

## Novel ablative polymer-based composite for aerospace applications

Luigi Torre, Maurizio Natali, Ivan Puri, and Marco Rallini

*A composite of ethylene-propylene-diene rubber and phenolic resin can be used to protect rocket and probe components at high temperatures.*

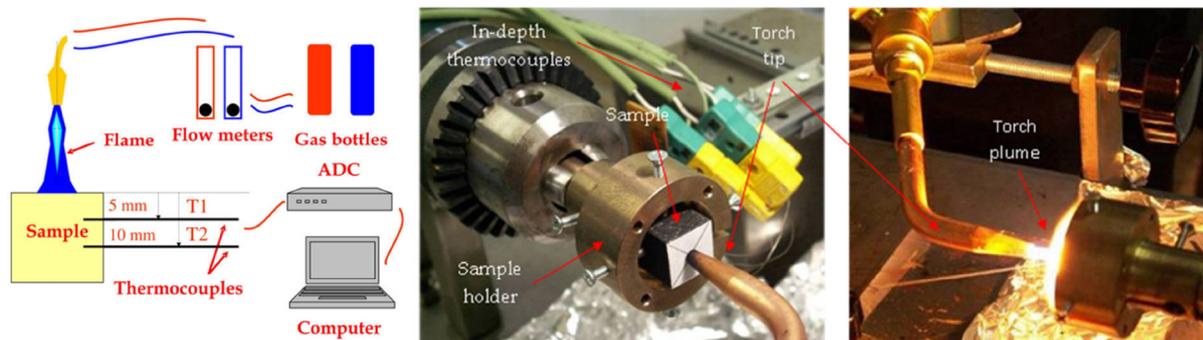
Ablative materials are designed to erode at extremely high temperatures. Such temperatures are experienced, for instance, by rocket and probe parts. The sacrificial materials thus protect components that would otherwise be damaged and are very important in the aerospace industry, i.e., where there is a great need for high-performing insulators that can protect against high heat fluxes.

Although some non-polymeric materials (e.g., high-melting-point metals, metal oxides, and carbides) have been successfully used for these applications, the available range of polymeric ablatives is much wider. Moreover, polymeric ablatives have a number of advantages compared with their non-polymeric counterparts, (e.g., their tunable density, lower cost, and higher heat-shock resistance). Polymer resins that have high char retention (e.g., phenolic resins<sup>1,2</sup>) are the most common matrices in the composite materials of rigid thermal protection systems (TPSs), i.e., that are used to protect probes during re-entry.

In addition, flexible TPSs are used as elastomeric heat-shielding materials (EHSMs) to protect the structural case of solid rocket motors from combustion gases. We recently published a comprehensive summary of 60 years of research efforts into the materials science of TPSs,<sup>3</sup> and in previous studies we have investigated the effects of using ethylene-propylene-diene rubber (EPDM)—reinforced with different types of polymeric<sup>4</sup> and inorganic<sup>5</sup> fibers—on the ablation properties of composites. For example, we evaluated the feasibility of replacing traditional aramid reinforcements, such as Kevlar or Twaron, with cheaper fibers (e.g., wollastonite) and achieved good results.

In this work,<sup>6</sup> we aimed to add a high char-yield phenolic resin to the EPDM matrix to further enhance the thermal resistance of elastomeric TPSs. Since the polar phenolic resin is not miscible in non-polar EPDM, we used a compatibilizer (vinyl triethoxysilane, VTES) to increase adhesion between the two components. In particular, to fabricate composites for testing, we processed the EPDM together with phenolic chopped fibers, nanosilica, plasticizer agent, VTES, and a liquid resol in a single-screw extruder. Once a homogeneous blend was obtained, we added a liquid peroxide as a vulcanizing agent. We thus fabricated composites that contained

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**Figure 1.** Left: Schematic illustration of the oxy-acetylene torch test bed system, in which the data is collected with the use of an analog-to-digital converter (ADC). Photographs show the details of the sample holder (center) and equipment, and testing of an ablative material (right). Reprinted with permission from Wiley.<sup>6</sup> T1, T2: Thermocouples.

20 and 40 parts per hundred resin (phr)—P20K and P40K, respectively—and a material that did not contain phenolic resin (for use as a benchmark).

We characterized our vulcanized samples in terms of their thermal stability, heat capacity ( $C_p$ ), and mechanical and ablative properties. For these measurements, we used an oxy-acetylene torch (with a heat flux of  $500\text{W}/\text{cm}^2$ ) to simulate a severe hyper-thermal environment (see Figure 1).<sup>3</sup> We applied the flame to the face of a cubic sample at a distance of 15mm and acquired in-depth temperature profiles at 5 and 10mm from the hot surface. In terms of their thermal stability, we found the materials that had been modified with phenolic resin did not exhibit noticeably different performances than the benchmark sample in air or nitrogen. An increase in the resol content therefore did not produce a corresponding increase in the char yield of the composites. On

the other hand, the  $C_p$  values of the P20K and P40K composites were higher than the benchmark value, indicating that an increase in resol content caused an increase in the  $C_p$ . This correlation arises because of the greater endothermal energy absorbed by the phenolic phase.

