Development of carbon foam from phenolic resin via template route

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Carbon foams fall in the class of porous, cellular high temperature non-metallic materials with interconnected porosity. In present work, carbon foams have been prepared using commercially available polymeric foams as templates and thermosetting phenolic resin as carbon source. The prepared preform has been carbonized at different temperatures up to 1400°C in inert atmosphere to form carbon foam with interconnected porosity. The removal of volatiles at different temperatures has been studied using FTIR. The effect of heat treatment temperature on density and volume shrinkage has been studied. Thermal stability of carbon foam has been examined by TGA. The porosity of carbon foam has been measured using water porosity and kerosene porosity. Surface morphological studies have been carried out using SEM, which showed that the pores are uniformly distributed and highly interconnected throughout the structure. Compressive strength of the foam has been found to increase with heat treatment temperature.

Keywords: Carbon foam, Template, Resin, Carbonization, Porosity, Surface morphology, Compressive strength

Carbon foams are rigid, porous materials consisting of an interconnected network of ligaments. These consist of solid struts arranged in space to form polyhedral cellular voids forming relatively isotropic cells. They can have open cell structure where pores are interconnected to one another or closed cell structure where pores are isolated from one another. There are several types of carbon foams, depending on the raw material (precursor) and the manufacturing process employed to produce the foam. The major categories are reticulated vitreous carbon foam (RVC), graphitic carbon foam and non-graphitic carbon foam.

Carbon foams fabricated by pyrolyzing thermosetting resin derived polymer foams yield reticulated carbon network or skeleton which is known as RVC or reticulated vitreous carbon. RVC is composed of glass-like carbon with a high void volume (up to 97%), low density and rigid structure. High resistance to combustion, good electrical conductivity and chemical inertness to a wide range of acids, bases and organic solvents are some of the special properties of carbon foam. It finds use as porous electrodes, as filters for metal and gas filtration, in storage batteries, as scaffolds for biomolecule detection, in semiconductor manufacture and as field emission cathodes and for thermal insulation in aerospace vehicles.

The processing routes for preparation of carbon foams have been classified into main three methods, i.e., replica, sacrificial template and direct foaming method. Open cell polymeric foams having the foam lamellae separating neighbouring cells all ruptured, resulting in a structure comprising a network of struts with continuous air passages could be used as precursor or template for carbon foams. The cell size distribution of the precursor foam is an important factor determining the cell size distribution of the resultant carbon foam. Vinton et al. and Franklin et al. showed that the cell structure of RVC is nearly the same as that of the precursor foam. The impregnating resins used are generally phenolic resins, epoxy resins or furfuryl alcohol. The carbonization rate of furfuryl alcohol impregnated polyurethane foams could be higher than that for foams infused with phenolic and epoxy resins. But the carbon yield of phenolic resin is found to be higher than that of other resins. In the present work carbon foam has been synthesized by template route. Open cell polyurethane foams were used as precursors or templates and phenolic resins as carbon source. The polymeric foam is usually made of polyurethane, but other polymers such as polyvinyl chloride, polystyrene, cellulose and latex have been tested successfully as well. The organic foam must possess reproducible and suitable properties, such as the ability to regain its shape after squeezing, limited tolerances for the cell size and size distribution and complete and clean burn-out during sintering.

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Experimental Procedure

Reticulated vitreous carbon foams were synthesised by impregnating commercially available polyurethane foams by phenolic resin. The overview of the template route for making carbon foam is shown in Fig. 1. The reticulated network structure of PU foam was first cleaned with distilled water and dried at 100°C. The cleaned PU foams were impregnated with phenolic resin. The viscosity of the phenolic resin was controlled by methanol. The excess resin from the impregnated PU foams was removed time to time to get uniform foam structures. Impregnated PU foams were cured at 150ºC overnight to enhance the degree of cross linking between phenolic chains. The cured foams were heat treated in inert atmosphere at different temperatures, i.e., 300°C, 500°C, 700°C, 1000°C, 1200°C and 1400°C to study the pyrolysis behaviour of foam. Up to 1000°C the foams were heat treated in N\textsubscript{2} atmosphere at slow heating rate 25ºC/h and that up to 1400°C were heat treated in Argon atmosphere at heating rate of 100ºC/h after 900°C.

Characterization

The changes in density were measured by ratio of mass of sample to the total volume it occupied. The porosity of all samples at each stage was found by water porosity and kerosene porosity. The thermal stability of the foams was studied by TGA (Mettler TG-50) and open furnace. The surface morphology of carbon foams like cell structure, size and shape of cell, pore wall thickness, etc were evaluated by SEM (HITACHI-S3000N). The compressive strength was measured by INSTRON 5500R.

Result and Discussion

Pyrolysis of the foam constituents and the impregnated foam

A critical point in the process is the production of a uniform ‘green’ (i.e. unfired) coating on the polymeric cellular structure, especially as it contains sharp corners at the strut edges. Moreover, incomplete removal of the excess resin slip before firing leads to the presence of some closed cells in the final carbon foam, altering its mechanical properties and permeability behaviour. Firing must be conducted at an appropriately slow rate during the elimination of the polymeric template, to avoid creating stresses and macro defects in the final carbon foam structure.

