar to EPDM and NBR–EHSM, with an appropriate filler or fiber. Their unique advantage respect to the others is their excellent compatibility with composite propellant, as polyurethane is normally used as a binder in composite propellant.

Respect to reinforcement materials, Kevlar fibers convey high thermal resistance to rubbers, converting them in excellent EHSMs. Other fibers such as carbon fibers, polyimide, polyetherimide, and polyphosphazene may behave as good as Kevlar. However, they are far more expensive. Conventional fillers for EHSM are fumed silica, expanded graphite, perlite, and organically modified layered silicates with a high aspect ratio, such as Cloisite brand. These reinforcements have in general a significant effect on increasing insulation properties, as pointed out in this review. Fumed silica has very low thermal conductivity, which can be explained by its high porosity and nanoscale porous structure. It is readily available at a low cost and can be easily formulated into rubbers. Expanded graphite is a platelet-like graphite that can host polymer chains intercalated between graphite plates. Although the addition of graphene in styrene-butadiene rubber (SBR) has remarkably reduced the backface temperature elevation during the ablation testing of the ablatives [101], no reports on ablative behavior were found for other rubbers. Conversely, perlite and nanoclays are utilized because of offering good enough insulating properties at very low cost. POSS and carbon nanotubes are nano reinforcement that showed the best results; however, they are very expensive today and not used widespread in commercial systems.

3 Future trends

It was highlighted that the ablation of insulator materials depend not only on its inherent properties but also on extrinsic conditions such as thermal, chemical, and mechanical factors related to theoretical or practical environment variables [34]. In this sense, a detailed work by Zhu et al. [102] has indicated that the high degree of development of research on TPS is not only focused on materials but includes a thorough analysis of heat transfer coefficients and modeling. For example, to optimize thickness, a numerical calculation of the

dynamic ablation of the EPDM-based insulation material in SRMs was carried out [103]. The degradation kinetics also influences performance: EPDM with carbon black as mineral filler were thoroughly characterized in this respect. It was found that the EPDM and the NBR rubber degradations represent a complex process, where there are conversion regions with a constant value of the apparent activation energy [104]. Overall, results showed that among the insulators for rocket motors there is an assortment of alternatives depending on the rocket size, configuration, time of flight, propellant, and case material. Clearly, material performance depends not only in its inherent physical–chemical properties but also on the utilization conditions of SRM.

New materials are continuously under development, particularly in composites of rubber materials with nanofibers and to a lesser extent with nanoparticles [105]. The use of graphite with rutile and modified fumed silica has been reported, with which properties can be modified in a wide range [106]. The use of various reinforcements together opens wider possibilities for obtaining efficient EHSM. Arabpol *et al.* [44] have used fumed silica, organoclay, and short carbon fibers in NBR, achieving ablation rates comparable to those obtained with EPDM or even lower. Carbon composites via a low-temperature carbonization of NBR elastomer compounds and highly filled with various carbon fillers and dispersed silicon carbide (SiC) were developed. These composites were intended for low-temperature carbonization of the elastomer compounds to generate a compact carbon structure with low thermal conductivity [107]. Although these composites still have limited application in rocket motor tubes, as they have displayed very low elongation at break, they constitute a promising lead for future research. Nanocomposites based on polyetherimide (ULTEM™ 1010) with nanoclay as filler and flame-retardant additives have displayed enhanced ablation and thermal properties, rendering ablation rates as low as 0.07 mm/s at a heat flux of 100 W/cm² [108,109]. Other novel materials are polyphosphazenes [46,110], even though these materials are still expensive and not extensively available.

Combinations of standard materials are continuously being developed, such as aramid fiber reinforced silica aerogel composites (AF/aerogels), which have been shown to possess low density, remarkable flexibility, and excellent thermal insulation properties [52]. These encouraging results from the use and the combination of different additives justifies continued research in the field of insulators.

3.1 New challenges and opportunities with graphene

As mentioned earlier, missiles and solid rocket motors (SRMs) contain different flexible liners (PU, EPDM, NBR, NR, SBR, and silicone) or rigid (epoxy resin, phenolic among others) inside their combustion chambers. Reinforcements (silica, aramid fiber, carbon fiber, etc.) are necessary to achieve desired properties as thermal protections for the hot gases coming from the combustion of oxidizing agents (such as ammonium perchlorate (AP-NH₄ClO₄), ammonium nitrate (NA-NH₄NO₃), ammonium dinitramide (ADN), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)). The main objective of thermal protections is to protect the combustion chamber from the thermal and erosive effects of particles from the combustion of the highly energetic solid propellant. In this sense, nanomaterials such as graphene have emerged as a promising alternative [111,112]. Graphene is an attractive reinforcement due to its high mechanical strength, low density, high surface area, and chemical functionality. Graphene oxide (GO) and reduced graphene (rGO) have been incorporated into elastomeric and rigid compositions to increase their physical, thermal, and ablative properties [113,114]. They have also been incorporated in propellant not only to add physical properties but also to contribute to the rheological, thermal, and combustion parameters [115–117]. GO and rGO have high combustion enthalpy (32.8 kJ/g of carbon–oxygen reaction), high thermal, and electrical conductivity favoring the dissipation of electrostatic energy. They also act as a combustion catalyst or as a combustion catalyst support [116,117]. Graphene platelets have also been incorporated in EPDM matrix for improved fire retardancy and thermal conductivity [118].