Photographs of our samples after torch exposure are shown in Figure 2. We found the introduction of resol promoted charred layers that had a limited adhesion to the virgin substrate. The P20K and P40K samples exhibited lower in-depth temperatures and we thus confirmed an increased insulation capability, which we partially attribute to the higher  $C_p$  values. We also infer that, in the presence of phenolic resin, a larger volume of pyrolysis gases helped to reduce the temperature of the char (i.e., via a transpiration cooling process). In the composites with increasing phenolic-resin contents, however, we observed that the char had a tendency of detaching from the virgin material.

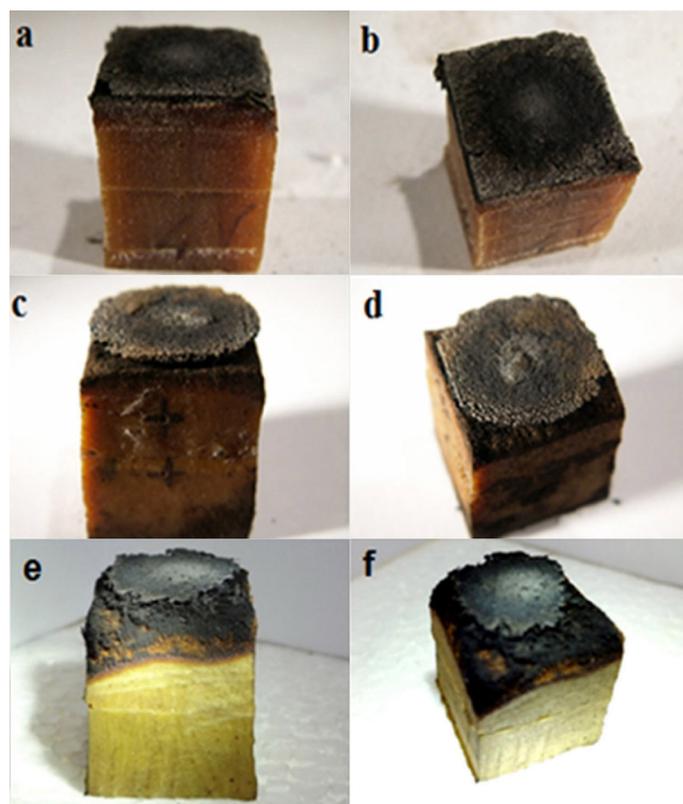
In our tensile property tests (conducted following the ASTM D412 standard), we found that the P20K sample exhibited an increased maximum strength, maximum deformation, and elastic modulus compared with the benchmark sample. These results highlight the toughening effect of the phenolic resin. In the P40K case, the increased proportion of phenolic resin enabled a higher deformation before fracture, but also resulted in a severe reduction in the elastic modulus and maximum strength.

In summary, we have developed a new ablative polymer composite for the development of EHSMs. In our composite we combine EPDM with phenolic resin. We have also characterized our materials to test how they will perform in this intended application, and we found that they exhibit suitable thermal and tensile properties. In light of our results, and considering our previous findings on the use of boron-containing fillers, we believe that the material formulation will be optimized by considering the synergy among phenolic resins and self-healing materials (such as boron carbide). In the next stage of our work, we plan to test this hypothesis.

## Author Information

**Luigi Torre, Maurizio Natali, Ivan Puri, and Marco Rallini**  
University of Perugia  
Terni, Italy

Luigi Torre is an associate professor of materials science and technology and is currently president of SAMPE Global. His main research activities are related to the characterization and development of polymer composites and nanocomposites. He has published more than 140 papers in international journals, edited books, and proceedings.



**Figure 2.** Photographs of the composite samples, obtained after the oxy-acetylene torch test. (a, b) The benchmark composite (i.e., composite made up of ethylene-propylene-diene rubber, phenolic chopped fibers, nanosilica, plasticizer agent, vinyl triethoxysilane, and a liquid resol). Samples containing an additional 20phr (i.e., 20 parts per hundred rubber) and 40phr phenolic resin are shown in (c, d) and (e, f), respectively. Reprinted with permission from Wiley.<sup>6</sup>

Maurizio Natali has a degree in physics and received a PhD in material science, for which he focused on nanostructured ablative bulk molding compounds. He has spent the last five years working in the field of ablative materials and has gained wide experience in the formulation and advanced characterization of polymeric heat-shielding materials.

Ivan Puri graduated in materials engineering from the University of Perugia in 2012 and received his PhD in civil engineering and innovative materials in 2015. He is now a research fellow at the University of Perugia and is involved in the development of models for ablation phenomena.

Marco Rallini graduated cum laude in materials engineering from the University of Perugia in 2009 and received his PhD in civil engineering and innovative materials in 2013. He is now a research fellow at University of Perugia. His work focuses on the development of high-temperature composite materials.

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