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Review
Mesophase AR pitch derived carbon foam: Effect of temperature, pressure and pressure release time

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For the carbon foam production, mesophase pitch pellets are heated up in a reactor in an aluminum mold to specified pressures and finally pressure released to obtain green carbon foam samples. The green foams were then stabilized and carbonized. The effects of various temperatures, pressures and pressure release times on production of carbons foams are investigated. The samples are subjected to SEM, mechanical testing, mercury porosimetry analysis and bulk density determination for characterization. For the processing temperatures of 553, 556, 566 and 573 K, the densities of the foams produced were 380, 390, 410 and 560 kg/m^3 respectively. The compressive strengths of the respective samples were increased from 1.47, to 3.31 MPa for the lowest and highest temperatures. The processing pressures were 3.8, 5.8, 6.8 and 7.8 MPa. The bulk density and the compressive strength of the carbon foams produced were changed from 500 to 580 kg/m^3, and 1.87 to 3.52 MPa for the lowest and highest pressures respectively. Pressure release times of 5 s, 80 s, 160 s and 600 s are used to produce different carbon foam samples. The densities and the comprehensive strengths measured for the highest and lowest pressure release times changed from 560 to 240 kg/m^3 and 3.31 to 2.16 MPa respectively. The pore size distribution of all of the products changed between 0.052×10^{-6}m and 120×10^{-6}m. Increase in temperature and pressure increased the bulk density and compressive strength of the carbon foams. The mercury porosimetry results show % porosity increase with increasing temperature and pressure. On the other hand, increase in pressure release time decreased the bulk density, compressive strength of the carbon foam.

1. Introduction

Generally, carbon foam is low-density porous material (air-like material), which may simplistically be characterized as an interconnected open cell structure. One of the fields of recent developments of advanced materials technology has been driven by the requirements for improved strength, low weight and low cost in structural engineering materials. In this respect mesophase carbon fibers offered new frontiers with its graphitizable characteristics in composite forms with other materials. The underlying processing principle behind carbon fiber production is to align the aromatic molecules by passing them through a spinneret [1]. Production of carbon foams from mesophase pitch opened a new frontier in the field of advanced carbon materials. One way of carbon foam production was to subject the mesophase bulk to bubble-growth due to temperature increase under pressure subjecting the molecules to stress to form junctions, ligaments, cell and cell walls [2]. Subsequent pressure release insures open cellular interconnected structure. Carbonized and graphitized foams result in a lightweight, high compression strength, and high thermal conductivity material, which may easily be tailored to different industrial applications. The fact that the graphine layers are stretched in the foam matrix in sense mimics natural composites thus provides extensive application areas. Carbon foam is widely used in many industrial areas such as: in aerospace and defence industries, optical benches and lightweight mirrors, thermal

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protection systems, heat transfer systems, lightweight antennas, stealthy materials and lightweight armor. Moreover, commercial carbon foam is used in composite tooling, abrasive tools, battery and fuel cell electrodes, brake disks, engine components, catalytic converters, heat exchangers, energy absorbing crash barriers, structural insulated panels, high temperature insulation, fire doors and blocks, bone surgery material and tooth implants [3]. Much research is being undertaken in order to improve the properties of carbon foam materials and to extend the application areas [4–7].

The bulk density of carbon foam ranges from 200 kg/m^3 to 700 kg/m^3. Carbon foam has a highly porous structure and has a uniform distribution of pore sizes (average between 10×10^{-6}m and 500×10^{-6}m), usually containing very little closed porosity, and mostly above 90% of the pores are open [8]. However, deviations from these preferable properties are possible by changing the operating conditions and the precursor [9,10]. For example, by varying the pressure applied, the size of the bubbles formed during the foaming will change, beside the density and strength. Moreover, other properties can be affected [11].

Mesophase pitch based carbon foams are proving to be popular in the field of carbon materials, for the case of carbon foams its popularity is due to producing high pore structure, high thermal conductivity and low density [12–14].

In this study, effect of temperature, pressure and pressure release time on the properties of mesophase pitch based carbon foams, are investigated.

