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Development of Asbestos-free and Environment-Friendly Thermal Protection for Aerospace Application

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Thermal protection systems (TPS) are components designed to protect the internal and external areas of a rocket motor from high temperatures. There has been studies in Brazil of resin-based polybutadiene hydroxylated (HTPB) loaded with asbestos since the 1970s. Nevertheless, asbestos has been banned in several countries because it is severely harmful to the human health. In this context, the development of asbestos free in flexible thermal protection (FTP) is extremely important. This study evaluates the use of Expanded Perlite (PExp) as an asbestos substitute. Lower densities were observed, which become a very interesting achievement for the aerospace field. Samples with 5 phr of Expanded Perlite showed similar results when comparing with 47 phr of fillers in PTF reference on oxy-acetylene torch test, and a reduction about 20 % of mass loss rate in test with solid propellant, thus showing that Expanded Perlite can replace asbestos in FTP.

Keywords: *asbestos replacement, expanded perlite, polybutadiene hydroxylated, thermal protection.*

1. Introduction

Rocket structures suffer extreme internal and external heating during operation. The temperature can achieve 3000 ºC in the combustion chamber, near the nozzle region. Thus, it is a critical subject in space programs. To overcome this crucial situation, Thermal Protection Systems (TPS) are designed to reduce the temperature and heat flow by ablation during propellant combustion or reentry[1-9].

In general, there are two groups of TPS: rigid TPS and flexible TPS. Rigid TPS materials are basically phenolic resins, ceramics and metals. Typical flexible TPS are made of polyurethane resins, elastomers, silicon, etc. Rigid protections show higher mechanicals properties in comparison to the flexible protections, nevertheless when considering the protection ability**,** each one of them has particularities that define its application[6-7,10-13,14].

A typical rocket motor, Figure 1, consists basically of three components: nozzle, igniter, and the motor case. The nozzle is responsible for the expulsion of the combustion gases, and the igniter starts the burning process of the solid propellant in the combustion chamber. The motor rocket is a cylindrical tube that carries the solid propellant.

As a single material is unable to meet all thermal, physical-chemical and mechanical requirements, a wide variety of materials have been used jointly as TPS, for protection of the internal and external components of a rocket motor [14,16].

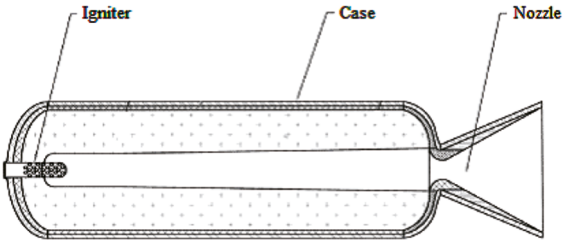

Figure 1. Components of a rocket motor[15].

One of this are the polymeric materials, mostly composites, have been widely used as TPS due to their mechanical properties, ablation rate, low density, among others essential characteristics for space application[2,4-6,8,11,17,18].

Elastomers such as Acrylonitrile Butadiene Rubber (NBR) and Ethylene Propylene Diene Monomer (EPDM) with reinforcement materials have been employed as matrix in ablative composites. However, they are unable to form char, a protective layer that is very resistant to mechanical erosion. The addition of cork, silica and carbon fiber used as matrix reinforcement can improve significantly the ablative properties[4,19].

The Brazilian Space Program has successfully been developing TPS applied to motor rockets since 1975. These TPS are usually made of a hydroxyl-terminated polybutadiene

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(HTPB) matrix with asbestos as the main reinforcement. The asbestos has been used due to its excellent thermal properties[20].

Over the years, asbestos has been proved very harmful to the human health, and thus has been banned in several countries. Attempts to substitute this material in TPS systems have continuously been made in the aerospace field. A Brazilian study[21] evaluated by thermal analysis the use of different contents of hydrated alumina silicate (SA) and expandable graphite (GE) in the liner. Thermomechanical analysis (TMA) showed that the thermal expansion coefficients of the liners with SA were lower than the liners with asbestos. Liners containing SA presented the highest tension values in the performed mechanical tests. The thermal stability of liners, evaluated by thermogravimetric analysis (TGA), showed that the filler replacement practically didn't affect the activation energy (Ea) obtained for the decomposition. The authors concluded that SA can replace asbestos with improvement of properties, although the SA reinforcement resulted in a considerable lower elongation until rupture. At this moment, there is no conclusion related to ablative performance because samples were not tested.