Overall, revisiting knowledge constitutes a road mark for future developments on specialty polymers and nanocomposites. This short review aims to impulse research on high-temperature resistant composites made from commonly available materials [119,120]. For example, fumed silica is used as filler in EHSM and common additive in industry and presents the same level of thermal conductivity of super critically dried aerogels. If conveniently compacted, an exceptional high heat-resistant material could be obtained easily [121]. Overall, new opportunities are continuously under way [122], which greatly encourages keeping on with research.

4 Conclusion

From this short review, we could conclude that PU–EHSM is an emerging alternative to EPDM–EHSM because of their easier processability, reinforcement possibilities, and compatibility with composite propellant. At the same time, the fact that Kevlar/EPDM is still the classic insulator has been highlighted, considering numerous reports and previous extensive laboratory studies. One of its advantages is that EPDM exhibits the lowest density among elastomers, thus maximizing the payload of a SRM. Indeed, the lowest values reviewed for the ablation rate have been recorded for EPDM-based EHSM (0.015 mm/s), compared to 0.13 and 0.06 mm/s for NBR-based EHSM and PU–EHSM, respectively. Although the ablation rate is the key parameter for assessing thermal resistance of an insulator, it is important to notice that insulator properties also depend on other properties, such as ballistic configuration, and on the operating conditions of the rocket motor.

Nitrile rubber is still used as an insulation liner for solid SRM, although not to the extent of the EPDM-based EHSM, according to the comparative number of studies. Regardless of the recognized benefits of EPDM and NBR–EHSM, other insulators may also be convenient, such as PU–EHSM. For instance, it would not be necessary to utilize Kevlar/EPDM for short-range SRMs, in which the insulator endures the erosion effect of the hot gases and particles for only a very short period, usually measured in seconds. In these conditions, a PU–EHSM with appropriate filler could perform adequately, with the advantage of eliminating compatibility issues at the interface insulator-binder (as binders are mostly of polyurethane nature in composite propellants). In this way, bonding problems at the interphase insulator-binder could be avoided. Moreover, PU–EHSM can be easily casted or sprayed onto the inner surface of SRM, which is an important advantage compared to NBR and EPDM-based EHSM, which has to be processed in a different way.

Another way of improving PU–EHSM performance in comparison to other type of EHSM is the inclusion of nanomaterials, such as nanofillers and nanofibers. Then critical properties that determine EHSM success are significantly improved and possibilities for PU use as EHSM are broaden.

Conflict of interest: The authors declare no conflict of interest.

