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Study of thermal protection materials in solid propellant rocket engines

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Abstract. Thermal insulation is widely employed to prevent catastrophic breakdowns that may take place during rocket mission. Its success highly dependent on the optimization of the polymeric ablative composition in the insulator that used in solid rocket motors systems (SRMs). Currently, a massive amount of researches have been conducted to improve thermal protection efficiency through advanced composite materials, especially those applied in rocket engine insulation. This paper gathers and investigates many of the recently published data regarding conventional insulators like nitrile rubber (NBR), ethylene-propylene-diene-monomer rubber (EPDM), silicone rubber, and polyurethane (PU) as elastomeric heat shielding materials (EHSM). Besides, a comparison between these selected insulators is conducted based on tensile strength, elongation, ablation rate, thermal conductivity, and density shows the effect of these properties on the total effectiveness of the insulation. This article is of great importance to readers interested in the domain of heat-shielding materials, covering the recent advanced composite materials used for ablative insulating systems in SRMs. Moreover, future trends including the employment of innovative fillers, like metal-organic frameworks (MOFs), in rubber composites are also discussed.

Keywords: Thermal insulation, Solid rocket motors, Ablation rate, NBR, EPDM, Polyurethane, Silicon rubber, Ablative TPS, Polymeric ablative, MOF.

1. Introduction

Solid rocket motors (SRMs), as an integral component providing the required thrust for rockets, play an essential role in serving both civilian and military purposes. Throughout the SRM initiation, ignition of the propellant takes place releasing a massive amount of gases accompanied by a huge amount of thermal energy and the temperature reaches 3000 K. Such a high temperature would cause a severe failure of the motor structure if it reached the outer rocket motor casing. Hence, a thermal protecting layer (insulation) is a part and parcel of being placed in the design of SRMs between the propellant and the metal case along with a liner to keep the structure intact and secure as demonstrated in figure 1. A thermal protection system (TPS) would provide a durable heat shield, protection, against the whole structure failure from excessive heating [1].

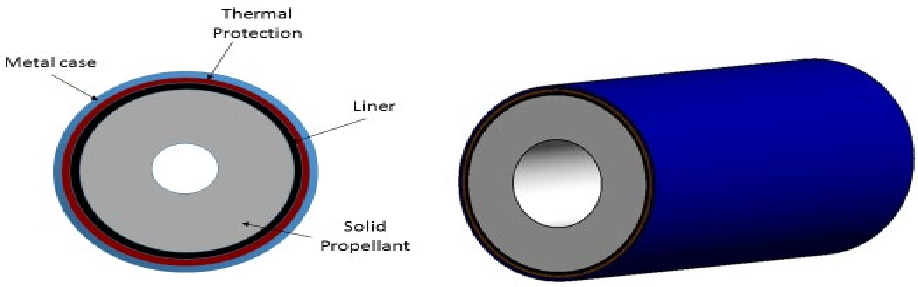


Figure 1. Different parts of a solid rocket engine cross-section [2].

The thermal protection system mainly consists of an elastomers base, reinforcement materials, flame retardants, plasticizers, and vulcanizing agents. The technique used for the preparation of TPS are performed on a two-roll mill. A mill consists of two metal hollow cylinders that rotate horizontally but in opposite directions. The separation of the two cylinders ranges from 0.25 mm to 2 mm. Rubber was masticated on a two-roll mill at 55 °C for 15 minutes with the rotor speed set to 15 rpm. The other ingredients were added to the rubber gradually. Once a uniform rubber compound was produced the vulcanization agents were blended with rubber on the two-roll mill until a perfect blend is achieved. After the mixing process was complete, the compounds were removed from the two-roll mill and vulcanized in the molds at a certain temperature and pressure according to the Rheometer analysis. The TPS should have certain specifications to match the main requirements for thermal protection. Table 1 demonstrates different essential requirements in thermal protection for solid rocket motor systems from different literature sources such as density, thermal conductivity, ablation rate, shelf life, and tensile strength. Its noticed differences in the required value for each property because it depends on the requirements and the constraints of the mission, such as a tight mass budget (Which may require giving density precedence over other properties) or a lengthy operational time (which may require giving thermal properties precedence over other properties) [3].