2. Experimental

Mitsubishi AR naphthalene-based mesophase pitch (Table I), with a softening point of 556 K, was used to produce carbon foam. For the foam production mesophase pitch pellets are introduced into a cylindrical aluminum mold having a predetermined shape and size. The reactor was washed with nitrogen to provide an inert atmosphere. Then the reactor was pressurized, and at a specific pressure foams are produced at different temperature and pressure levels. Finally pressure was released in order to obtain green carbon foam samples. The green foams were removed, stabilized by a flow rate of 0.5×10^{-5}m^3/s dry air up to 583 K. The regime applied had various soak times and heating rates. At the beginning of the stabilisation the heating rate was 0.017 K/s. This rate was gradually decreased to 0.02 K/s as the temperature increased. A total of 90000 s stabilization time was achieved. Stabilised carbon foam samples were carbonized by heating up to 1323 K under nitrogen atmosphere. The effect of process temperatures of 553, 556, 566 and 573 K were investigated on carbon foam structure and properties at a constant pressure and pressure release time: 6.8 MPa and 5 s respectively. The effect of pressures of 3.8, 5.8, 6.8 and 7.8 MPa were investigated on carbon foam structure and properties at a constant temperature and pressure release time: 573 K and 5 s respectively. The effect of pressure release times of 5 s, 80 s, 190 s and 600 s were also investigated on carbon foam structure and properties at a constant temperature and pressure; 573 K and 6.8 MPa respectively.

TABLE I Properties of AR mesophase pitch

Appearance	Pellets (black)
Softening point	548–568 K
Density	600–700 kg/m^3
Solubility in water	Insoluble

The samples were characterized by scanning electron microscopy (JEOL JSM-840), mercury porosimetry (Micromeritics Autopore II 9220). The porosity results are the amount of porosity that is exposed. Therefore, it does not take in to account the closed porosity which are not accessible to the mercury porosimetry measurements. Compressive testing was conducted by an Instron Model 1195 Tension/Compression tester. Densities of all samples were also determined according to ASTM-C559.

3. Results and discussion

3.1. Effects of temperature

The scanning electron microscopy photographs of the carbon foams produced at 553,556, 566 and 573 K temperatures at 75 magnifications are given in Fig. 1. In the production process 6.8 MPa atmosphere and 5 s pressure release times were used.

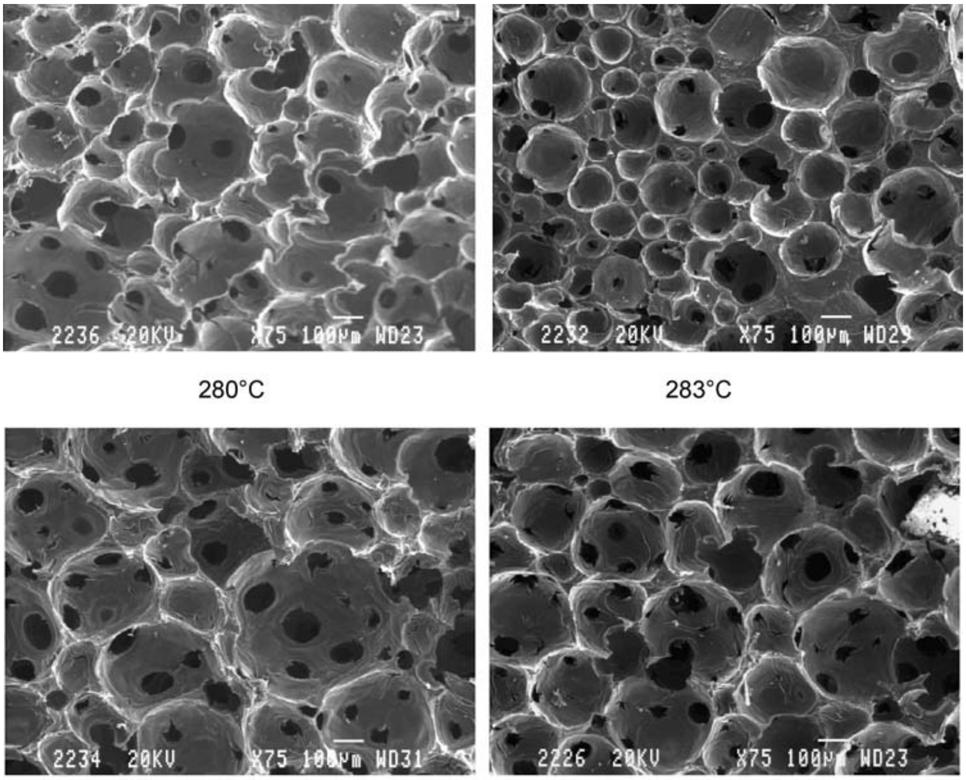
As can be seen from SEM images of carbon foams, process temperature affected the cell structure of the samples. In the range of temperatures used in these experiments, the temperature was increased as cell formation became more regular and uniform. The cell geometry improved to more spherical formation with better intracellular connection via pores.