In Brazil, judicial disputes have been taken place over the years about the prohibition of asbestos. There are still debates whether all types are indeed prejudicial. However on November, 29, 2017, asbestos was banned in Brazil[22]. Even if in a hypothetical scenario, asbestos is liberated in Brazil, the foreign market would force its replacement. Latest tendencies point to the asbestos banning, favoring the human health and preserving the environment[23]. According to Jargin[24], asbestos replacement studies must be kept aside from the industry interests.

Of all the classic materials applied to polymeric matrices, Expanded Perlite (PExp) has been the reinforcement least applied to TPS. It is commonly used in thermal and acoustic insulation. Perlite is a generic term for siliceous rocks that are usually composed of minerals rich in SiO_2 e Al_2O_3. Perlite is an insulation material of inorganic origin that is light, fire resistance, and present good thermal and acoustic insulation properties[25-29].

The characteristic that differentiates perlite from other rocks is that when heated, usually between 900 and 1100 ºC, its structures undergoes a light softening and the loss of humidity (2 to 5%). Water molecules vaporize leaving a cellular structure, which increases the material in volume by 10 to 30 times. This material is then called PExp and the new expanded structure is responsible for its low mass and excellent thermal and acoustic insulation[25,29].

PExp is very attractive to the insulation industry because, besides its porous insulating configuration, it is fire and chemical resistant[25,30]. The hollow spaces inside the PExp structure act as a barrier to conductive and convective heat transfer. Voids reduce energy flow in the conductive heat transfer process. These factors contribute to make PExp a good substitute for asbestos, with the advantage of being a low cost product[27].

Thus, there is a need for environmental and health requirements for the replacement of asbestos and a commercial necessity, considering the possibility of Brazil failing to act in the international aerospace market, with the supply of motor rockets, due to the prohibition of these countries in relation to the presence of asbestos. In this context the use of Expanded Perlite can be a suitable solution to the problem, opening new study fronts for this type of material and consequently in the development of new products, not only for the aerospace sector, but for all the sectors in which asbestos had great participation.

The study of asbestos replacement in the composition of Flexible Thermal Protections will serve as a basis for future research on formulations based on polyurethane and epoxy resin, which make up other parts of the motor rockets, such as adhesive coating for solid composite propellant, top inhibitions among others. Thus, this paper proposes the study of asbestos substitutes, with the understanding that the data obtained with these materials will be the starting point for the continuous improvement of thermal protection processes, allowing a multiplier effect, when applied to similar systems.

2. Materials and Methods

2.1 Materials

The most significant materials used in this study are: Hydroxyterminated Polybutadiene resin (HTPB), from Liquiflex, Brazil (Hydroxyl number 0,82 mmol/g); Expanded Perlite (PExp) SF22, from Schumacher Insumos, Brazil; and Toluene Diisocyanate (TDI) type Voranate T80, from Isopol, Brazil.

2.2 Formulations

Samples of TPS without asbestos (PExp-1 to PExp-5) were prepared according to Table 1. TPS binder and TPS Reference refer to the formulation without filler and the usual asbestos TPS, respectively.

2.3 Sample preparation

Initially, fillers were heated to 110 ºC during 2 hours to eliminate the moisture present, according to internal procedure. HTPB resin and plasticizer Dibutyl phthalate (DBP) were also heated to approximately 60 ºC. Thereafter, HTPB resin, plasticizer DBP, catalyzer Iron(III) acetylacetonate $Fe(C_5H_7O_2)_3$, and respective fillers were weighted according to the formulations, and homogenized by mechanical stirring.

All the samples (mechanical and ablation tests) were cured for 24 hours at 60 ºC and then subjected to additional post curing, at ambient conditions during 7 days, to achieve the ultimate mechanical properties according to internal procedure. For the mechanical tests, the samples were in

Table 1. Compositions of samples used.