Table 1. Thermal protection specifications for rocket engines [3].

Property	Tam and Bell	Ahmed et al	Bhuvaneswari et al
Density (g/cm^3)	<1.3	<1.5	<1.5
Thermal conductivity (W/mK)	<0.26	0.2-0.5	0.17-0.21
Tensile strength (MPa)	≥ 3.5	≥ 0.5	Not available
Ablation rate (mm/s)	(0.05-0.2)^a	0.09-0.2	0.09-0.2
Shelf life (years)	Not available	≥ 10	≥ 10

^{a} Mach from (0.254-1.143)

This article highlights the role of polymeric ablatives such as elastomeric materials as most common used constituent in TPS, and the recent research worked on increasing the elastomeric materials performance. In addition, this paper compared various elastomeric heat shield materials (EHSM) with different reinforcements and fillers which are used to insulate rocket engines. Moreover, a new trend for TPS performance enhancement by using different synthetic MOFs is presented.

2. Polymeric ablative TPS

Since the 1960 attention to the development of rocket motors have been considered as many studies focused on studying and assessment of polymers used in heat insulation systems [4]. These polymers are essential in the thermal insulation performance where it reacts as ablative polymers. The ablation reaction occurs through the thermal decomposition of the polymeric materials; it yields some non-flammable gases at the site of the reaction which decreases the amount of flammable gases present and the char layer as a product. The char layer is produced from the carbonization reaction of the ablative polymer then it covers the surface of the thermal insulator to protect the underlying materials from the heat source. The inner layer of the thermal insulator is repeatedly exposed to the high heat generated by the rocket propulsion reaction, the volume of the virgin material is reduced while the char layer is increased. Furthermore, the ablation rate of TPS decreases with the slow consumption of the char layer, which depends on its stability and compactness [5].

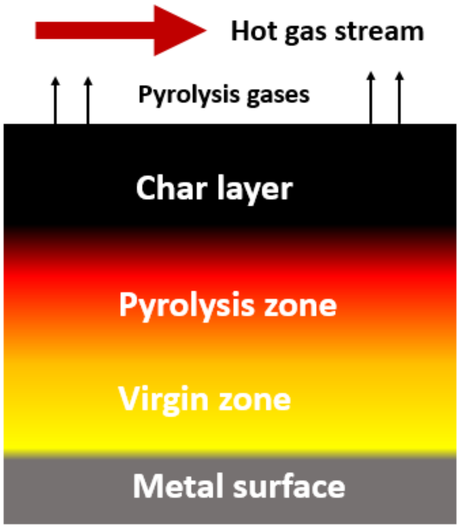


Figure 2. The three major zones emerged throughout the ablation procedure.

Figure 2 depicts the three main zones created during a TPSs ablation process:

- Charring zone: The first area to be affected by the intense heat produced by the burning of solid propellants, which forms the char layer.
- Pyrolysis zone: This area divides the virgin zone from the charring zone, which is where the pyrolysis and decomposition processes of TPS occur.
- Virgin TPS zone: A region where TPS is unreacted.

Polymeric ablative materials serve as insulators to the SRMs at extremely high temperatures and are efficient to create passively cooled missile combustion chambers. Compared to inorganic polymers, organic polymers have advantages such as lower density, decent mechanical strength, strong resistance to heat shock, and abilities to insulate heat. Because inorganic polymers used in ablative TPS such as ceramics or metals miss their efficiency at high temperatures and show brittleness which limits them from being used as an insulator.

The used organic elastomers materials for producing HSM such as foamed rubbers and composite materials made of rubber, fabric, or fiber [6]. Rubbers have a low thermal resistance around 350°C. Therefore, they cannot withstand harsh conditions like those in a rocket motor, which include extremely high temperatures, pressures, and erosion from fast-moving flows. However, adding numerous additives to the rubbers might improve their ability to withstand heat. The materials added to the ablative polymer should have stable char forms, high char shear strength, low density, low thermal conductivity, high temperature resistance, and a good erosion performance [7].

