

# Study of Modified and Improved Carbon Phenolic and Carbon Elastomeric Ablative Composites

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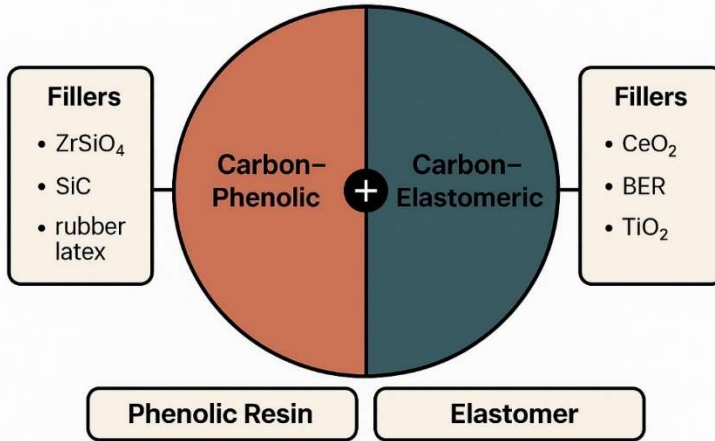
**Abstract.** This article presents a structured comparative review of carbon–phenolic and carbon–elastomeric ablative composites used in thermal protection systems for aerospace and hypersonic applications. The review critically examines the influence of various ceramic, metallic oxide, and polymeric fillers on ablation behaviour, char formation, mechanical integrity, and erosion resistance. Reported studies employing oxy-acetylene torches, plasma wind tunnels, flames, and laser ablation are systematically analyzed using metrics such as linear ablation rate (LAR), mass ablation rate (MAR), heat flux, and exposure duration. The role of hybrid filler systems in enhancing char stability and thermal resistance is discussed through mechanistic correlations between filler chemistry, char microstructure, and ablation performance. Key challenges in data normalization and cross-comparison are highlighted. Finally, the article outlines specific future research directions, including multi-physics ablation modelling, AI-assisted material design, graded thermal protection architectures, and in-situ diagnostics, to advance the development of next-generation ablative composites.

## 1 Introduction

Ablative composites are essential materials in high-temperature engineering applications, particularly in aerospace and rocketry, where structural components are exposed to extreme thermal and mechanical loads. These materials function as sacrificial barriers that absorb and dissipate heat through controlled material removal, thereby protecting the underlying structure from catastrophic failure. Among the various ablative systems, carbon–phenolic and carbon–elastomeric composites have attracted considerable attention for their superior thermal stability, mechanical strength, and resistance to oxidative degradation. Carbon–phenolic composites are widely used in re-entry vehicle nose cones, rocket nozzles, and heat shields, while carbon–elastomeric composites find applications in flexible thermal protection systems due to their resilience and toughness.

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Fig. 1 illustrates the structure and classification of ablative composites, distinguishing between carbon–phenolic and carbon–elastomeric systems. The diagram highlights the core materials and filler reinforcements used in each type: carbon–phenolic composites incorporate fillers such as zirconium orthosilicate ( $ZrSiO_4$ ), silicon carbide (SiC), and rubber latex, which enhance thermal stability, erosion resistance, and char strength, with phenolic resin serving as the rigid matrix material. In contrast, carbon–elastomeric composites utilize fillers like cerium oxide ( $CeO_2$ ), bismaleimide epoxy resin (BER), and titanium dioxide ( $TiO_2$ ) to improve oxidation resistance, tensile strength, and flexibility, supported by an elastomeric matrix that provides superior resilience under dynamic thermal conditions.



**Fig. 1.** Structure of carbon–phenolic and carbon–elastomeric ablative composites.

Despite their proven performance, conventional ablative composites often face challenges, including limited erosion resistance, suboptimal char-layer integrity, and moderate mechanical properties under high-heat-flux conditions. To address these limitations, recent research has focused on incorporating functional fillers and hybrid reinforcements to tailor the thermal and mechanical behaviour of ablative materials. The inclusion of ceramic and metallic oxides as fillers has been shown to improve thermal conductivity, enhance char formation, and reduce ablation rates by forming thermally stable protective layers.

The choice of material used in ablative composite is rigidly related to its properties and the conditions in which the composite will work; no individual material can fulfil such a wide range of operational conditions so efficiently [1]. In the last few decades, a huge variety of ablative materials have been studied, developed, optimized, and used in different conditions as required [2]. Ablation is a heat and mass transfer process in which a large amount of heat is dissipated in a very short period with a sacrificial loss of material. Ablation consists of convection, radiation, conduction, and diffusion of chemical species. The need for these materials was first recognized during the missile's development, when it failed to reach the target due to the missile skin's disintegration caused by aerodynamic heating. Ablative materials are also used to protect rocket nozzles, thermal protection systems, and ship hulls from high-heat environments [3].