Component	TPS Binder(phr)	TPS Reference(phr)	TPSPExp-1(phr)	TPSPExp-2(phr)	TPSPExp-3(phr)	TPS Pexp-4 (phr)	TPSPExp-5(phr)
HTPB	100	100	100	100	100	100	100
TPS reference fillers	-	47.0	-	-	-	-	-
DBP	-	2.11	-	-	-	-	-
$Fe(C_5H_7O_2)_3$	0.016	0.016	0.016	0.016	0.016	0.016	0.016
PExp	-	-	1.0	2.0	3.0	4.0	5.0
TDI	7.50	7.50	7.50	7.50	7.50	7.50	7.50

phr: Parts per Hundred Rubber, unit of measure used in all components.

accordance with ASTM D412 Standard[31], for the OAT tests, the samples were diameter of 125 mm and 6 mm of thickness. For Propellant Ablation Tests the dimensions of the samples were diameter of 50 mm and height of 40 mm with a square internal piece of solid propellant with 10 mm of side and 40 mm of length.

2.4 Methodology

Morphology of expanded perlite particles: The shape of perlite particles was evaluated in an optical stereomicroscope Carl-Zeiss, model Discovery V12.

Characterization by Fourier Transform Infrared Spectroscopy (FT-IR): FT-IR spectra of PExp samples were collected in a FT-IR Spectrum One PerkinElmer Spectrometer, in the mid-infrared region (4000 to 550 cm^{-1}). The spectra were obtained by transmission mode and the resolution 4 cm^{-1}. Samples were prepared as KBr pellets (0.8:400 mg KBr).

Characterization by Thermal Analysis: Thermogravimetric analysis (TGA) was performed to evaluate the PExp thermal stability. Three samples of (4.860 ± 0.432) mg were placed and pressed in a platin sample holder. Analysis were carried in a Simultaneous Thermal Analyzer SDT TA Instruments Q-600, under a nitrogen flow of 50 mL/min, from 30 to 1000 ºC, at a heating rate of 10 ºC/min.

Filler characterization by granulometric analysis: The granulometric analysis was performed in a MASTERSIZER 2000 equipment (MALVERN Instruments), in aqueous (water) medium. Environmental conditions were: temperature from 19.2 to 20.1 ºC, and relative humidity between 36.5 and 37.4 %.

Mechanical tests, hardness, and density determination: Five samples were tested for elongation and ultimate strength in a ZWICK 1474 mechanical tester, according to the ASTM D412 Standard[31]. Hardness tests were carried in an INSTRON S1 tester, according to the ASTM D2240-05 Standard[32]. Density of three samples was determined by the principle of Archimedes.

Oxy-Acetylene Torch Testing (OAT): Ablation tests were performed with an oxy-acetylene torch, according to the ASTM E285-08 Standard[33]. The oxyacetylene burner provides a flow of steady hot gas that simulates the propellant combustion inside the motor rocket chamber. The torch heat flux was approximately (800 ± 20) W/cm^2.

Propellant Ablation Test: The Figure 2 shows the testing apparatus that allows the investigation of the samples ablative performance in association to the propellant combustion. Subsequently to the combustion in ambient condition, the formed char layer is weighted. Replicates (15 of each sample) were analyzed for the TPS reference formulation e for the TPS PExp-5. TPS PExp-5 was selected because of the superior OAT result. Analysis conditions measured during the test: burn rate (0.94 + 0.02) mm/s and mass flux (0.160 + 0.03) g/s.

This test, an adaptation of an internal procedure, consists of subjecting the sample to a parallel mass flow and reaction products generated during the combustion of the solid propellant in order to evaluate the wear on the TPS reference and TPS Pexp-5 formulations. During combustion of the propellant, some chemical species such as CO_2, H_2O, OH are generated in addition to Al_2O_3 particles that cause both the surface oxidation of the samples and the mechanical erosion from the mass flow and impact of the alumina particles. The ablation process under the action of the propellant is influenced by the burn area, internal pressure, gas flow and temperature so that the temperature will directly influence the oxidation process and the gas flow will act directly in the mechanical erosion of the surface already weakened by the oxidative process[34,35].

Figure 2. Propellant Ablation Test apparatus.