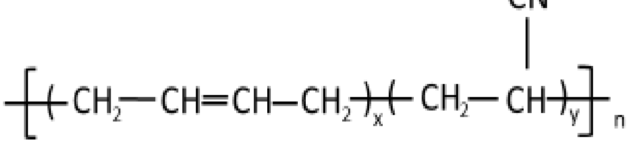
2.1. Main polymer based in HSMs of SRMs

The four different polymers based on HSMs are NBR, EPDM, silicone rubber, and PU elastomer [4]. The following section studies the thermal insulation behavior of each polymer based on HSMs and the role of added selected materials, which match the main requirements required in the TPSs, in the thermal resistance property enhancement.

2.1.1. NBR-based HSMs. NBR consists of copolymer butadiene and acrylonitrile. It is a polar rubber that is widely used in the evolution of HSM for rocket engines. The polarity in acrylonitrile allows good adhesion with other materials, as shown in figure 3. For TPS, NBR is frequently utilized as a polymeric matrix due to its low thermal conductivity, easy processing, appropriate mechanical strength, and excellent thermal resistance properties [8].

Several methods were utilized to improve NBR characteristics. For example, Morteza Fini Bidgoli et al. [8] created a new TPS by adding (15phr) of silica aerogel with NBR rubber. The linear and mass ablation rates of TPS were decreased by (29%) and (15%) respectively due to the excellent thermal stability and residual char tenacity for silica aerogel. Besides, silica aerogel has been successful in lowering the insulation back-face temperature. The combination of NBR rubber with the chopped polyimide fiber (PI) by using an oxygen plasma to modify the PI surface. As the amount of (PI) fiber content rises the ablation rate is decreased due to the high thermal resistance of (PI). The interfacial interactions between PI fibers and the NBR matrix are improved by plasma treatment, which effectively increases the roughness of (PI) fibers and forms numerous polar groups on the surfaces leading to the enhancement of the mechanical properties of TPS. PI-filled NBR provides better insulation compared to Kevlar-filled NBR. This approach, it is concluded, offers superior ablative and charring properties as an HSM [9].

The thermal insulation with various phenol formaldehyde concentrations with NBR was mixed by using an internal dispersion kneader and a two-roll mixing mill. It was noted that the improvement of the ablative resistance for thermal insulation becomes significant. Besides, the amount of phenol-formaldehyde in the rubber matrix increased along leads to a rise in the shore A hardness and tensile strength. This results because phenol formaldehyde is a polar structure and this polarity depends on the hydroxyl group on the benzene ring. NBR and phenol formaldehyde are both organic polar compounds that are probably compatible with one another [10]. Table 2 lists some of the NBR composites that are utilized as an insulating materials for rocket motors.



$$-\left[\left(CH_2-CH=CH-CH_2\right)_x\left(CH_2-\overset{\overset{CN}{|}}{CH}\right)_y\right]_n-$$

Figure 3. Chemical structure of NBR rubber.

2.1.2. EPDM-based HSMs. Ethylene, propylene, and a diene component are combined to form the terpolymer that is EPDM rubber, as shown in figure 4. Recently, a lot of researchers have developed high-thermal insulating materials for use in rocket engine applications using elastomeric composite materials based on EPDM. The EPDM has appealing anti-oxidative degradation, low density, and protective qualities because of its backbone chain saturation. Besides, the EPDM is distinguished by being Lightweight, low ablation rate, and flexible at relatively low temperatures. Nevertheless, EPDM, unlike NBR, cannot achieve good adhesion with other materials because of its non-polar structure, but EPDM is still used as an insulation for SRM. Therefore some additives are added to the EPDM to improve its polarity such as using Maleic anhydride [11].

