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Low-density microcellular carbon foams

RICHARD W. PEKALA*, ROBERT W. HOPPER
Lawrence Livermore National Laboratory, Livermore, California 94550, USA

A method has been developed to produce vitreous carbon foams having both low densities (0.03 to 0.10 g cm^{-3}) and small cell sizes ($\sim 20\,\mu$m). This process involves the replication of a porous sacrificial substrate, i.e. sodium chloride. The salt is pressed initially into bars and sintered to give a structure with continuous porosity. The pores are infused with a phenolic solution, the solvent is evaporated, and the resin is pyrolysed within the salt substrate. Extraction of the salt and freeze drying lead to the final carbon foam. The substrate serves two purposes in this process: (1) it prevents shrinkage of the foam during pyrolysis, and (2) it dictates the cell size of the foam.

1. Introduction

The synthesis and characterization of low-density microcellular foams is an area of growing interest at Lawrence Livermore National Laboratory. Potential applications for these materials require (1) a density of less than 50 mg cm^{-3}, (2) a maximum cell size of 35 μm, (3) a chemical structure composed of atoms with atomic numbers less than nine, (4) dimensional stability, and (5) machinability. A survey of commercially available foams revealed that these requirements are generally outside of the state-of-the-art [1]. Thus, one of the principal goals of this research has been to develop a new method for producing carbon foams which approach the above requirements.

A number of methods can be used to generate low-density carbon, foams. Phenolic microballoons can be stabilized with an appropriate binder and pyrolysed to form syntactic carbon foams. Benton and Schmitt used this approach to produce carbon foams with high compressive strength and low density (i.e. > 500 psi (3.445 N mm^{-2}) at 180 mg cm^{-3}) [2]. A reticulated carbon foam results from the pyrolysis of a selectively oxidized polyurethane foam which has been swollen in a reactive monomer [3]. In each of these cases, processing parameters can be used to control the morphology, density, and cell size distribution of the final foam. Nevertheless, it is difficult to meet *simultaneously* the aforementioned cell size and density requirements.

In this paper, a substrate replication process for producing carbon foams is described. A variety of porous substrates have been used throughout our research (e.g. glass, metal powders, fumaric acid) but we have found finely divided sodium chloride to be the most convenient. After classifying the sodium chloride into the desired size range, substrates are cold pressed into the shape of bars and sintered. A phenolic polymer solution is then wicked into the pores and the resin is pyrolysed inside the substrate to a temperature of 700° C. Water is used to leach the sodium chloride and the final foam is produced by freeze drying. Major advantages of this process include (1) the ability to control foam density without having to account for the shrinkage which accompanies pyrolysis of free-standing polymer foams, and (2) preselection of cell size in the carbon foam through control of the particle-size distribution in the substrate.

2. Materials and methods

2.1. Substrate production

All substrates were produced from sodium chloride purchased from Morton Thiokol, Inc., Chicago (Extra fine 325). Morton EF325 salt is a food-grade product pulverized to -325 mesh ($< 44\,\mu$m) and contains 1.75 wt % tricalcium phosphate to prevent caking [4]. The as-received salt was classified further by passage through an air classification system (Acucut Model A-12, Donaldson Co., Minneapolis, Minnesota) to remove both the fines and large particles. Fig. 1 compares the particle-size distribution of the salt before and after classification. Particle size was determined using the MSA (Mine Safety Appliances Co., Pittsburgh, Pennsylvania), a gravitational and centrifugal sedimentation instrument which measures the Stokes' diameter of the particles. Analyses were conducted in benzene, and the data were averaged from three separate runs.

The particle-size distribution has been narrowed after classification, and the mean particle size (MSA 50th percentile) increases from 15 to 17 μm. BET surface areas of the two fractions were measured using nitrogen adsorption and showed a significantly lower surface area for the classified salt (0.71 compared to 1.24 m^2 g^{-1}). These data corroborate the MSA data and indicate a partial removal of the fines.