Among the various types of polymeric matrices used in ablatives, the burnt matrix is relatively weak, even when using a high-char retention resin such as a phenolic; the charred polymer can be mechanically removed by the frictional action of atmospheric gases or rocket combustion products [1]. The charring material is the material that pyrolyzes, which is the most commonly used material for atmospheric re-entry. Most ablative material consists of

fibrous composites with organic resins as binders [3]. To assist the char retention, a wide range of reinforcements can be added to the matrix. Fibers made of carbon, refractory oxides, mineral asbestos, or glass are typically used. Micron-sized powdered fillers also play a very important role [1]. The extent of char removal by mechanical ablation depends on the in-plane shear strength and on the severity of the aerodynamic surface shear [4]. Rayon carbon fabric-reinforced phenolic (C-Ph) composites are widely used thermal protection systems due to the low thermal conductivity of the rayon fabric and the high char yield of the phenolic resin. In general, carbon-phenolic composites exhibit better ablation resistance and continue to improve ablative performance as the composite structure becomes thinner, enabling greater payload and fuel efficiency [5].

Development of high-temperature protection materials and carbon elastomeric ablative work as flexible heat-shielding materials with high elongation at break. The ablation resistance of rubber-based elastomeric composites is reduced compared to the brittle phenolic resin-based composites [6]. The organic polymer content decomposes in a hyperthermal environment, along with the rise in volatile components, namely, methanol, water, and carbon dioxide, followed by the conversion of silicone to a hybrid siliceous and carbonaceous char [7]. Ablative materials are used to protect certain structural parts or equipment from the intense hypothermal environmental conditions. Mostly, such composites are used in the aerospace industry. The thermal protection system (TPS) of space vehicles and long-range ballistic missiles protects them from hypersonic atmospheres encountered during their missions, which are composed of ablative, highly endothermic sacrificial materials [8]. The lower ablation resistance of rubber-based TPMs occurs due to the stresses between the pyrolysis zone and the generated char layer caused by the pyrolysis gases. Pyrolysis gases easily remove the char layer by the action of high-speed incoming shear heat flux [9]. The 1 wt.% addition of MWCNTs to the rubber matrix has remarkably reduced the backface temperature elevation during ablation testing of the ablatives. The linear and mass ablation resistances also diminished.

The thermal stability and heat absorption capability of the polymer composites also improved with increasing the filler-to-matrix ratio [10]. Oxyacetylene ablation tests are used to study the ablation properties of materials [11]. This method is intended to screen the most obvious poor materials from further consideration. Since the combustion gases more closely resemble the environment generated in rocket motors, this test method is more applicable to screening materials for nozzle and motor liners than for aerodynamic heating. The environment for any specific high-temperature thermal protection problem is peculiar to that application. This test method is used to measure and describe the properties of materials, products, or assemblies in response to heat and flame under controlled laboratory conditions [12]. Mesoporous silica particles and carbon black were selected as fillers for a resol-type phenolic resin to be used as a matrix for ablative materials. Composites were processed with the modified polymer, and carbon fibers were used as continuous reinforcement. The ablative properties of the materials obtained were studied by the oxyacetylene torch test, and the ablated samples were observed by scanning electron microscopy.

Regarding dynamic mechanical properties, the addition of particles decreased the modulus and glass transition temperature of all the systems studied [13]. Analysis of ablative charring materials with blocking effect of pyrolysis gas and its thermal response mechanism are the main thermal protection methods of charring materials, and the study of internal temperature distribution and is helpful for the analysis of the thermal protection mechanism of charring materials, the thermal protection material can avoid direct contact between the external heat flux and the airframe or the blunt body, while on the other hand, it consumes heat due to the decomposition reaction within the material and surface ablation. In addition, the pyrolysis gas generated by the resin decomposition will act as a thermal barrier, thereby hindering heat transfer to the vehicles [14]. Improvements in fire resistance can also be

achieved through the lamellar structure of raw materials such as talc or montmorillonite. For talc, increasing the lamellar coefficient (lamellarity) and specific surface area improves fire resistance, while thermal resistance is unaffected [15].

The ablation performance of modified composites is governed by a coupled sequence of physicochemical processes linking filler chemistry to char evolution and erosion resistance. Ceramic fillers such as SiC, ZrSiO<sub>4</sub>, and CeO<sub>2</sub> promote the formation of thermally stable ceramic-rich char layers that act as diffusion barriers against heat and oxidative species. In phenolic systems, rigid ceramic networks enhance char strength and reduce mechanical erosion, whereas in elastomeric systems, oxide fillers and short fibers improve char cohesion and suppress peel-off under high-shear, high-heat-flux conditions. Hybrid filler systems further synergize these effects by combining oxidation resistance, thermal insulation, and mechanical reinforcement, thereby reducing both linear and mass ablation rates.