The most prevalent fiber in EPDM-based SRM liners is aramid (also known as Kevlar) pulp, which has been used successfully to reduce thermal conductivity, low density, and reinforce TPS. Moreover, kevlar in the EPDM rubbers enhances the mechanical requirements of thermal insulation, which guarantees higher resistance to erosion. Hence, kevlar shields the TPS from the exhaust gasses inside the rocket motors, by keeping TPS from degradation and the char residue can be used as a heat insulator, reducing the need for additional insulation. [12].

Multi-walled carbon nanotubes (MWCNTs) in the EPDM matrix leads to increase the elongation and tensile strength by (25.4%), and (24.7%) respectively. The secondary force between the matrix and MWCNTs, it will be necessary to use MWCNTs as reinforcement for EPDM because it will improve the mechanical properties. MWCNTs can enhance the ablation resistance of the EPDM insulation material. However, it is important to keep in mind that MWCNTs have good thermal conductivity, which means that adding more of them could have a negative impact on EPDM ability to withstand ablation from a heat transfer perspective. Abrasive efficiency can be increased by using fillers like carbon fiber (CF), silica, zirconium carbide, phenolic resin, and glass fiber [13]. Table 2 lists several of the EPDM mixtures that are applied as insulating materials for SRM.

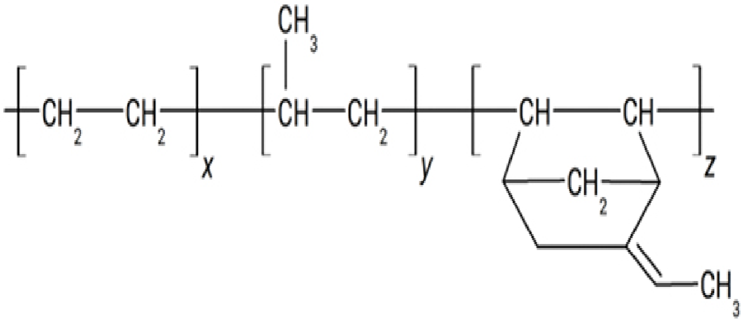


Figure 4. Chemical structure of EPDM monomer.

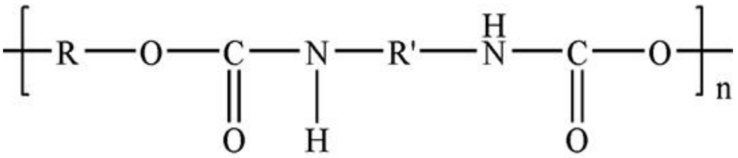
2.1.3 Silicone-based HSMs. Silicon rubbers are linear polysiloxanes that can be classified as either high-temperature vulcanized or room-temperature vulcanized silicone rubbers depending on how they cure. The silicon rubber most frequently used as a matrix for SRM is polydimethyl siloxane. Then, at higher temperatures, it decomposes with the release of volatile substances like (H_2O), (CO_2), and methanol. Meanwhile, silicon compounds like (SiO_2) and (SiC) make up the majority of the carbonaceous char that results from pyrolysis [14]. Silicone-based EHSMs are present in the most advanced insulator compositions. In particular, it uses expensive additives with silicone rubber, like carbon fibers and polyhedral oligosilsesquioxane (POSS), for special rocket engines. During silicones expose to extreme temperatures in an oxygen environment, they release an inorganic silica residue. Which acts as an insulating layer to shield the polymer surface from the effects of the heat flux from the outside. However, silicones limited applicability is a result of their weak mechanical characteristics[15].

Regarding ablation efficiency have found that silicone and EPDM can be blended (1:1), after (20s) of the oxy-acetylene ablation Test, the ablation rate was (0.06 mm/s), significantly lower than the EPDM insulations of (0.215 mm/s). This outcome emphasizes silicone value as an ingredient in EHSM formulations[16].The manufacture of a silicon rubber matrix containing octaphenyl polyhedral oligomeric silesquioxane, aluminum diethyl phosphinate, and ammonium polyphosphate. Hence, the addition of flame retardants systemically enhanced smoke suppression, thermal stability, flame retardancy, and linear ablation rate [10]. The incorporating silicone with zirconia (ZrO_2) or zirconium carbide (ZrC), (40phr) zirconium carbide and zirconia each reduced the ablation rate by (41%) and

(73%), respectively. whereas the ablated surface covered in ZrO_2, SiO_2, and SiC served as a strong barrier against oxygen dispersion and temperature navigation [17].