The classified salt is pressed into bars (20.0 cm × 2.5 cm × 1.0 cm) using a mould with four detachable sides-rails and a Carver laboratory press (Model C). The mould was plated with a nickel–phosphorus coating to inhibit corrosion. A one degree draft on the inner sides of the rails assisted in ejection of the salt bars from the mould. All substrates were

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*Present address: Air Products and Chemicals, Inc., Allentown, Pennsylvania 18105, USA.

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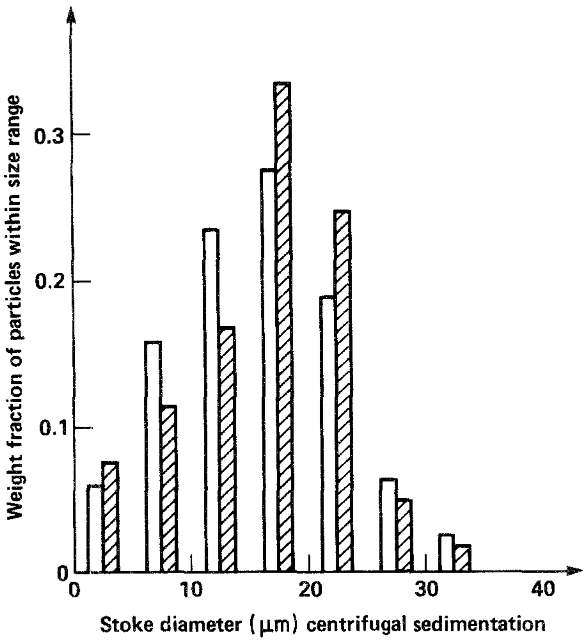

Figure 1 Particle-size distribution of Morton EF325 salt before and after air classification. Unshaded bars: as-received. Morton EF325 salt. Shaded bars: classified salt.

cold pressed at 2500 psi (17.225 N mm^{-2}) for 3 min. The substrates were typically 65% of theoretical density (i.e. 35% porosity). Substrate porosity was found to be approximately independent of the applied pressure over the range 2000 to 5000 psi (13.78 to 34.45 N mm).

All substrates were sintered in a Marshall three-zone tube furnace (Model 11893). The furnace was initially evacuated and the bars were placed under a partial pressure of argon during sintering. The substrates were heated at 1° C min^{-1} to 710° C and then held at the latter temperature for 12 h. The furnace was controlled with a multichannel programmer/controller (Micricon Model 823) and one K-type thermocouple (chromel–alumel) per hot zone. The control thermocouples could be maintained within $\pm 1^\circ$ C of the setpoint at a temperature above 400° C. K-type thermocouples at seven positions in the central zone were used to monitor the temperature near the specimens. Temperature uniformity was $\pm 5^\circ$ C and constant in time to $\pm 1^\circ$ C.

The sintering process results in a substantial reduction in surface area as compared to the original classified salt (0.30 compared to 0.71 m^2 g^{-1}). Final surface area is approximately independent of sintering temperature over the range 650 to 725° C, and very little densification occurs during the sintering process. Fig. 2 shows a scanning electron micrograph of a sodium chloride substrate after sintering under the above conditions. Significant necking between the particles is not observed, yet the substrates are noticeably stronger after sintering.

2.2. Polymer impregnation

A one-step, thermosetting phenolic polymer (29-104, Reichhold Chemicals, Buffalo, New York) was selected as the impregnating resin because of its good solubility, low intrinsic viscosity, and high carbon yield. Impregnating solutions were prepared by dissolving the phenolic polymer in tetrahydrofuran at the concentration necessary to achieve the desired foam density after pyrolysis. In most cases, a concentration of 25 to 30% wt/vol polymer was needed. Other polymers (e.g. epoxies) and monomers (e.g. furfuryl alcohol) could also be successfully carbonized to produce foams.

The sodium chloride substrates were partially immersed in the phenolic solution, and capillary action forced the solution into the pores. The substrates must be impregnated in this manner so that trapped air bubbles are avoided. After the pores of the substrate were completely filled with polymer solution, the bars were submerged and allowed to stand in the solution overnight. Prior experience with glass substrates of the same nominal pore size showed that the polymer molecules are subject to a filtering or chromatographic effect as evidenced by a change in translucence as a function of impregnation time. The overnight soak allows diffusion to give a uniform concentration of polymer throughout the substrate.