Figures 2 and 3 show TGA plots of polyurethane foam and phenolic resin respectively. As seen from Fig. 2, pyrolysis of polyurethane starts at 170°C and is intensified at around 200°C. Around 350°C the decomposition of polyurethane starts releasing components like diisocyanates and polyols. Other decomposition products are amines, olefins and carbon dioxide because of the destruction of the polymer chains\textsuperscript{11}. At 400°C decomposition of polyurethane results in around 5% yield. The phenolic resin gives 60% yield after pyrolysis as shown in Fig. 3. To retain the original porous structure of precursor foam, it is necessary to cure the impregnated phenolic resin in PU foam.

Figure 4 shows pyrolysis behaviour (weight and volume retention) of phenolic resin impregnated PU foam. As seen from the figure, the weight loss is maximum up to 600°C in accordance with Figs 2 and 3. It also leads to shrinkage resulting in strong cell formation. In the temperature range 600-1000°C the weight loss is negligible. Further heat treatment to temperature between 1000-1200°C, more weight loss is observed due to denitrogenation\textsuperscript{12}. However,
dimensional changes on heat treatment are not significant, thereby showing that the porous structure formed at 1000°C is retained at higher temperature.

Microstructure of the carbon foam

Figure 5 shows physical view of carbon foams at different temperatures. As such PU foam is in pink colour and when it is impregnated with phenolic resin, after curing it become reddish brown in colour. At 1000°C, the carbon foam produced has glassy colour. It is also noticed that the sound of carbon foam when it strike with ceramic tiles become more metallic or glassy with increase in heat treatment temperature.

The surface morphology of carbon foam is also studied with the scanning electron microscope (SEM). Figure 6 shows the pores are uniformly distributed throughout the structure, indeed shows the open cell and well organized cell structure without any cracks and stress-induced failure in carbon foam. SEM image shows that the pore diameter varies from approximately 200 µm to 500 µm. The pore wall thickness varies between 60 µm to 100 µm. The SEM
images also show that the pores are broken during sample preparation or machining. The diameter of pores of carbon foam decreases as the heat treatment temperature increases.

It is clearly seen that the surface of carbon foam cells are very clear without any pore on the pore wall. The foam cell size is relatively uniform throughout the structure.

**Thermal stability of the carbon foam**

The oxidation behaviour of carbon foam is checked with TGA in air up to 950°C. Figure 7 shows that the oxidation resistance of carbon foam increases with increase in heat treatment temperature. The open air furnace is also used to study the oxidation of carbon foam at 950°C socked for 2 h at the same temperature. The yield obtained is very near to the yield obtained by TGA. This shows that these foams can be used up to temperature of 550°C in open atmosphere. The thermal stability of carbon foams can be improved by providing certain types of antioxidative coatings on the carbon foam struts.

**Physical properties of the carbon foam**

The porosity of carbon foams at different heat treatment temperatures was determined by using kerosene porosity method and water porosity method. The porosity was found out by Eq. (1) as given below:

\[
\% \text{Porosity} = \frac{\text{Weight absorbed Kerosene/water}}{\text{Density of kerosene/water} \times \text{Volume of sample}} \times 100
\]

The results showed that the kerosene porosity is higher than that of water porosity as shown in Fig. 8. The porosity of carbon foam decreases as the heat treatment temperature increases because with increase in temperature the entire foam structure gets shrunk and some of the pores may get blocked with vitreous carbon. The kerosene porosity is higher than that of water porosity because the size of kerosene molecule is lower than water molecules.

The slope of initial, linear, part of curve is the young’s modulus the stress reaches a peak value at the end of the elastic region and corresponds to the yield strength or fracture stress. Crack initiate at the peak stress value and the materials tends to generate fragments as a result of these cracks. The compressive strength and modulus of the foam heat treated at different temperatures is given in Table 1.

As shown in Table 1, the compressive strength and modulus of carbon foam increases with increase in heat treatment temperature. The compressive strength increases with the relative density. The increase of relative density implies an increase of the thickness of cell wall or decrease of the length of the cell edge. A thicker cell wall and shorter cell edge promote higher compressive strength. However, for the foam derived from different types of precursors, this relation is not followed very well. In addition, the strength of carbon foam is also related to the type of porosity and interconnected network of porous structure. It is also seen in Fig. 3, the increase in temperature leads to more shrinkage resulting in strong cell formation and blocking of some pores. However, during heating, the expansion and gas evolution of the polymer lead to significant stresses that can damage the carbon foam surface if not carefully controlled, leading to carbon struts containing macroscopic flaws.

<table>
<thead>
<tr>
<th>HTT Temp, °C</th>
<th>Density, g/cc</th>
<th>Compressive strength, MPa</th>
<th>Modulus, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.103</td>
<td>0.12</td>
<td>5.58</td>
</tr>
<tr>
<td>500</td>
<td>0.090</td>
<td>0.05</td>
<td>3.98</td>
</tr>
<tr>
<td>700</td>
<td>0.109</td>
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<td>16.80</td>
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<tr>
<td>1000</td>
<td>0.112</td>
<td>0.10</td>
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<tr>
<td>1200</td>
<td>0.095</td>
<td>0.19</td>
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<tr>
<td>1400</td>
<td>0.092</td>
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<td>15.65</td>
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</table>
Conclusions
Carbon foam having highly interconnected porosity through the structure can be produced from phenolic resin by using template method. The pore size and total porosity of carbon foam can be controlled by using appropriate processing conditions.

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References