References

- [1] Zhu Q, Zhang C, Weibin Y. The influence of permeability on the ablation process for an ablative material. *Fractals*. 2019;27(6):1950105. doi: 10.1142/S0218348X19501056.
- [2] Zhu W. Review on active thermal protection and its heat transfer for air breathing hypersonic vehicles. *Chin J Aeronaut*. 2018;31(10):1929–53. doi: 10.1016/j.cja.2018.06.011.
- [3] Kumar CV, Kandasubramanian B. Advances in ablative composites of carbon based materials: A review. *Ind Eng Chem Res*. 2019;58:22663–701. doi: 10.1021/acs.iecr.9b04625.
- [4] Pinto JR, Sanches NB, Diniz MF, Santos RS, Oliveira JL, Dutra RCL. Expanded perlite/cork fillers applied to aerospace insulation materials. *An da Academia Brasileira de Ciências*. 2018a;90:3197–206. doi: 10.1590/0001-3765201820170964.
- [5] Pinto JR, Sanches NB, Santos RS, Oliveira JL, Dutra RCL. Development of asbestos-free and environment-friendly thermal protection for aerospace application. *Mat Res*. 2018b;21(6):1–9. e20170856. doi: 10.1590/1980-5373-MR-2017-0856.
- [6] Association for Standardization Test Methods. ASTM-E-285-08: Standard Test Method for Oxyacetylene Ablation Testing of Thermal Insulation Materials. Philadelphia: 2015.
- [7] Natali M, Kenny J, Torre L. Science and technology of polymeric ablative materials for thermal protection systems and propulsion devices: A review. *Prog Mater Sci*. 2016;84:192–275.
- [8] Hourt W. Plastics as heat insulators in rocket motors. *Ind Eng Chem*. 1960;52(9):761–3.
- [9] Koo J, Mensah T. Novel polymer nanocomposite ablative technologies for thermal protection of propulsion and reentry systems for space applications. In: Mensah TO, Wang B, Bothun G, Winter J, editors. *Nanotechnology commercialization: Manufacturing processes and products*. Hoboken, USA: Virginia Davis John Wiley & Sons; 2018.
- [10] George K, Panda B, Biswal M, Nayak S, Mohanty S. Ethylene propylene diene monomer rubber-based heat shielding materials for solid rocket motor: Impact of Kevlar fiber reinforcement on the thermal and mechanical properties. *Polym Adv Technol*. 2020;1–11. doi: 10.1002/pat.4857.
- [11] Natali M. Effect of Wollastonite on the ablation resistance of EPDM based elastomeric heat shielding materials for solid rocket motors. *Polym Degrad Stabil*. 2016;130:47–57. doi: 10.1016/j.polymdegradstab.2016.05.019.
- [12] Kesiya G, Panda V, Mohanty S, Nayak S. Recent developments in elastomeric heat shielding materials for solid rocket motor casing application for future perspective. *Polym Adv Technol*. 2017;1–14. doi: 10.1002/pat.4101.
- [13] Cosentino Garcia M, Silva FC, da Silva G, Sciamarelli J, da Costa Mattos E, Short A. Review about aerospace materials characterization -bonding agents and thermal insulation. *Propellants Explo Pyrotech*. 2020;45:1–11. doi: 10.1002/prep.201900407.
- [14] Quagliano Amado JC. Thermal resistance properties of polyurethanes and its composites: A short review. *J Res Updates Polym Sci*. 2019;8:85–93.