2.1.4. Polyurethane-based HSMs. PU is a multi-connected block polymer typically made up of chemically different parts, to produce urethane linkage (–NHCO–O–) from covalent bonds between hard and soft segments as shown in figure 5. These polymers experience a marked increase in hydrogen bonding as the number of urethane linkages increases. Additionally, by reducing intermolecular slippage, the inter-chain molecular forces contribute significantly to the material fatigue properties, durability, and flexibility of the polymers. When combined with the right filler, PU-EHSM could serve as solid rocket motors' thermal insulation with sufficient effectiveness. PU-EHSM is preventing the bonding problems between insulator and propellant. Besides, PU-EHSM is distinguished from NBR and EPDM- based EHSM as it can be casted or sprayed into the rocket engines easily which must be treated in a different way [4]. Regarding polyol, hydroxyl-terminated polybutadiene (HTPB) is frequently used due to its that has physical and mechanical characteristics like high tensile strength, a low glass transition temperature, and chemical resistance. Because of this, HTPB was employed in a variety of ways, including as a binder in the creation of composite propellants and as an inhibitor or thermal protection in rockets [18].

The mixture of (SiO_2), aluminium oxide(Al_2O_3), (ZrO_2), and thermal black as fillers in HTPB-based PU, the lowest ablation rate is (0.32 mm/s) at using (10%) from thermal black. Researchers have studied the behavior of an HTPB-based PU reinforced with POSS. They found that POSS molecules had a considerable impact on ablative resistance because they serve as precursors for the protective silica that forms when expose to high temperatures. But as we mentioned above, the POSS is very costly [19]. HTPB-based PU filled with polysiloxane and polycarbodiimide, which are fillers of the reactive type, these materials are used to shield the rocket motor from high-temperature ablation. Therefore, the type of organic-inorganic hybrid is enhanced PU with greater thermal stability and modulus than the original PU[20]. Table 2 includes a list of some of the PU composites utilized as shielding components for rocket engines.



$$\left[R-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-R'-\overset{H}{N}-\underset{\underset{O}{\|}}{C}-O \right]_n$$

Figure 5. Chemical structure of polyurethane elastomer.

2.2 Fillers and fibers used in EHSM

For nanofillers to be used with EHSM, proper fiber and filler mixing with rubber are essential for producing a thermal insulation composite that performs well. The primary requirement for compositions used in thermal insulation is the bond strength between the polymer and additives like CF, kevlar, and SiO_2. As the insulation composite is being created, it is also essential that these additives be uniformly distributed throughout. Typically, reinforcement to matrix proportion is no more than 20% since at that point the heat shielding properties start to deteriorate. Some simultaneous factors were involved, like the mixing technique, the interaction between filler, fiber, and matrix, fiber-fiber interaction, the interaction between fillers, and the surface area of the particle [21].

In the past, asbestos was once widely used as a reinforcement fiber in a variety of products especially elastomers. Without a doubt, asbestos fiber is no longer employed in the creation of composites due to its potential for cancer. Especially, Artificial fibers, such as fibers made of carbon, aramid, etc filled the gap found in polymer HSM due to their superior thermo-mechanical and ablation resistance qualities. The introduction of carbon fiber into the matrix, ablative TPS is more resistant to erosion and ablation, due to the enhancement charring mechanism and char reinforcing reaction. Aramid fibers are incorporated in the polymeric matrix due to having some advantages:

excellent tensile properties, high degree of thermal stability, limited density, poor thermal conductivity, and corrosion resistance. The two main morphologies of aramid short fibers are stapled fibers and pulp [22].