## 2 Scope and methodology

This work is intended as a comparative and critical literature review rather than an experimental investigation. Peer-reviewed journal articles published between 2000 and 2025 were analyzed, focusing on carbon–phenolic and carbon–elastomeric ablative composites evaluated under high-temperature testing conditions. Key comparison parameters include filler type, heat flux range, exposure duration, testing methodology, and reported linear and mass ablation rates. Due to variations in experimental setups and reporting standards, absolute normalization across all studies is not always feasible; therefore, performance trends and mechanistic insights are emphasized. This structured approach enables identification of dominant material design strategies, performance trade-offs, and research gaps in ablative composite development.

## 3 Carbon-phenolic ablative composites

Carbon–phenolic composites exhibit outstanding thermal and mechanical performance, making them highly effective in applications exposed to intense heat flux. The combination of high-tensile carbon fibers with the rigidity of phenolic resin results in composites that can endure extreme mechanical and thermal stresses without significant degradation [16]. Incorporating fillers such as silica, zirconium orthosilicate (ZrSiO<sub>4</sub>), silicon carbide (SiC), rubber latex, and graphene nanoplatelets further improves ablation resistance and enhances the structural integrity of the char layer [17]. The extent of these improvements is strongly influenced by factors such as filler particle size, concentration, and dispersion uniformity within the composite matrix.

Phenolic-based carbon composites can withstand heat fluxes as high as 30,000 W/cm<sup>2</sup> and have been used in rocket nozzles and spacecraft re-entry shields [18]. Ceramic additives like SiC and Zr compounds significantly improve char yield and oxidation resistance [19,20]. Phenolic–silica composites such as Aleastrasil and AQ60/I, used in European Space Agency (ESA) missions, have demonstrated superior ablation performance under atmospheric re-entry conditions [13-16]. Increase in wt. % of nanoparticles improves the ablation and insulation performance of carbon-phenolic composites, and there is no detectable deterioration in performance after adding carbon nanoparticles to the reinforced matrix [12].

Mesoporous silica particles are a new type of reinforcement obtained by sol-gel, which contain ordered porosity like that of a honeycomb with empty worm-like canals. Its unique properties, such as surface area, high pore content with a narrow distribution [2-10nm], and good chemical and thermal stability, make it potentially suitable as a reinforcement in thermal insulation materials [13]. The mechanical performance of the ZrB<sub>2</sub>–SiC-modified phenolic

composite reflects the modification effect of the particles on the phenolic resin and directly impacts the stability of the material during the ablation process. The composite's strength effectively improves. As the particle content increases, the material's bending strength increases steadily [25]. Table 1 presents the ablation performance of carbon–phenolic composites tested under various high-temperature conditions using methods such as oxy-acetylene torch, plasma wind tunnel, and laser ablation tests.

The results show that the composites exhibit significant reductions in both the linear ablation rate (LAR) and the mass ablation rate (MAR), depending on heat flux, temperature, and exposure duration. Oxy-acetylene torch tests conducted between 2000°C and 3000°C demonstrate LAR reductions ranging from 27% to 84.4% and MAR reductions from 8.5% to 81%, highlighting the strong influence of test parameters and material composition. Plasma wind tunnel testing produced a 60% LAR reduction under a heat flux of  $1.6 \times 10^6$  W/m<sup>2</sup>, while laser ablation tests at  $1 \times 10^7$  W/m<sup>2</sup> yielded lower LAR and MAR reductions of 29% and 43%, respectively. Overall, the data indicate that carbon–phenolic composites exhibit excellent thermal protection, with performance closely tied to filler content, test conditions, and ablation methodology.

**Table 1.** Characteristics of carbon-phenolic ablative composites.

References	Method of ablation test	Ablation characteristics	
		LAR reduction %	MAR reduction%
[24]	Oxy-acetylene torch test at 2000°C for 300s	84.4	81
[26]	Oxy-acetylene torch test at a heat flux of $4.28 \times 10^6$ W/m <sup>2</sup> for 30s	69.6	46.3
[27]	Oxy-acetylene torch test at ~2900°C	69	27
[28]	Oxy-acetylene torch test at 3000°C for 30s	62	-
[29]	Oxy-acetylene torch test for 60s	62	8.5
[30]	Plasma wind tunnel, heat flux of $1.6 \times 10^6$ W/m <sup>2</sup> for 50s	60	-
[31]	Oxy-acetylene torch test for 20s	43	-
[32]	Laser ablation, heat flux $1 \times 10^7$ W/m <sup>2</sup> for irradiation of 30-100s	29	43
[33]	Oxy-acetylene torch test for 30s	27	17