3. Results and Discussions

3.1 Particle morphology

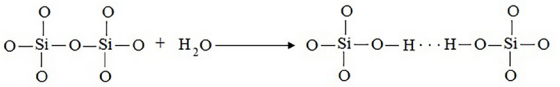
Figure 3 shows optical the stereomicroghaphic image of neat PExp.

The stereomicrography test of neat PExp (Figure 3) shows a porous structure. Such configuration accounts for the material low density and good insulation capacity, and provides good ablation resistance of the TPS PExp. This type of morphology helps to decrease the heat transfer to the lower layers, thereby reducing the pyrolysis process of the HTPB matrix and consequently improving the thermal and ablative resistance of TPS PExp[25,30,36,37].

3.1 Characterization by FT-IR

Neat PExp was characterized by FT-IR, in the medium region (MIR), to characterize its functional groups. Figure 4 shows the obtained FT-IR spectrum.

The presence of water molecules inside the PExp structure occurs due to its formation process and to the environmental humidity. Water interacts with the perlite structure to promote a chemical reaction that severs many Si-O bonds of the tetrahedral structure of perlite. The result is unstable hydrogen bonds **(Scheme 1)** which promote the perlite expansion under heating[38].



Scheme 1. H_2O molecules reaction with the tetrahedral structure of perlite[38]

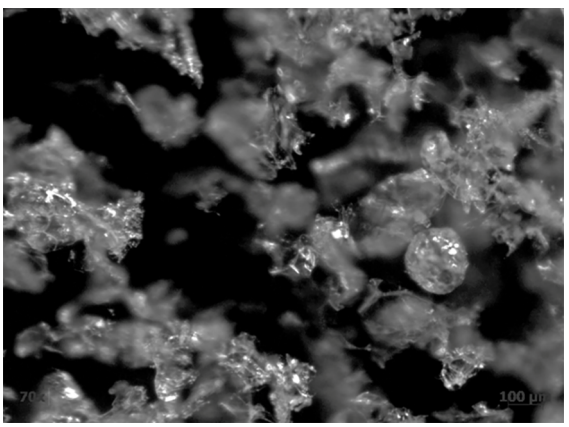


Figure 3. Stereomicrography of neat PExp. Magnification: 70x.

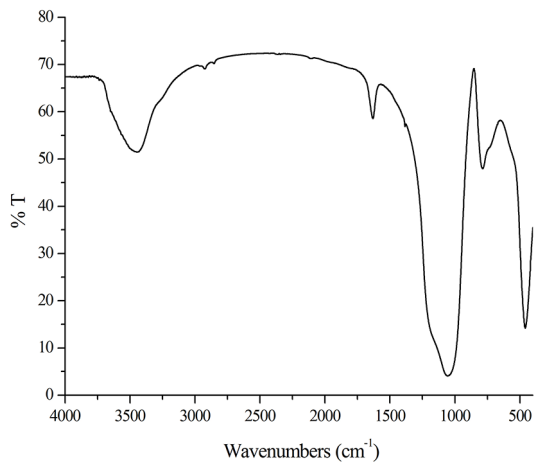


Figure 4. Transmission FT-IR/MIR Spectrum of neat PExp, prepared as KBr pellets (0.8:400 mg KBr).

The FT-IR Spectrum of neat PExp showed the presence of absorptions around 3447-2924 cm^{-1} that are attributed to the combination of hydroxyl (OH) group, silanol groups (Si-OH), and water adsorbed in the porous structure. These bands are in agreement with the molecules showed in Scheme 1 and in the literature[25,29]. An absorption at 1630 cm^{-1} shows the presence of water adsorbed as well. It should be noted that all of the above bands can also originate from the material used in the pellets. As well known, KBr salt is highly hygroscopic and it might affect the FT-IR spectrum causing enlargement and increase of bands intensity[39] in the region of 3400 and 1650 cm^{-1}.

Several other bands were detected as well: 1055 cm^{-1} and 786 cm^{-1}, assigned to the Si-O vibrational stretching of the Si-O-Si groups and of the Si-O-Al groups, respectively; and a band at 459 cm^{-1} from the Si-O-Si bonds, assigned to bending vibrations[39].