For fillers and flame retardants specifically, it should be noted before using these additives that there is compatibility between them and the polymer HSM. Otherwise, the mechanical characteristics of TPS may suffer severe degradation. Numerous of these compounds have high levels of flame retardation due to their chemical makeup, which includes aluminum, bromine, phosphorus, antimony, chlorine, and boron. These elements are the basis for about (95%) of all additives, which are used as boron oxides, antimony oxides, and alumina trihydrate. Antimony trioxide and halogen-containing compounds are two synergistic flame retardants that are frequently added to EPDM composites to increase their flame retardancy. Halogen-type materials during burned would emit corrosive or toxic byproducts, posing a threat to human health and the environment. Moreover, the trend is to use organic or nanomaterials as a retardant flame in place of halogen compounds to enhance the properties of polymer HSM in terms of thermal and mechanical properties and also to prevent damages caused by the combustion of halogen compounds [23].

In recent years, nanoscale materials have been used instead of traditional materials such as nanosilica, nanoclay, nanofibers, and carbon nanotubes. because of the high surface area of nanomaterials enhancement mechanical and thermal properties for TPS. Moreover, the modern reinforcement materials for TPS represented by polyamide, polyimide, polysulfonamide, or polybenzoxazol. It has been proven to improve thermal insulation behavior and give better performance for ablative requirements[4].

3. A Comparative study of the different EHSMs

Table 2 lists the thermal, physical, and mechanical characteristics of insulators made of silicon, PU, NBR, and EPDM rubber. The ablation rate is viewed primarily based on thermal behavior found by recent studies as a condition for EHSM. According to the reviewed data, the erosion rate for NBR insulations, varied from (0.06 mm/s to 0.235 mm/s); for EPDM insulations, varied from (0.015 mm/s to 0.21 mm/s); for PU insulations, it varied from (0.13 mm/s to 0.346 mm/s); for silicon insulations, it varied from (0.045 mm/s to 0.02 mm/s). Although these results are from different materials, different mixing conditions, as well as different test conditions, they showed that the performance of NBR, EPDM, PU based HSM is very close when compared to each other. In addition, the table shows the mechanical characteristic of the insulation as an essential comparison factor because it is just as important as the thermal resistance. Hence, improving the mechanical properties of EHSM helps it withstand physical stress, vibration, and aging to maintain its overall performance as an SRM insulator. It was observed that (MPI) and (SiC) improved the mechanical properties when added to the NBR and EPDM matrix, the tensile strength reach about 18 MPa and 12 MPa respectively. Beside, observed the tensile strength for PU matrix and silicon rubber compositions is lower than the tensile strength for NBR and EPDM compositions. And also, comparing the results of density and thermal conductivity for NBR, EPDM, and PU based HSM, they demonstrated that there is little difference when compared to each other. It has been noticed that the mechanical characteristics deteriorate with increasing concentration of additives, which is a drawback of conventional additives. The development of effective flame retardants is inevitable.

These days, people are more aware of the fire risks associated with polymeric materials, and as a result, a variety of environmentally friendly flame retardants FRs are becoming more popular. In the past decade, a new type of flame retardant has been found, which is a hybrid of transition metal ions and organic groups in the form of bonds called metal-organic frameworks MOFs. In contrast to other inorganic FRs, MOFs are a series of organic-inorganic hybrids whose organic component improves the adhesion between additives and polymers without requiring any more organic additives. The mechanical performance will often be worsened by the incompatibility of inorganic FRs filling with polymer. The mechanism of MOFs as flame retardant, the extraordinary chemical makeup of MOFs is responsible for their excellent smoke suppression and flame resistance performance. During the exposure of the MOFs to high temperatures, they decompose to metal oxides, carbonized MOFs, and released gases. The MOFs particles release some non-flammable gases like CO_2 and NH_3, which may reduce and that dampen the amount of combustible gases. Metal oxides have a catalytic effect that helps to promote char formation and prevent smoke release. Besides, coherent and compact char layers prevent pyrolysis products, combustible gases, and oxygen from changing and harming the pristine matrices. In recent articles, MOFs-based flame retardants were applied in epoxy resin (EP), polyurethane (PU), and poly (lactic acid) (PLA). Notable MOF classes include (ZIFs), (MILs), and (UiOs), all of which are blended directly into polymers to study their flame retardancy. TGA tests showed that the addition of MOFs significantly improved pure matrix thermal stability by reducing the thermal degradation of the matrix. Also, the composites had a higher char yield than the pure matrix, suggesting that MOFs played a significant role in the formation of char in matrix/MOFs composites [24,25]. In recent years, most articles have focused on thermal protection layers using different materials for rocket engine applications. Researchers have not used MOFs as flame retardants for TPS in rocket engines, so we recommend utilized of MOFs within insulating components due to the aforementioned MOF advantages of higher flame retardancy.