Densities, compressive strengths, and total porosities of carbon foams obtained for the stabilized foams produced at four different temperatures, are compiled in Table II

The density of carbon foam increased with increasing temperature. As is well illustrated in the literature, the process of foaming involves alignment of ligaments under generated stress by the evolving volatiles at moderate temperatures and pressures. Therefore, bubble growth is an effective mechanism affecting foam formation together with viscosity [3, 5]. As the temperature is increased, more volatiles are evolved and kept under pressure. When the pressure is released, volatiles are released to finalize the cell geometry and interconnections between cells. At

TABLE II Some properties of Carbon foam samples produced at various temperatures

Temperature (K)	Bulk density (kg/m^3)	Compressive strength (MPa)	Total porosity (%)
553	380	1.47	44.9
556	390	1.59	45.1
566	410	2.10	45.4
573	560	3.31	80.6



280°C 283°C

293°C 300°C

Figure 1 SEM photographs of carbon foam samples produced at various temperatures.

the same time, the remaining foam shrinks due to release of the stress after the loss of volatiles resulting in to more compact structure at higher temperatures. In this process higher temperatures generated higher stress for a more efficient alignment and subsequently better compaction to increase the density. At higher temperatures the pitch has a lower viscosity and higher volatile release which causes formation of more pores with smaller size. At lower temperature due to the comparatively higher viscosity and lower volatile release, less number of pores releasing comparatively a high flow of gases most probably results. Also during the process, the foam expands in adiabatic conditions resulting in cooling due to thermodynamics, which is expected to contribute to the hardening of the pitch. Thus the cooling effect is expected to be faster at lower temperature. The net effect of the cooling is expected to result in smaller pores. However, at the lower temperatures the viscosity and compaction play a more effective role on the foaming process compared to the cooling effect. The effect of process temperature on the density of foams produced in this study is in similar trend to the data reported in literature [2–15].

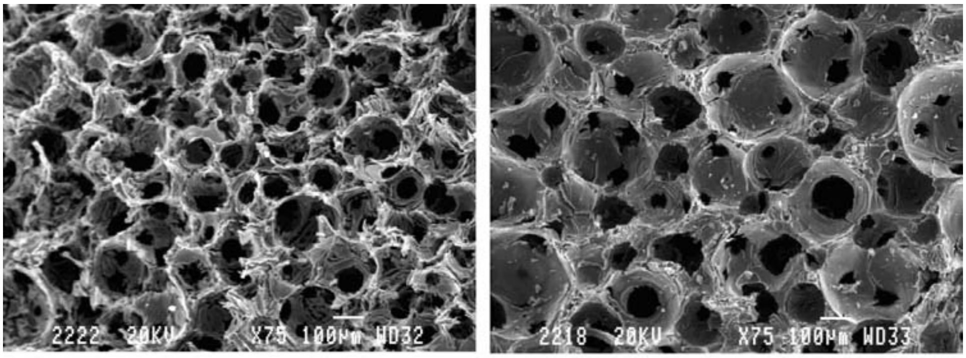
The compressive strengths of the four samples increased with increasing temperature, which is in parallel behaviour with the density increase with increasing temperatures. This confirms that under increased stress a better compaction is achieved resulting in considerable increase in the compressive strength. The total porosity also increases slightly with increasing temperature for the first three process temperatures but increased steeply to level of 80.6% at 573 K, which is nearly double the previous process temperature.