#### 4 Carbon-elastomeric ablative composites

Elastomeric ablative composites formulated from polymers such as nitrile butadiene rubber (NBR), styrene-butadiene rubber (SBR), silicone rubber, and ethylene propylene diene monomer (EPDM) are widely used in aerospace applications due to their superior flexibility, resilience, and shock-absorption capabilities [34–40]. The incorporation of fillers such as CeO<sub>2</sub>, SiC, BER, and TiO<sub>2</sub> has been shown to significantly enhance thermal resistance, tensile strength, and char layer integrity [35]. Specifically, CeO<sub>2</sub> contributes to oxidation resistance and heat reflection, SiC enhances hardness and erosion resistance, while BER improves elasticity and fiber–matrix adhesion. These elastomeric systems perform effectively under moderate heat flux and dynamic thermal environments, where flexibility and controlled material degradation are essential. However, their overall performance is

influenced by factors such as the type of base polymer, filler dispersion, and processing techniques. Under high-speed shear heat flux, the char layer in elastomeric ablatives tends to peel off, reducing protective efficiency. To mitigate this issue, short fibres are often integrated into the polymer matrix to strengthen the composite and improve both its ablative stability and thermomechanical properties [7].

The combination of elastomers and thermosets, such as nitrile-butadiene rubber (NBR) and PR, in the form of polymer blends or composites, represents a promising formulation in the design of elastomer-based TPMs. In general, NBR is widely used in elastomeric TPMs because it has good compatibility with resins and fillers, which ensures high char yield (fibers and metal oxides) [9]. Functional rubber composites, such as electroactive and magnetoactive rubber composites, are promising for advanced engineering applications in robotics and sensing [41]. Talc is a filler that interacts with the elastomer matrix. Unlike flux, it increases the dynamic viscosity of compounds and exhibits a significant Payne effect. Flux itself does not increase dynamic viscosity and does not exhibit a Payne effect. However, flux in the presence of talc can cause a synergistic increase in viscosity, and interactions are involved in the formation of the filler network. This is due to “blend overload,” too much filler relative to the polymer matrix, making the usually passive filler (flux) into an active filler [15].

Table 2 summarizes the ablation performance of carbon-elastomeric composites evaluated using various thermal testing methods, primarily the oxy-acetylene torch and flame tests. The results reveal considerable reductions in both linear ablation rate (LAR) and mass ablation rate (MAR), depending on heat flux intensity and exposure duration. Oxy-acetylene torch tests show LAR reductions ranging from 30.76% to 71.6%, while oxy-acetylene flame tests conducted at heat flux levels between  $4.15 \times 10^6$  and  $4.57 \times 10^6$  W/m<sup>2</sup> for 30 seconds achieved LAR reductions of up to 54% and MAR reductions reaching 64.4%. These variations reflect the influence of filler composition, polymer type, and test conditions on ablative performance. Although some studies did not report full ablation data, the overall trend indicates that carbon-elastomeric composites exhibit effective thermal resistance and material stability under moderate-to-high heat flux, validating their suitability for aerospace applications requiring flexibility and controlled degradation.

**Table 2.** Characteristics of carbon-elastomeric ablative composites.

References	Method of ablation test	Ablation characteristics	
		LAR reduction %	MAR reduction%
[34]	Oxy-acetylene torch test	71.60	-
[35]	Oxy-acetylene flame test at a heat flux of $4.152 \times 10^6$ W/m <sup>2</sup> for 30s	54	30
[36]	Oxy-acetylene flame test at a heat flux of $4.57 \times 10^6$ W/m <sup>2</sup> for 30s	53.6	64.4
[37]	Oxy-acetylene flame test at a heat flux of $4.57 \times 10^6$ W/m <sup>2</sup> for 30s	31	-
[38]	Oxy-acetylene torch test for 30s	30.76	-
[39]	-	-	28
[42]	-	-	10.7

## 5 Conclusion

This review demonstrates that strategic modification of carbon–phenolic and carbon–elastomeric ablative composites using ceramic, metallic oxide, and hybrid fillers significantly enhances thermal protection performance. Reported reductions in linear and mass ablation rates are primarily attributed to improved char-layer integrity, enhanced oxidation resistance, and controlled material regression under high-heat-flux conditions. Carbon–phenolic composites remain superior for extreme thermal environments that require rigid structural stability, whereas carbon–elastomeric composites offer advantages in applications that demand flexibility and impact resistance.

Despite extensive experimental literature, major research gaps remain. Future efforts should focus on: (i) multi-physics modelling that couples heat transfer, chemical degradation, gas diffusion, and mechanical erosion; (ii) AI-assisted optimization of filler combinations and compositions; (iii) development of graded and multifunctional thermal protection systems; and (iv) implementation of in-situ diagnostics for real-time char evolution and temperature monitoring. Addressing these challenges will enable predictive material design and accelerate the development of lightweight, durable, and cost-effective ablative systems for next-generation aerospace and hypersonic vehicles.

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