Once the substrates were removed from the polymer solution, they were placed on perforated stainless steel racks in a Lindberg three-zone tube furnace (Model

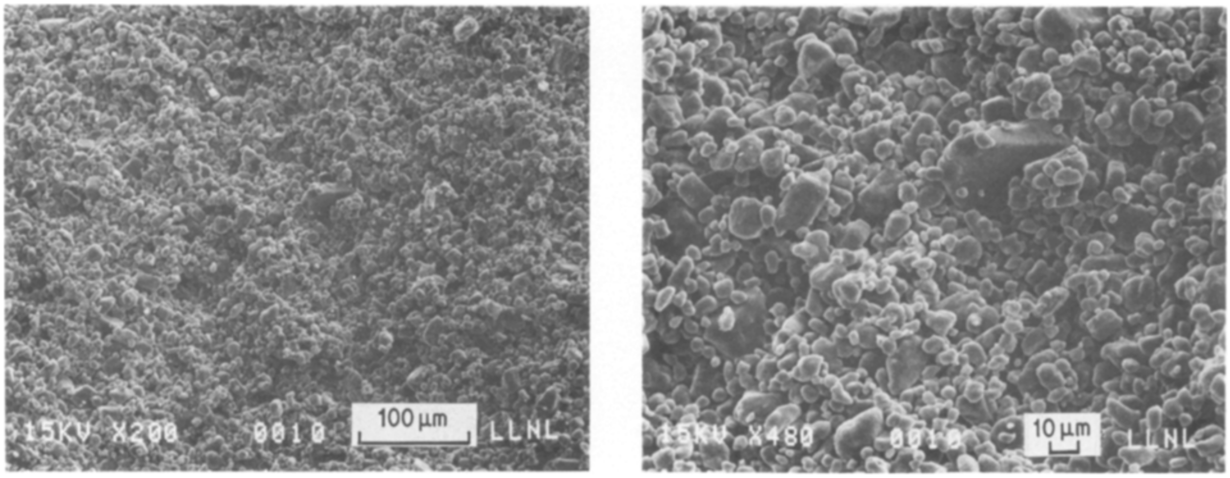

Figure 2 Scanning electron micrographs of the fracture surface of a sodium chloride substrate sintered for 12 h at 710° C.

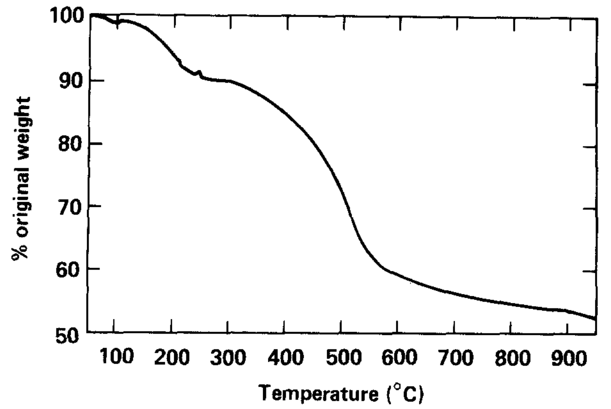

Figure 3 Thermogravimetric analysis of phenolic polymer 29-104 powder heated at 10° C min^{-1} under nitrogen.

5465 6-V-S). The furnace was flushed initially with argon and then purged with the gas while heating to 700° C at 1° C min^{-1}. The samples were held at this temperature for 2 h and were then slowly cooled back to room temperature over a period of 16 h. Provisions for temperature control were similar to those used for sintering salt.