- [15] López Rivilli P, Berrier L, Donalisio E. Development and fabrication of an elastomeric thermal protection with seal for solid rocket propellant. Córdoba, Argentina: IX Congreso Argentino de Tecnología Espacial; April 26–28, 2017.
- [16] Pinto JR, Sanches NB, Santos RS, Oliveira JL, Dutra RCL. Expanded perlite/cork fillers applied to aerospace insulation materials. *An da Academia Brasileira de Ciências*. 2018;90(3):3197–206. doi: 10.1590/0001-3765201820170964.
- [17] Bhuvaneswari C. Ethylene-propylene diene rubber as a futuristic elastomer for insulation of solid rocket motors. *Def Sci J*. 2016;56(3):309–20.
- [18] Donskoy A. Silicon organic heat-shielding materials for aircraft external surfaces. In: Zaikov GE, editor. *New approaches to polymer materials*. vol. 5392, Hauppauge, NY, USA: Nova Publishers; 1995.
- [19] Natali M, Rallini M, Puglia D, Kenny J, Torre L. EPDM base-heatshielding materials for solid rocket motors: A comparative study of different fibrous reinforcements. *Polym Degrad Stabil*. 2013;98(11):2131–9. doi: 10.1016/j.polymdegradstab.2013.09.006.
- [20] Natali M, Kenny J, Torre L. Thermoset Nanocomposites as ablative materials for rocket and military applications. *Structure, properties, and applications, thermosets*. 2nd edn. Amsterdam, The Netherlands: Elsevier; 2018. p. 477–509.
- [21] Bhowmick A. *Current topics in elastomers research*. Boca Raton, USA: CRC Press, Taylor & Francis Group, LLC; 2008.
- [22] Satyaprasad P. Missile propulsion systems. *Indian Inst Met Ser*. 2017;1:305–30. doi: 10.1007/978-81-10-2143-5_15.
- [23] Dimitrienko Y. Effect of finite deformations on internal heat-mass transfer in elastomer ablating materials. *Int J Heat Mass Transf*. 1997;40(3):699–709. doi: 10.1016/0017-9310(96)00146-9.
- [24] Kumar S, Mahulikar S. Selection of materials and design of multilayer lightweight passive thermal protection system. *J Therm Sci Eng Appl*. 2015;8(2):021003. doi: 10.1115/1.4031737.
- [25] Gajiwala H, Hall S. Precursor compositions for an insulation, insulated rocket motors, and related methods, EP3375817 (A1). Plymouth, MN 55442 (US): Orbital ATK, Inc.; 2018.
- [26] Murakami LM. Off-line TLC-IR (UATR) characterization of additives in EPDM rubber. *Polym Test*. 2019;79(1–11):106042. doi: 10.1016/j.polymertesting.2019.106042.
- [27] Da Maia JV. Influence of gas and treatment time on the surface modification of EPDM rubber treated at afterglow microwave plasmas. *Appl Surface Sci*. 2013;285(Part B):918–26. doi: 10.1016/j.susc.2013.09.013.
- [28] Sanches NB, Diniz MF, Alves LC, Dutra JCN, Cassu S, Azevedo MF, et al. Avaliação da aplicabilidade de técnicas FT-IR de reflexão (UATR) e de transmissão para a determinação do teor de acrilonitrila (AN) em NBR. *Polímeros (São Carlos Impresso)*. 2018;18:249–55. doi: 10.1590/S0104-14282008000300011.
- [29] Dutra JN. Surface modification of EPDM rubber by reactive argon-oxygen plasma process. *Mol Cryst Liq Cryst*. 2003;374:45–52. doi: 10.1080/713738292.
- [30] Gladysz G, Chawla K. *Voids in Materials. From unavoidable defects to Design Cellular Materials*. Amsterdam, The Netherlands: Elsevier; 2015.