3.2 Characterization by thermal analysis

Figure 5 shows the TGA analyzes of neat PExp. TGA profile shows a mass loss of (4.637 + 0.424) mg or (4.6 ± 0.6) %, from 50 ºC to 980 ºC. This mass loss relates to the evaporation of water molecules present at the surface of neat PExp[29,40] and confirms that neat PExp is basically perlite. According to Celik[41], the water loss mechanism happens in three distinct steps due to the porous structure of the PExp. Initially, at 250 ºC occurs the first water loss from the surface and from the more superficial porous. The second dehydration step occurs between 250 and 550 ºC, which are related to the water from the internal porous. Third step happens between 550 e 950 ºC, and is related to the dissociation of the OH groups bonded to the oxygen atoms.

3.3 Filler characterization by granulometric analysis

Table 2 presents results from the granulometric analysis of the PExp.

The value that best represent the PExp granulometric results is average d(0.5), because the d(0.9) e D[4.3] values may contain errors that suggests higher levels due to possible agglomerations. Thus, granulometric analysis indicates that PExp present the average d(0.5) of (53 ± 1) μm.

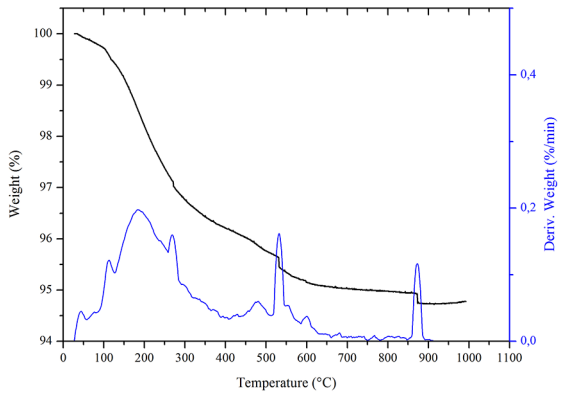


Figure 5. PExp TGA Thermal profile.

Table 2. Granulometric distribution of the PExp sample.

Sample	Distribution (μm)			Diameter médio (μm)
	d (0.1)	**d(0.5)**	**d(0.9)**	**D[4.3]**
PExp	15 ± 1	53 ± 1	158 ± 1	76 ± 1

d(0.1) = 10% in volume present values lower than indicated.
d(0.5) = 50% in volume present values lower than indicated.
d(0.9) = 90% in volume present values lower than indicated.
D[4.3] = mediam particle diameter.

3.4 Mechanical properties and density

Figure 6 shows optical stereomicroghaphs of neat PExp disperse in HTPB matrix and Table 3 shows results from the mechanical tests and density determination for all the formulations.

Figure 6 displays particles of PExp in the HTPB matrix. Darker regions suggest that some particles did not disperse properly in the matrix. Such areas cause variations in ablative and mechanical properties because these properties depend on good particles dispersion, according to Kallergis[42].

Figure 7 presents the tensile strength versus elongation profile for the TPS binder, TPS reference and TPS PExp samples.

The examination of Table 3 and Figure 7 indicates differences between the mechanical properties of the formulations. TPS reference shows higher values that can be attributed to the filler content. Fillers reinforce the HTPB matrix, however they can affect negatively the density as it increases its values[42]. For aerospace application, this is definitely undesirable.

Kallergis[42] in your research explain that perlite possibly forms a second phase with the matrix due to clusters, decreasing the mechanical properties as can be seen in Table 3.

According to Verbeek[43] and Li[44] the properties of composites are extremely dependent of presence of filler and their characteristics such as particle size, distributions, shape, interactions matrix filler and nature of filler. The evaluation of tensile strength in Table 3 for TPS PExp-1 to 5, is possible to observe the percolation phenomenon, because of significant change in physical properties after TPS PExp-3[45,46].

The percolation phenomenon can be used to explanation the particle-particle of expanded perlite in HTPB matrix and is the responsible for the decliner of the tensile strength according the quantity of perlite is increase, i.e the excessive amount of particle causes resin-poor area around the perlite that leads to weak stress transfer between the HTPB matrix and perlite that causes a decrease of tensile strength[43,45,47].

Furthermore, increasing the PExp concentration affects significantly the density due to its content, porosity and to the low granulometry of the perlite[41,42,48]. Even so, the density of the TPS PExp samples showed lower results than the TPS reference.