2.3. Extraction and freeze drying

The carbon-coated substrates were placed in desiccators and evacuated. Water is admitted to the desiccators after the initial evacuation step. This procedure prevents internal regions of undissolved salt resulting from trapped air. The salt solution was continuously stirred during the extraction process, and it was replaced with fresh water every 8 to 16 h. The foams were transferred after 48 h from water to a 0.4 M nitric acid solution. A 36 h acid wash was necessary to dissolve the tricalcium phosphate used as an anticaking agent in Morton EF325 salt. The foams were then placed back into water, and a specific ion probe (Model 701A, Orion Research) was used to monitor the Na$^+$ concentration. The foams were considered ready for freeze drying if the Na$^+$ level was less than 10^{-5} m.

The water-filled foams were placed on a stainless steel tray in the freeze dryer (Model 62012343, The Virtis Co., Gardiner, New York) and frozen at an initial shelf temperature of − 40° C. The shelves of the freeze dryer were programmed to heat from − 40 to 0° C in 4 days. The shelves were then heated to 40° C at a rate of 5° C h^{-1}. The foams were held at the latter temperature for approximately 16 h and then removed from the freeze dryer. A typical pressure of 50 mtorr existed throughout the process.

It should be noted that low-density carbon foams with small cell sizes are severely damaged if simply dried in air. The capillary forces associated with the moving liquid–vapour front in the foam cause cell disruption, cracking, and general collapse. For this reason, replica carbon foams must be freeze dried or critical point dried.

3. Results and discussion

The morphological and chemical properties of the carbon foams are primarily derived from the substrate and the heat-treatment temperature. Because the substrate volume does not change during pyrolysis, the final foam density is a function of polymer degradation at various temperatures. The phenolic polymer generally leaves behind 50% of its original mass as a carbon char when slowly pyrolysed to 700° C in argon. We have used thermogravimetric analysis (TGA) to model degradation of the polymer inside the sodium chloride substrate. Fig. 3 shows the TGA curve for phenolic polymer 29-104 when heated at 10° C min^{-1} in nitrogen. In general, the degradation is completed by 700° C and the major by-products are evolved near 450° C.

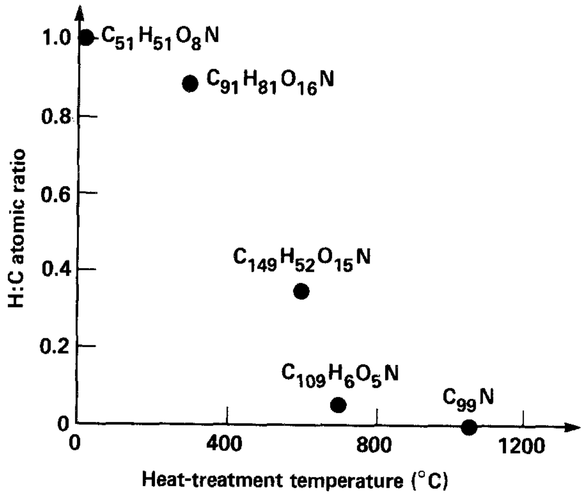

Figure 4 Empirical formulas and H : C ratios for foams pyrolysed at various heat-treatment temperatures.

The change in chemical structure which accompanies pyrolysis of phenolics has been widely studied [5, 6]. Rapid weight loss between 300 and 500° C involves the formation of intermolecular crosslinks and the elimination of small molecules such as water, carbon monoxide, methane, and phenol. At 500° C, the original phenolic has generally been transformed into an aromatic ladder polymer containing one hydrogen atom for every two carbon atoms. As the temperature is increased, hydrogen is gradually eliminated and the H : C ratio becomes characteristic of a given heat-treatment temperature. For cure temperatures above 600° C, the atomic composition was found to change little with time after the first two hours of carbonization. Fig. 4 displays the empirical formula and H : C ratios of foam pyrolysed to various temperatures within the sodium chloride substrate. All foams were carefully dried before each combustion analysis.

The H : C datum point at 1050° C resulted from the pyrolysis of a carbon foam previously heated to 700° C within a sodium chloride substrate. Thermal expansion mismatches, the melting point of sodium chloride (825° C), and rapid densification by sintering (> 750° C) prohibit us from pyrolysing above 700° C within the substrate. Nevertheless, we were interested in the effects of pyrolysing the 700° C carbon foam to higher temperatures. Pyrolysis of the foam to 1050° C resulted in no detectable shrinkage or density change.