- [31] Paglia L. Carbon-phenolic ablative materials for re-entry space vehicles: Plasma wind tunnel test and finite element modeling. *Mater Des*. 2016;90:1170–80. doi: 10.1016/j.matdes.2015.11.066.
- [32] Natali M, Puri I, Kenny JM, Torre L, Rallini M. Microstructure and ablation behavior of an affordable and reliable nanostructured phenolic impregnated carbon ablator (PICA). *Polym Degrad Stabil*. 2017;141:84–96. doi: 10.1016/j.polymdegradstab.2017.05.017.
- [33] Sureshkumar M, Bhuvaneswari CM, Kakade SD, Gupta M. Studies on the properties of EPDM-CSE blend containing HTPB for case-bonded solid rocket motor insulation. *Polym Adv Technol*. 2008;19(2):144–50. doi: 10.1002/pat.988.
- [34] Elwan I, Jabra R, Arafeh M. Preparation and ablation performance of lightweight phenolic composite material under oxyacetylene torch environment. *J Aerosp Technol Manag*. 2008;10:e3118. doi: 10.5028/jatm.v10.935.
- [35] Prasertsri S, Amnuay P, Sripan K, Nuinu P. Role of hydroxyl-terminated polybutadiene in changing properties of EPDM/ENR blends. *Adv Mat Res*. 2013;844:349–52. doi: 10.4028/www.scientific.net/amr.844.349.
- [36] Deuri A, Bhowmick A, Ghosh R, John B, Sriram T, De S. Thermal and ablative properties of rocket insulator compound based on EPDM. *Polym Degrad Stabil*. 1988;21(1):21–8.
- [37] Allred LD. Asbestos free insulation development for the space shuttle solid propellant rocket motor (RSRM). 4th aerospace materials, processes and environmental technology. Huntsville, AL; United States; 2000.
- [38] Kablov V. Development and study of elastomer heat-shielding materials containing zirconium dioxide. *Russ J Appl Chem*. 2017b;90(3):401–5. doi: 10.1134/s1070427217030120.
- [39] Rajeev R. Studies on thermal degradation of short melamine fibre reinforced EPDM, maleated EPDM and nitrile rubber composites. *Polym Degrad Stabil*. 2013;79(3):449–63. doi: 10.1016/s0141-3910(02)00361-0.
- [40] Bassyouni M. Ablation and thermo-mechanical investigation of short carbon fiber impregnated elastomeric ablatives for ultrahigh temperature applications. *Pol Degrad Stabil*. 2014;110:195–202. doi: 10.1016/j.polymdegradstab.2014.08.032.
- [41] Bidgoli M, Arabgol F, Kokabi M. Ablation behavior of elastomeric insulator based on nitrile rubber containing silica or silica-clay aerogels. *Iran Polym J*. 2020;29:985–96. doi: 10.1007/s13726-020-00855-z
- [42] Balachandran M, Bhagawan SS. Mechanical, thermal and transport properties of nitrile rubber (NBR)–nanoclay composites. *J Polym Res*. 2012;19(2):9809. doi: 10.1007/s10965-011-9809-x
- [43] Kim J. Characteristics of nitrile–butadiene rubber layered silicate nanocomposites with silane coupling agent. *J Appl Polym Sci*. 2003;89(10):2633–40.
- [44] Arabgol F, Kokabi M, Bahramian AR. Ablation behavior of organoclay-NBR insulator: Modeling and experimental. *Fire Mater*. 2018;42(7):859–72.
- [45] Liu Y. Ablation and mechanical investigation of heat vulcanizing silicone rubber (HVSr) composite containing carbon fibers. *J Polym Eng*. 2017;37(5):521–8. doi: 10.1515/polyeng-2016-0130.