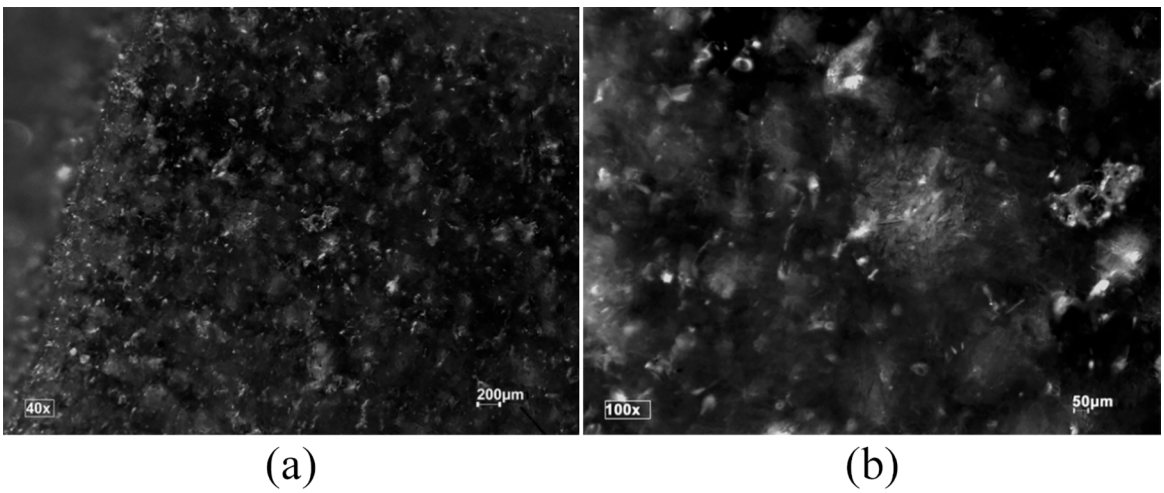


Figure 6. Stereomicrographs of PExp disperse in HTPB matrix. Magnification: A) 40x and B) 100x.

Table 3. Results from mechanical tests and density determination.

Sample	σ (MPa)	ε (%)	E (MPa)	H (Sh.A)	ρ (g/cm³)
TPS Binder	1.23 ± 0.10	116 ± 15	2.15 ± 0.05	47 ± 1	0.930 ± 0.001
TPS Reference	1.98 ± 0.17	157 ± 11	3.57 ± 0.44	58 ± 1	1.151 ± 0.001
TPS PExp-1	1.25 ± 0.07	131 ± 9	2.16 ± 0.15	50 ± 1	0.932 ± 0.004
TPS PExp-2	1.26 ± 0.04	141 ± 6	2.18 ± 0.06	48 ± 1	0.934 ± 0.004
TPS PExp-3	1.49 ± 0.04	145 ± 4	2.54 ± 0.11	48 ± 1	0.941 ± 0.003
TPS PExp-4	1.39 ± 0.03	120 ± 8	2.85 ± 0.07	51 ± 1	0.947± 0.001
TPS PExp-5	1.22 ± 0.06	130 ± 6	2.56 ± 0.09	50 ± 1	0.951± 0.001

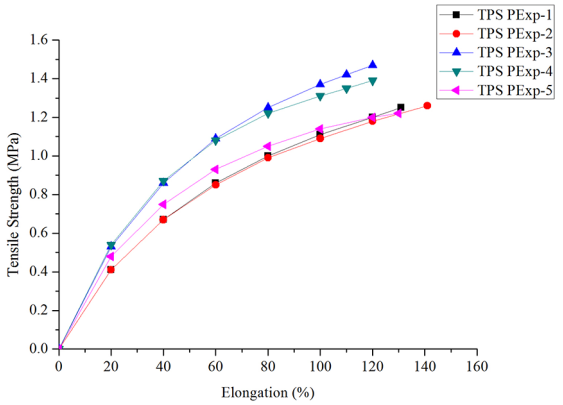


Figure 7. Tensile strength versus elongation profile for the TPS PExp samples.