The X-ray diffraction patterns for both foams show an amorphous carbon structure, but there are subtle differences. These differences were not studied in detail but presumably reflect the further elimination of

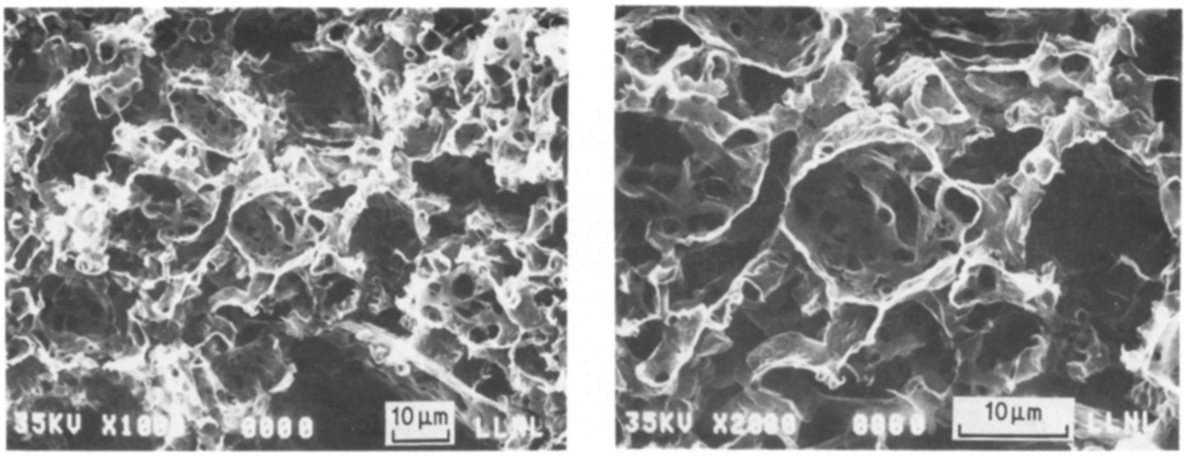

Figure 5 Scanning electron micrographs of the web structure of a 700° C carbon foam.

hydrogen and a reduction of the spacing between "planes" of carbon atoms in the glassy structure. No graphitization was detected. Transmission electron microscopy of thin carbon flakes obtained by crushing a 1050° C foam was featureless at a resolution of approximately 5 nm, and selected-area electron diffraction always showed an amorphous pattern.

An examination of the morphological properties of the above foams was also conducted. Figs 5 and 6 show scanning electron micrographs of the 700 and 1050° C foams, respectively. The structures on this scale are essentially the same, consisting of interconnected webs. It seems evident that the polymer film initially coating the salt (rather uniformly) develops holes and pulls back from them, leaving ribbon-like webs with thick edges. The thickness of the webs may be estimated at a few tenths of a micrometre. No evidence of microscopic foam damage resulting from the freezing or drying processes was observed.

The surface area of the foams was analysed by nitrogen adsorption using the BET method. The 700° C carbon foam was found to have a surface area of 544 $m^2 g^{-1}$. The surface area of the 1050° C sample was reduced to 33 $m^2 g^{-1}$. This tremendous difference in surface area also explains the hygroscopic nature of the 700° C foam. If the latter sample is dried under vacuum at 300° C for 4 h, an 8% weight loss results. In the 1050° C sample, there was no detectable change in mass.

Mercury intrusion porosimetry was used to assess the cell size distribution of the foams. These experiments were performed on a Micromeritics AutoPore 9200. A maximum pressure of 30×10^3 psi (206.7 $N\,mm^{-2}$) was obtained and corresponds to a minimum pore diameter of approximately 6 nm. Fig. 7 plots cumulative volume fraction with respect to pore diameter for the 700 and 1050 °C carbon foams. These curves have been normalized for differences in bulk density and show that there is a larger fraction of small pores (< 1 μm) in the 700° C sample. A calculation of the median pore diameter by volume reveals a value of 6.79 μm for the 700° C sample and 8.17 μm for the 1050° C sample. Although these values are well within our initial objectives, Fig. 7 shows that a substantial number of cells have diameters greater than 35 μm. It is possible that these experiments do cause damage to the foams, in which case the apparent distribution would be skewed toward the high side.