Table 2: Comparison between NBR, EPDM, silicone, and PU-based HSM [4].

	Compositions	Ablation rate (mm/s)	Thermal conductivity (W/mK)	Tensile strength (MPa)	Elongation (%)	Density (kg/m^3)
Nitrile rubber matrix	0% PR/NBR-50%PR/NBR	0.235/0.095	0.07-0.185	-	-	1.03-1.14
	NBR/15phr Silica aerogel	0.108	0.172	8.2	1040	1.190
	NBR/6phr KP –NBR/8 phr MPI	0.137-0.05	-	15.4-18.2	666.6-768.7	-
	NBR/6% SCF	0.06	0.08	4.75	22	-
EPDM matrix	25 phr CF /25 phr KP /EPDM	-	0.198	11	7.4	1.16
	30phr KP/EPDM	0.015	0.171	9.35	11.7	1.185
	10 phr KP /5phr MWCNT /EPDM	0.092	-	6.28	385	1.120
	EPDM /20phrSiC	0.21	-	12.09	716	1.081
Polyurethane matrix	12% AL_2O_3 /HTPB	0.13	0.26	2.393	469.1	-
	HTPB/5% Cloisite20A	0.42	-	1.375	640	-
	33 wt.% POSS/ HTPB-HTPB based(PU)	0.247-0.346	-	-	-	-
Silicon rubber	40 phr ZrC/silicon / 40 phr ZrO_2	0.045/0.02	-	4.46/4.38	83.3/78.7	-
	20 phr ASCF /40 phr Wollastonite	0.041	-	-	-	-

Abbreviations: PR: phenolic resin. KP: Kevlar pulp. (-): not analyzed. phr: parts per hundred resin. FS: Fumed silica. ASCF: Aluminum Silicate Ceramic Fiber. MPI: modified polyimide. SiC: silicon carbide.

4. Conclusion

This article evaluated various EHSM types as potential SRMs insulation candidates and their usefulness in real-world applications. This paper also covers materials, that have attributes like higher thermal stability and ablation capabilities, which might be used in the future. Actually, the lowest result for ablation rate was recorded at (0.06 mm/s) for NBR-based (EHSM). Elastomers would be the preferred choice among various polymeric ablatives and the characteristics of shielding composite materials can be modified to some extent by the suitable selection of fillers, reinforcements, and additives. In previous decades, nitrile rubbers were used for almost of heat shielding applications in SRMs due to their being polar and therefore compatible with additives and thus enhancing the thermal and mechanical characterization of HSMs. The synthesis of rubber materials with nanoparticle stiffening agents yields a new design for TPS. Elastomeric materials, such as PU elastomeric composites, now play a bigger role in hypersonic flying missions. The advantage of PU elastomer is simple to pour or spray onto the internal layer of the SRM when compared to the other elastomers. The ablation rate for PU-based EHSM and thermal conductivity was recorded at (0.13 W/mk) and (0.26 mm/s) respectively, which are near to the result obtained from NBR and EPDM-based EHSM. Aramid fibers, CNTs, and PI fibers can replace the high-performance asbestos fibers used as reinforcement in EHSMs. Advancements in these substances can be obtained by adjusting the reinforcement concentration, incorporating multiple additives, optimal fiber loading percentage, and suitable processing techniques. Future trends focus on using metal-organic frameworks emerged as a replacement for halogens flame retardants due to their simple processability and compatibility with the matrix base for composite materials.

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