3.2. Effects of pressure

The scanning electron microscopy photographs of the carbon foams produced at 3.8, 5.8, 6.8 and 7.8 MPa pressures are given in Fig. 2 In all these experiments the temperature was kept at 573 K and pressure release time at 5 s. As it can be observed from the SEM photomicrographs of carbon foams obtained at 3.8 MPa, the number of pores in a cell is relatively less, compared to high-pressurized foam samples. This reflects an undeveloped structure, with less interconnection of cells, which result in decreased porosity. For other three higher pressures, more open-celled, interconnected porous structure and better alignment of mesophase molecules are observed.

The improvement is attributed to favourable foaming process conditions substantiated by the morphological observations, density and compressive strength measurements.

Densities, compressive strengths, and total porosities of carbon foams obtained at four different pressures are compiled in Table III. It is observed that the density and porosity of the carbon foam increased with increase in operating pressure. According to the mercury porosimetry analysis, the total porosity of the material was determined to be as high as 86% at 7.8 MPa.



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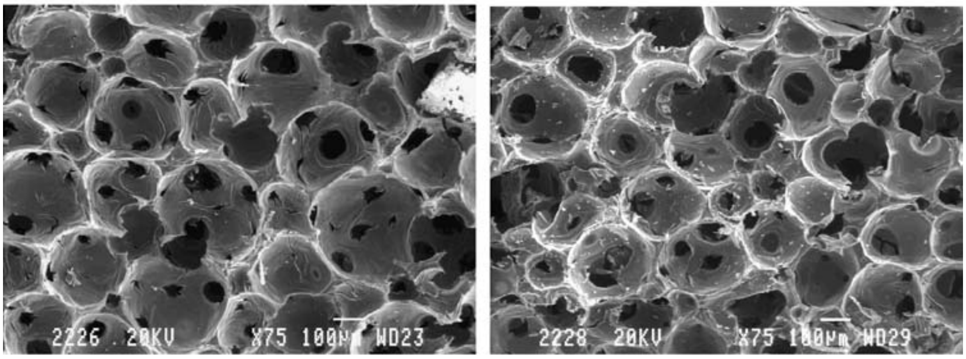

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Figure 2 SEM photographs of carbon foam samples produced at various pressures.

Higher stress created on the bubbles at higher pressures causes suppression of the bubbles. While depressurizing rapidly from high pressure to atmospheric pressure, the bubbles are subjected to greater stress, resulting in the opening of connections between cells and causing an increase in porosity. The release of higher stress results in compaction thus increase in the density. This explains the enhancement of the mechanical properties for the increasing operating pressure. Low-pressurized carbon foams, having an undeveloped texture with cracks, have relatively low compressive strengths. Since the high content of cracks in the foam structure will adversely affect mechanical properties [2].

3.3. Effects of pressure release time

The scanning electron microscopy photographs for foams produced at pressure release times of 5 s, 80 s, 190 s and 600 s are given in Fig. 3. For the pressure release time experiments, the temperature of the autoclave was kept constant at 573 K and pressure was kept at 6.8 MPa.

The changes in pressure release time basically affect the formation of porous structure. All carbon foam samples exhibit a varying degree of interconnected, open-celled and spherical porous morphology. Typical porous structure of carbon foam can be observed for the carbon foam obtained for pressure release time of 5 s. On the other hand, with increasing pressure release time deviations from spherical structure and an increasing number of cracks in the foam structure are observed.

Densities, compressive strengths, and total porosities of carbon foams obtained at four different pressure release times are compiled in Table IV

