Fabrication and analysis of HNBR-Silica / Carbon Phenolic ablative composites as an effective thermal protection system (TPS)

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Abstract: The hydrogenated nitrile butadiene rubber (HNBR) based thermal protection systems (TPS) were successfully developed using silica phenolic and carbon phenolic as fillers by filler particle size variation and fixing filler amount in different formulations. Both the TPS were characterized for their confirmations and functional properties using various analytical techniques. The fabricated composites demonstrated improved mechanical, thermal and ablative properties that can meet requirements of aerospace industry for specific applications. A comparative study was also carried out to perceive the effects of particle size of the filler on thermo-mechanical and ablative properties showing that with decrease of the particle size of the filler, mechanical properties and thermal stability increased, while ablation rate decreased. Furthermore, silica phenolic based composites had better mechanical, thermal and ablative properties as compared to its counterpart carbon phenolic TPS.

1. Introduction
The increasing demands of thermal protection system (TPS) in aerospace and defense industry focused the scientists and engineers to develop thermal protections / insulations that can withstand at high temperature and pressure environments [1, 2]. Usually, these thermal protections are composed of special materials having ablative properties, shielding the space vehicles and defense ammunition from thermal destruction during exposure at high temperatures and flow of flame [3, 4, 6].

Literature has revealed that ablative materials are used to protect certain structural parts or equipment from the intense hypothermal environmental conditions [2, 5, 6]. Mostly, such composites are used in aerospace industry [7]. Thermal protection system (TPS) of space vehicles and long range ballistic missiles is to protect them from hypersonic atmospheres, encountered during their missions, are composed of ablative materials that are highly endothermic sacrificial materials [8, 9].

Rubber itself cannot survive the severe environments such as high temperature, pressure and high-speed flow erosion. These properties can be improved by incorporation of some fillers. Silica and carbon phenolic fillers may be incorporated into the rubber to improve its ablative as well as mechanical properties [9-10]. Elastomeric ablative materials with a rubber matrix are widely used in heat shields. Thermal insulation by ablation is achieved through the degradation of the material itself and the formation of a refractory char on the material surface, thereby hindering the transfer of heat into the interior of material [11-12].

The above-mentioned description, convinced us to study the effects of carbon and silica phenolic fillers in hydrogenated nitrile butadiene rubber (HNR) for thermal protection applications. It was
significant part of research to explore, whether these fillers can improve the thermal protection at high
temperature or not. Other than this a comparative study was also carried out to perceive the effects of
particle size of the filler on thermo-mechanical and ablative properties of both fabricated composites.

2. Experimental

2.1 Materials
The material utilized in this work includes Hydrogenated Acrylonitrile Butadiene Rubber (HNBR)
(having CAN content 29% and density 1.1 gm/cm$^3$), Silica Phenolic and carbon Phenolic (as fillers,
mesh size 30 to 70 mesh), Sulphur (curing agent), ZnO, Steric acid (activators), Tetramethylthiuram
disulfide (TMTD), Dibenzothiazyle Disulphide (MBTS) (accelerator), Dioctyl Phthalate (DOP)
(Platicizer) and Phenyl Naphtylamine (PBN) (anti-oxidant).

2.2 Fabrication of HNBR based ablative composites
The fabrication of HNBR based ablative composites was done by mixing the ingredients in optimized
quantities as shown in Table 1. 11 different recipes were prepared, 1 neat sample without filler
incorporation and 5 samples for each filler, fixing its amount at 20 phr with mesh size variation from
30 mesh to 70 mesh.

After mixing of all ingredients, curing of the vulcanized HNBR was carried out by using
compression molding machine at 165 °C and pressure 10 MPa. After curing, the sample sheets of
fabricated ablative composite were prepared for characterization.

| Material  | A/U    | Amount |
|-----------|--------|--------|
| HNBR      | Phr*   | 100    |
| S         |        | 3      |
| ZnO       |        | 10     |
| Stearic Acid |      | 2      |
| Fillers   |        | 20     |
| MBT       |        | 2      |
| DOP       |        | 5      |
| TMTD      |        | 1      |
| PBN       |        | 2      |

*Parts per hundred rubber

3. Characterization
Fabricated ablative composites were characterized by using following instruments:

3.1 Mechanical Properties
Mechanical properties like tensile strength and elongation at break was carried out by using
INSTRON-4465, UK according to ASTM D412-98a standards.