3.5 Ablative properties

Figure 8 shows photographs of TPS PExp-5 sample before and after oxy-acetylene torch ablation test.

Figure 8-B illustrates the TPS PExp-5 sample with a central orifice after oxy-acetylene torch ablation test. It occurs during the pyrolysis under certain conditions of mass flux and heat from the torch. Thereby, the burn time and ablation rate parameters can be estimated to determine the final thickness of the TPS[33].

Table 4 and Figure 9 show the ablation test results, burn time and ablation rate for some formulations. The choice of TPS PExp-1, 3 and 5 was according to percolation phenomenon, how is the result with minimum, medium and maximum amount of perlite in HTPB matrix. According to the ASTM E285-08 Standard[33] burn time refers to the time taken to burn-through the sample while the ablation rate represents the burning distance as a function of time (mm/s). Results were evaluated statistically by using the Chauvenet Criterion[49,50].

Materials with good ablative properties present high burn time and low ablation rate[14]. In this context, TPS reference and TPS PExp-5 are the ones with the best results. Considering the results and in view of the filler content of each formulation, the efficiency of the expanded perlite is evident as the addition of 5.0 phr in the HTPB matrix was enough to improve the ablative properties, practically at the same level as the TPS reference.

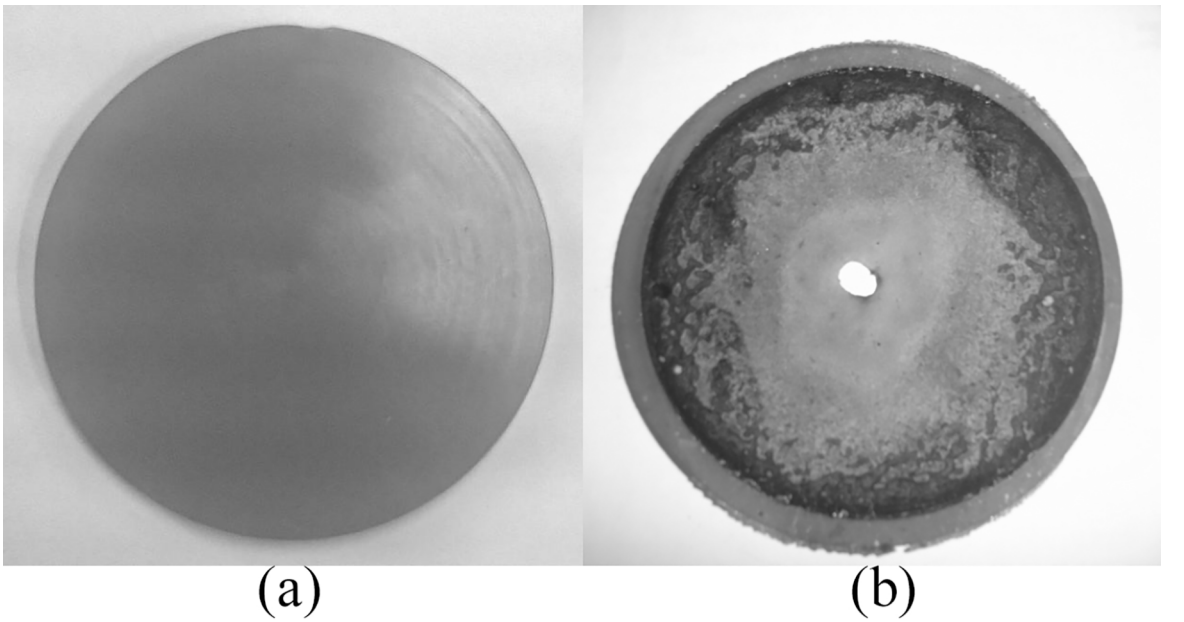


Figure 8. Photographs of TPS PExp-5 sample: A) before; and B) after oxy-acetylene torch ablation test[33].

Table 4. Results for burn time and ablation rate for the different samples.