- [46] Alex A, Bhuvaneswari S, Sreenivas N. Short silica fibre-reinforced polymethylsilsesquioxane-phenolic interpenetrating networks: Exploration for use as ablative thermal protection system in aerospace. *Polym Bull.* 2019;76:3941–56. doi: 10.1007/s00289-018-2579-4.
- [47] Wu S. EPDM-based heat-shielding materials modified by hybrid elastomers of silicone or polyphosphazene. *High Perform Polym.* 2019;31(9–10):1112–21. doi: 10.1177/0954008318824861.
- [48] Gao L, Liu L. Ablation behavior of silicone rubber-benzoxazine-based composites for ultra-high temperature applications silicone. *Polymers.* 2019;11(11):1844. doi: 10.3390/polym1111844.
- [49] Xie F. Degradation and stabilization of polyurethane elastomers. *Progr Polym Sci.* 2019;90:211–68. doi: 10.1016/j.progpolymsci.2018.12.003.
- [50] Benli S. Effect of fillers on thermal and mechanical properties of polyurethane elastomer. *J Appl Polym Sci.* 1998;68:1057–65.
- [51] Lee J. Characterization of ablative properties of thermoplastic polyurethane elastomer nanocomposites. Thesis. Austin, Texas, USA: The University of Texas at Austin; December 2010.
- [52] Li Z. Flexible silica aerogel composites strengthened with aramid fibers and their thermal behavior. *Mater Des.* 2016;99:349–55. doi: 10.1016/j.matdes.2016.03.063.
- [53] Liu C, Kim J, Kwon Y. Comparative investigation on thermal insulation of polyurethane composites filled with silica aerogel and hollow silica microsphere. *J Nanosci Nanotechnol.* 2016;16:1703–7.
- [54] Han Z, Xi Y, Kwon Y. Thermal stability and ablation behavior of modified polydimethylsiloxane-based polyurethane composites reinforced with polyhedral oligomeric silsesquioxane. *J Nanosci Nanotechnol.* 2016;16(2):1928–33. doi: 10.1166/jnn.2016.11986.
- [55] Yu F. Study on the ablation materials of modified polyurethane/polysiloxane. China: National Sun Yan-Tsen University; 2004. Thesis available at: https://etd.lis.nsysu.edu.tw/ETD-db/ETD-search/view_etd?URN=etd-0817104-151504.
- [56] Lee J. Flammability study of thermoplastic polyurethane elastomer nanocomposites. 50th AIAA/ASME/ASCE/AHS/ASC structures, structural dynamics, and materials conference; 2019. doi: 10.2514/6.2009-2544.
- [57] Bocchio JA, Escobar MM, Quagliano Amado JC. Ablative properties of polyurethanes reinforced with organoclay. *Polym Eng Sci.* 2020;60:630–5. doi: 10.1002/pen.25321.
- [58] Allcorn E, Natali M, Koo J. Ablation performance and characterization of thermoplastic polyurethane elastomer nanocomposites. *Compos Part A: Appl Sci Manufact.* 2013;45:109–18. doi: 10.1016/j.compositesa.2012.08.017.
- [59] Ho W. Thermoplastic polyurethane elastomer nanocomposites: Morphology, thermophysical, and flammability properties. *J Nanomat.* 2010;2010:583234. 11 p. doi: 10.1155/2010/583234.
- [60] Dai Z. Synthesis and thermal properties of antimony doped tin oxide/waterborne polyurethane nanocomposite films as heat insulating materials. *Polym Adv Technol.* 2010;22(12):1905–11. doi: 10.1002/pat.1690.
- [61] Ding H. Inherently flame-retardant flexible bio-based polyurethane sealant with phosphorus and nitrogen-containing polyurethane prepolymer. *J Mat Sci.* 2016;51(10):5008–18. doi: 10.1007/s10853-016-9805-y
- [62] Ghosh K. Light weight HTPB-clay nanocomposites (HCN) with enhanced ablation performance as inhibition materials for composite propellant. *Def Technol.* 2020. doi: 10.1016/j.dt.2020.03.011, in press.
- [63] Schiariti D, Bellomi P. Inner coating layer for solid-propellant rocket engines, WO2019073436 (A1). Rome, Italy: AVIO S.P.A.; 2019.
- [64] Awad M, Nasser M. Effect of insulation layer composite and water adsorption on bonding performance. *Heat Adv J Chem-Section A.* 2020;3(3):370–7. doi: 10.33945/SAMI/AJCA.2020.3.15.
- [65] Farajpour T, Abdollahi M. Improvement in adhesion between ethylene-propylene-diene terpolymer (EPDM)-based elastomer and polyurethane coating using epoxy-polysulfide copolymer as adhesion promoter. *Polym Sci, Ser A.* 2018;60(5):655–62. doi: 10.1134/s0965545x18050048.
- [66] Boonstra B. Role of particulate fillers in elastomer reinforcement: A review. *Polymer.* 1979;20(6):1–704. doi: 10.1016/0032-3861(79)90243-x
- [67] Rallini M, Kenny JM. Nanofillers in polymers. *Modif Polym Prop.* 2017;3:47–86. doi: 10.1016/b978-0-323-44353-1.00003-8.
- [68] Milhomem G. Experimental studies of heat insulation materials for hybrid propellant rocket motors. Experimental studies of heat insulation materials for hybrid propellant rocket motors. 24th ABCM International Congress of Mechanical Engineering. Curitiba, PR, Brazil: December 3–8, 2017.
- [69] Rallini M. Thermal and ablation properties of EPDM based heat shielding materials modified with density reducer fillers. *Compos Part A: Appl Sci Manufact.* 2018;112:71–80. doi: 10.1016/j.compositesa.2018.05.031.
- [70] Iqbal N. Ablation, thermal stability/transport and mechanical investigations of modified nanokaolinite impregnated acrylonitrile butadiene rubber composites. *J Compos Mat.* 2013;48(10):1221–31. doi: 10.1177/0021998313484948.
- [71] Sanoj P, Kandasubramanian B. Hybrid carbon-carbon ablative composites for thermal protection in aerospace. *J Compos.* 2014;825607. 15 p. doi: 10.1155/2014/825607.
- [72] Koo J, Mensah T. Novel polymer nanocomposite ablative technologies for thermal protection of propulsion and reentry systems for space applications. In: Mensah TO, Wang B, Bothun G, Winter J, editors. *Nanotechnology commercialization: Manufacturing processes and products.* Hoboken, USA: Virginia Davis John Wiley & Sons; 2018.
- [73] Liu C, Kim J, Kwon Y. Comparative investigation on thermal insulation of polyurethane composites filled with silica aerogel and hollow silica microsphere. *J Nanosci Nanotechnol.* 2016;16:1703–7.
- [74] Bourbigot S, Flambard X. Heat resistance and flammability of high performance fibres: A review. *Fire Mater.* 2002;26(4–5):155–68. doi: 10.1002/fam.799.
- [75] Jaramillo M, Koo JH, Natali M. Compressive char strength of thermoplastic polyurethane elastomer nanocomposites. *Polym Advan Technol.* 2014;25(7):742–51. doi: 10.1002/pat.3287.
- [76] Singh S. Development of polyimide-nanosilica filled EPDM based light rocket motor insulator compound: Influence of