3.2 Thermal Conductivity
Thermal conductivity was carried out using guarded hot plat according to ASTM C177-97.

3.3 Thermal Stability
Thermal stability was characterized by using TGA Q50, TA Instruments, and USA according to
ASTM D6370-99. Linear ablation rate was found using oxyacetylene torch method according to
ASTM E-285-80.
4. Results and Discussion

4.1 Physical Properties

4.1.1 Density. Density of fabricated ablative composites increases with decrease in filler particle size for both fillers, the result is shown in figure 1. This increase in density is due to increase in surface area and good compaction of filler with matrix material as the particle size decreases. Moreover, density of the fabricated composite is also dependent on the specific gravity of additives and since specific gravity of silica Phenolic (1.23) is higher than neat sample of HNBR having specific gravity (1.035). It can also be concluded that silica phenolic gives slightly higher values of the density as compared to its counterpart.

![Figure 1: Density (g/cm³) of fabricated composites](image1)

4.1.2 Hardness. The effect of particle size variation on the hardness of the composite is shown in the figure 2. It is quite evident that hardness of ablative composites increases as the particle size of the filler decrease for both types of the fillers. This increase in hardness is because more rigid filler particles replace the relatively softer part of the rubber which also lowers the elasticity of the polymeric chains of the rubber. It can also be concluded that silica Phenolic filler gives slightly higher values of the hardness as compared to carbon Phenolic.

![Figure 2: Hardness of fabricated composites](image2)
4.2 Mechanical Properties

4.2.1 Tensile Strength. The effect of particle size variation on the tensile strength of the fabricated ablative composite is shown in the figure 3. It is evident that tensile strength of composites increases as the particle size of the filler decrease for both types of fillers. This increase in tensile strength can be explained by the fact that rubber filler interaction improves as the particle size of the filler decreases i.e. smaller the particle size higher will be interaction. It can also be concluded that silica Phenolic gives slightly higher values of the hardness.

![Figure 3: Tensile strength of fabricated ablative composites](image)

4.2.2 Elongation at break. The effect of particle size variation on the elongation at break of the composite is shown in the figure 4. It is clear that elongation at break of fabricated ablative composites decreases as the particle size of the filler decreases for both types of fillers. Since elongation at break measures the elastic behavior of the material, this decrease in elongation at break is because more rigid filler particles replace the relative softer part of the rubber which also lowers the elasticity of the polymeric chains of the rubber. Moreover, Silica phenolic filler gives lower values of the elongation at break in comparison to its counterpart Carbon Phenolic.

![Figure 4: Elongation at break (%) of fabricated composites](image)

4.3 Thermal Properties

4.3.1 Thermal stability analysis using TGA. Thermal stability comparison of fabricated ablative composite using silica / carbon phenolic as filler is shown in figure 5 and 6, respectively. Results obtained by TGA indicate that composites had superior thermal stability than the neat matrix of HNBR by filler particle size variation for both fillers.
4.3.2 Thermal conductivity. The effect of particle size variation on the thermal conductivity of the composite is shown in the figure 7. It is clear that thermal conductivity of fabricated ablative composites decreases as the particle size of the filler decreases for the both types of the fillers. Moreover, Silica phenolic filler gives lower values of the elongation at break in comparison to its counterpart Carbon Phenolic. Decrease in thermal conductivity was due incorporation of non conducting fillers which actively blocks the path of thermal energy flow as compared to neat HNBR.

4.4 Linear Ablation Rate
The figure 8 shows the effect of filler particle size variation on the linear ablation rate on ablative composites. It gives clear picture that as the particle size of the filler decreases, linear ablation rate also decreases. Results showed incorporation of silica/carbon phenolic fillers into HNBR helps to considerably reduce erosion rate because as the fabricated composites melt, they tend to produce a more viscous layer of residue that binds to substrate. It can also be concluded that Silica phenolic filler gives good ablation results as compared to its counterpart carbon phenolic.
5. Conclusions

It can be depicted from experimental study that tensile strength of fabricated composites increases with the decrease the particle size of both fillers. However, silica phenolic gives better strength as compared to its counterpart carbon phenolic. The elongation at break decreases with the decreases of the fillers size, while an increase in the values of initial modulus of the composite was found as filler particles became coarse to fine. The general increasing trend among density and hardness was also found as filler particles became coarse to fine.

Results of thermal conductivity of composites showed a gradual decrease when size of filler particles is decreased. TGA results indicated that thermal stability of newly fabricated ablative composites was improved as compared to neat sample. Similarly, results of linear ablation rate also showed the effectiveness of HNBR composites as compared to blank HNBR.

From the test results, it can be concluded that in general, physico-mechanical, thermal and ablative properties of HNBR based composites can be improved effectively for optimal and desired results by decreasing particle size of the filler. Furthermore, silica phenolic filler has presented better results as compared to its counterpart carbon phenolic.

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