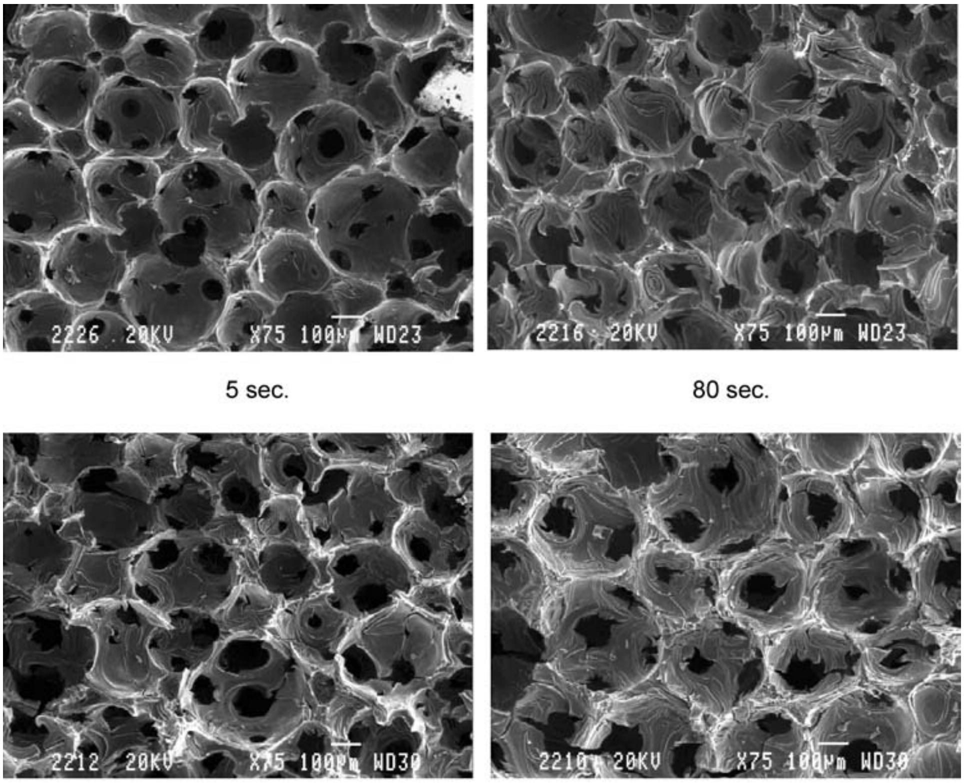
The bulk density of the produced carbon foams decreased progressively from 560 to 240 kg/m^3, as the pressure release time was increased from 5 to 600s. The measured density range is in general agreement with the densities reported in literature [2–11–12].

TABLE III Carbon foams density measurements, compressive strengths and total porosities for samples produced at different pressures

Pressure (MPa)	Bulk density (kg/m^3)	Compressive strength (MPa)	Total porosity (%)
3.8	500	1.87	65
5.8	540	2.52	69
6.8	560	3.31	80
7.8	580	3.52	86

TABLE IV Carbon foam density measurements, compressive strengths, and total porosities for samples produced at different pressure release time

Pressure release time (s)	Bulk density (kg/m^3)	Compressive strength (MPa)	Total porosity (%)
5	560	3.31	80
80	510	2.92	70
190	370	2.59	58
600	240	2.16	37



5 sec. 80 sec.

190 sec. 600 sec.

Figure 3 SEM photographs of carbon foam samples produced at various pressure release times.

Mercury porosimetry analysis shows that the porosity of the foams decreased from 80 to 37% for the lowest and highest pressure release times, as shown in Table IV The pore sizes of the foam samples varied between 0.0052×10^{-6}m and 120×10^{-6}m.

Generally, the average pore diameter of carbon foams exhibits an increasing trend with increasing pressure release time. By increasing the pressure release time, the alignment and orientation of mesophase molecules are affected adversely. This results in decreasing stress, which may allow for the expansion of the pores due to the tendency of opening less number of pores.

From the density and porosity measurements, it is clear that the foaming process is operating much more efficiently as the pressure release time is reduced. At the faster pressure release times, the volatiles seem to exert enough driving force and open comparatively more uniform and interconnected pores. At longer pressure release times the driving force is reduced, and thus the volatiles are preferably routed and they widen the pores relatively more than in the case of faster release rates.

The compressive strength values of the carbon foams obtained at different pressure release times were measured to be between 3.31–2.16 MPa as presented in Table IV With increased pressure release times, cell walls and ligaments became weaker in structure so that carbon foams became weak in strength as well when compared to more rapidly depressurized foam samples. This was further realized with the increased number of cracks in the foam structure and decreased porosity with increasing pressure release time.

4. Conclusions

Operating pressure and pressure release time affect foam properties such as pore structure, density and compressive strength of the carbonized foams. Higher density, increased compressive strength and a more interconnected open celled porous structure are obtained at higher pressures. A more interconnected open-celled porous structure is formed for shorter pressure release times. Carbon foam with tailorable mechanical characteristics is obtained from a mesophase pitch.

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