- polyimide–nanosilica loading on thermal, ablation, and mechanical properties. *Compos Part A*. 2013;44:8–15.
- [77] Jia X. Ablation and thermal properties of ethylene-propylene-diene elastomer composites reinforced with polysulfonamide short fibers. *J Appl Polym Sci*. 2019;113(1):283–9. doi: 10.1002/app.29470.
- [78] Samatadze AI, Parakhin IV, Tumanov AS. Heat-protective properties of materials based on polyheteroarylenes. *Polym Sci Ser D*. 2016;9(2):243–7. doi: 10.1134/s1995421216020192.
- [79] Patton R, Pittman CU, Wang L, Hill JR, Day A. Ablation, mechanical and thermal conductivity properties of vapor grown carbon fiber/phenolic matrix composites. *Compos Part A: Appl Sci Manufact*. 2002;33(2):243–51. doi: 10.1016/s1359-835x(01)00092-6.
- [80] Georges K. Recent developments in elastomeric heat shielding materials for solid rocket motor casing application for future perspective. *Polym Adv Technol*. 2018;29:18–21.
- [81] Singh H, Sekhar H. Solid rocket propellants: science and technology challenges. Thomas Graham House, Milton Road, UK: Royal Society of Chemistry; 2017.
- [82] De P, Choudhury N, Dutta K. Thermal analysis of rubber and rubbery materials. Shrewsbury: Rapra Technology; 2010.
- [83] Guo M, Li L, Xi K, Liu L, Ji J. Effect of multi-walled carbon nanotubes on thermal stability and ablation properties of EPDM insulation materials for solid rocket motors. *Acta Astronautica*. 2019;159:508–16. doi: 10.1016/j.actaastro.2019.01.047.
- [84] Li L. Characteristics and formation mechanism of compact/porous structures in char layers of EPDM insulation materials. *Carbon*. 2018;127:498–509. doi: 10.1016/j.carbon.2017.10.091.
- [85] George K. Recent developments in elastomeric heat shielding materials for solid rocket motor casing application for future perspective. *Polym Advan Technol*. 2017;29(1):8–21. doi: 10.1002/pat.4101.
- [86] Yang L. A volumetric ablation model of EPDM considering complex physicochemical process in porous structure of char layer. *Open Phys*. 2017;15:344–53.
- [87] El-Dakhakhny A. Effects of aramid fibers and colloidal particle fillers in composite ethylene propylene diene monomer rubber thermal insulators for rocket motor insulation. *J Compos Mat*. 2017;52(15):1989–95.
- [88] Zhang Z. Study on thermal and mechanical properties of EPDM insulation. Proceedings of the 2016 International Conference on Mechanical Engineering and Control System (MECS2016). 15–17 April 2016; Wuhan, China.
- [89] Winya N, Hansupalak N. A comparison between the effects of sepiolite and silica on mechanical properties and thermal stability of NR/EPDM blend. *MATEC Web Conf*. 2016;69:04003. doi: 10.1051/mateconf/20166904003.
- [90] Ahmed A, Hoa S. Thermal insulation by heat resistant polymers for solid rocket motor insulation. *J Compos Mat*. 2012;46(13):1549–59.
- [91] Chu H, Sheu S, Chou S. Experimental study of ablative materials by oxyacetylene flame flow system. *J Propul Power*. 2011;27(5):1108–13. doi: 10.2514/1.b34055.
- [92] Yezzi C, Moore C. Characterization of Kevlar/EPDM rubbers for use as rocket motor case insulators. 22nd Joint Propulsion Conference. Huntsville, Alabama, USA: June 16–18; 1986. doi: 10.2514/6.1986-1489.
- [93] Han Z, Xi Y, Kwon Y. Thermal stability and ablation behavior of modified polydimethylsiloxane-based polyurethane composites reinforced with polyhedral oligomeric silsesquioxane. *J Nanosci Nanotechnol*. 2016;16(2):1928–33. doi: 10.1166/jnn.2016.11986.
- [94] Kim H, Kim C, Kwon Y. Ablation and fire-retardant properties of hydroxyl-terminated polybutadiene-based polyurethane-g-polyhedral oligomeric silsesquioxane composites. *High Perform Polym*. 2015;27(6):749–57. doi: 10.1177/0954008314559554.
- [95] Iqbal SS. Exfoliated sodium montmorillonite reinforced elastomeric nanocomposites: Ablation, thermal transport/decomposition/transitions and mechanical aspects. *Int J Mater Mech Manuf*. 2018;6(1):19–25. ISSN: 1793-819810.18178/ijmmm.2018.6.1.340.
- [96] Nawaz R, Rashid N, Ali Z, Khan A, Nazir MS, Ul-Haq N. Effects on thermal and ablative properties of phenolic resin (Novolac) blended acrylonitrile butadiene rubber. *Fiber Polym*. 2018;19(6):1318–26. doi: 10.1007/s12221-018-8075-5.
- [97] Farrukh S, Tahir NA, Hussain A, Ayoub M, Rafiq M, Khan MH. Fabrication and analysis of HNBR-silica/carbon phenolic ablative composites as an effective thermal protection system (TPS). *IOP Conf Series: Mat Sci Eng*. 2018;458:012015. doi: 10.1088/1757-899x/458/1/012015.
- [98] Chukov D, Stepashkin A, Salimon AI, Kaloshkin SD. Highly filled elastomeric matrix composites: Structure and property evolution at low temperature carbonization. *Mater Des*. 2018;156:22–31. doi: 10.1016/j.matdes.2018.06.034.
- [99] Guan Y. Study on ablative properties and mechanisms of hydrogenated nitrile butadiene rubber (HNBR) composites containing different fillers. *Pol Degrad Stabil*. 2011;96(5):808–17. doi: 10.1016/j.polymdegradstab.2011.02.010.
- [100] Zhao Y, Hu S, Lu W, An G, Wu Z, Wu D, et al. Nitrile butadiene rubber-based heat-shielding insulations for solid rocket motors. *High Perform Polym*. 2014;27(2):153–60. doi: 10.1177/0954008314541819.
- [101] Iqbal SS, Sabir A, Islam A, Bukhari S, Yasir M, Bashir MA, et al. Effect of graphene for ablation study of advanced composite materials for aerospace applications. *Key Eng Mater*. 2018;778:118–25. doi: 10.4028/www.scientific.net/kem.778.118.
- [102] Zhu Y, Peng W, Xu R, Giang P. Review on active thermal protection and its heat transfer for airbreathing hypersonic vehicles. *Chin J Aeronaut*. 2018;31(10):1929–53. doi: 10.1016/j.cja.2018.06.011.
- [103] Xu Y. Dynamic simulation of insulation material ablation process in solid propellant rocket motor. *J Aerosp Eng*. 2015;28(5):04014118. doi: 10.1061/(asce)as.1943-5525.0000452.
- [104] Samaržija-Jovanović S. Ethylene–propylene–diene rubber-based nanoblends: Preparation. *Charact Appl Springer Ser Polym Compos Mat*. 2016;9:281–349. doi: 10.1007/978-3-319-48720-5_9.
- [105] Maiti M, Bhattacharya M, Bhowmick A. Elastomer nanocomposites. *Rubber Chem Technol*. 2018;81(3):384–469. doi: 10.5254/1.3548215.
- [106] Azizi S. Performance improvement of EPDM and EPDM/Silicone rubber composites using modified fumed silica,