Sample	Filler content (phr)	Burn time (s)	Ablation rate (mm/s)
TPS Binder	0	6.8 ± 0.1	0.94 ±0.02
TPS Reference	47.0	9.5 ± 0.5	0.68 ± 0.02
TPS PExp-1	1.0	8.0 ± 0.4	0.80 ± 0.03
TPS PExp-3	3.0	8.5 ± 0.2	0.75 ± 0.01
TPS PExp-5	5.0	9.2 ± 0.4	0.70 ± 0.04

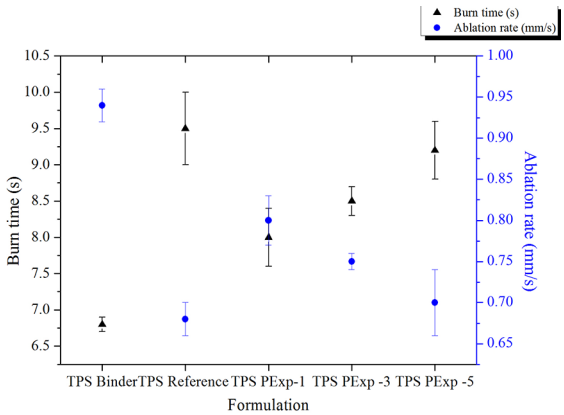


Figure 9. Burn time and Ablation rate with an oxyacetylene torch for the formulation studied

Table 5 shows TPS Reference and TPS PExp-5 rates of mass loss in propellant ablation test. Only these formulations were tested considering the preliminary good results of TPS PExp-5, and due to samples costs and availability. This test evaluates char layer resistance during propellant combustion. It simulates what actually happens inside real combustions chambers, unlike what occurs with the OAT test[14].

Table 5 results agree with Kallergis[42]studies as they confirm the pyrolysis characteristics of expanded perlite particles. TPS composition with expanded perlite as the filler provides a char layer more resistant to the heat and the mass flux generated by the propellant combustion.

Results of the PExp samples, Figure 9 and Tables 4 and 5, are in agreement with the literature[14], to diminish the ablation rate and thus increase the burn time it is a requirement to create a stable char layer. This layer in the surface reduces the heat flow, the oxygen diffusion, and consequently the thermal degradation of the material more internal layers[42,48]. According to Sheu[51], the use of asbestos fibers in the reference material helps the anchoring of the char layer during the pyrolysis process of the organic matter. Thus, it difficults the heat flow and the oxygen diffusion to the internal layers. Moreover, the presence of SiO_2 assists in the generation of an uniform inorganic layer that acts as a momentary barrier to the ablation process. Nevertheless, these fillers tend to increase the material thermal conductivity allowing for faster heating of the lower layers, thereby causing an increase in degradation rate[7,52].

Table 5. TPS Reference and TPS PExp-5 rates of mass loss in propellant ablation test.

Sample	Rate of Mass Loss(g/s)
TPS Reference	0.041 ± 0.001
TPS PExp-5	0.033 ± 0.001

The presence of PExp creates a stable and resistant char layer, with the advantage of being light and insulating due to the natural porous structure. Furthermore, its particle sizes allow a better accommodation of the filler in the HTPB matrix, reducing the sites that the matrix would occupy and, thus, creating a more effective inorganic layer against the heat flow and oxygen diffusion. Consequently, it minimizes the pyrolysis of internal layers and, this way, the thermal protection consumption. These results demonstrate that PExp has potential to substitute asbestos in insulating materials[42,48].

4. Conclusions

The ablation tests results of oxy-acetylene torch and under the action of the gases generated by the combustion of the solid propellant show that the Expanded Perlite performance as ablative filler in the HTPB matrix is adequate to replace asbestos as a component of thermal protections. It also has the additional advantage of reducing the material density, which is also of great value for the aerospace industry.

This replacement also solves the severe problem of having to use asbestos, a product known to be carcinogenic, allowing Brazil to remain in the international space market.

However, regarding the mechanical properties of the PExp formulations, the performance was not as good as the reference TPS with asbestos. This can be credited to the fact that this material does not present reinforcing characteristics for the HTPB matrix. However, the use of PExp in TPS formulations is still considered feasible because its flap configuration allows the mechanical properties presented.

In an attempt to resolve the problem of low mechanical properties, other studies are being developed by this group to make the use of perlite more attractive, by the addition of compatibilizing agent to improve the interaction of PExp in the HTPB matrix. This will be the goal of a new publication.

5. Acknowledgments

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