- titanium dioxide and graphene additives. *Polym Test*. 2020;84:106281. doi: 10.1016/j.polymertesting.2019.106281.
- [107] Chukov DI. Highly filled elastomeric matrix composites: Structure and property evolution at low temperature carbonization. *Mater Des*. 2018;156:22–31. doi: 10.1016/j.matdes.2018.06.03.
- [108] Kim S. Evaluation of a modified fused filament fabrication material for use as thermal protection, SAMPE Conference Proceedings. Charlotte, NC: Society for the Advancement of Material and Process Engineering – North America; May 20–23, 2019.
- [109] Ramgobin A. Thermal degradation and fire behavior of high performance polymers. *Polym Rev*. 2019;59(1):55–123. doi: 10.1080/15583724.2018.1546736.
- [110] Zou W, Basharata M, Ullah SD, Zhang S, Abbas Y, Wei L, et al. Preparation and performances of novel polyphosphazene-based thermally conductive composites. *Compos Part A: Appl Sci Manufact*. 2019;119:145–53. doi: 10.1016/j.compositesa.2019.01.024.
- [111] Rui L, Wang J, Peng Shen J, Hua C, Yang GC. Preparation and characterization of insensitive HMX/graphene oxide composites. *Propellants Explos Pyrotech*. 2012;35:1–7. doi: 10.1002/prep.201200199.
- [112] Iqbal SS, Sabir A, Islam A, Zain-ul-Abdeen Bukhari S, Yasir M, Bashir A, et al. Effect of graphene for ablation study of advanced composite materials for aerospace applications. *Key Eng Mater*. 2018;778:118–25. doi: 10.4028/www.scientific.net/KEM.778.118.
- [113] Chehroudi B. Nanotechnology and applied combustion: Use of nanostructured materials for light-activated distributed ignition of fuels with propulsion applications. *Recent Pat Space Technol*. 2011;1(2):107–22. doi: 10.2174/1877611611101020107.
- [114] Dillier CAM, Demko AR, Sammet T, Thomas JC, Petersen EL, Grossman K, et al. Burning rate and ignition delay times of AP/HTPB-based solid rocket propellants containing graphene – Propulsion and energy forum. 52nd AIAA/SAE/ASEE joint propulsion conference, Salt Lake City, Utah, USA: July 25–27, 2016. doi: 10.2514/6.2016-4690.
- [115] Zhang X, Zheng J, Fang H, Zhang Y, Bai S, Guansong H. Al₂O₃/graphene reinforced bio-inspired interlocking polyurethane composites with superior mechanical and thermal properties for solid propulsion fuel. *Ciência e Tecnologia de Compósitos*. 2018;167:42–52. doi: 10.1016/j.compscitech.2018.07.029.
- [116] Nasir K, Memon AW, McBainand SF, Son F. Graphene oxide/ammonium perchlorate composite material for use in solid propellants. *J Propuls Power*. 2016;32(3):682–6. doi: 10.2514/1.b35815.
- [117] Pazat A, Barrès C, Bruno F, Janin C, Beyou E. Preparation and properties of elastomer composites containing “Graphene”-based fillers: A review. *Polym Rev*. 2018;58(3):403–43. doi: 10.1080/15583724.2017.1403446.
- [118] Araby S, Su X, Meng Q, Kuan HC, Wang CH, Mouritz A, et al. Graphene platelets versus phosphorus compounds for elastomeric composites: Flame retardancy, mechanical performance and mechanisms. *Nanotechnology*. 2019;30(38):385703. doi: 10.1088/1361-6528/ab2a3d.
- [119] Pedreira S, Pinto JR, Campos E, da Costa Mattos E, Santos de Oliveira Junior M, Sampaio de Oliveira J, et al. Methodologies for characterization of aerospace polymers/energetic materials – a short review. *J Aerosp Technol Manag*. 2016;8(1):18–25. doi: 10.5028/jatm.v8i1.576.
- [120] Sanches NB, Diniz M, Mattos EC, Cassu SN, Dutra RCL. Infrared spectroscopy applied to materials used as thermal insulation and coatings. *J Aerosp Technol Manag*. 2013;5:421–30. doi: 10.5028/jatm.v5i4.265.
- [121] Feng J. Study of thermal stability of fumed silica based thermal insulating composites at high temperatures. *Compos Part B Eng*. 2011;42(7):1821–5. doi: 10.1016/j.compositesb.2011.06.023.
- [122] Vilela Salgado MC, Belderrain CMN, Devezas TC. Space propulsion: A survey study about current and future technologies. *J Aerosp Technol Manag*. 2018;10:e1118. doi: 10.5028/jatm.v10.829.