The MSA analysis of classified salt revealed no large particles. In a sieve analysis, however, approximately 7% of the salt is retained on a 400-mesh screen (37 μm opening). Non-quantitative optical microscopy showed both large grains and agglomerates of small ones. The latter generally break up when dispersed ultrasonically for MSA analysis. The extent to which they contribute large cells to the foam depends on how well the pressing operation disrupts them and how well the polymer molecules penetrate their small

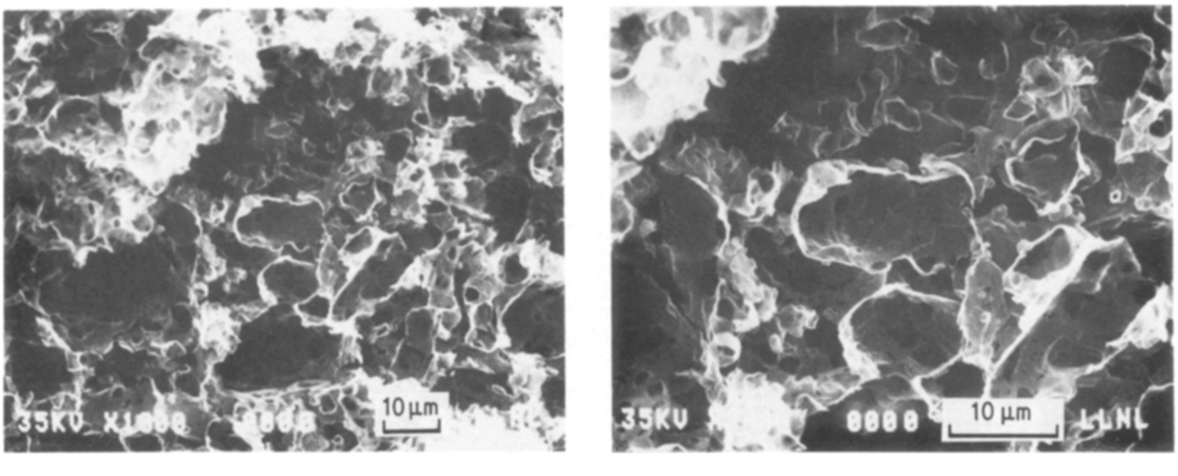

Figure 6 Scanning electron micrographs of the web structure of a 1050° C carbon foam.

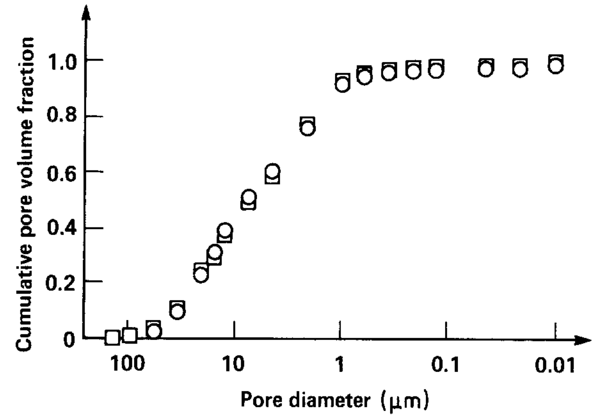

Figure 7 A plot of cumulative volume fraction against pore diameter for (○) 700 and (□) 1050° C carbon foams.

interstices. These factors have not been examined carefully, but large cells observed in SEM usually have the appearance of being a replica of a single large salt grain. We believe that the large grains remaining in the classified salt are the main source of large cells in the foams. Other factors may also contribute. For example, the degradation of selective webs during pyrolysis may result in the coalescence of small neighbouring cells into a much larger cell.

The mechanical integrity of the carbon foams is sufficient for machining operations, yet special procedures are required. Most foams are cut on an EMCO FB-2 mill (Maier and Co., Hallein, Austria) with a fine-toothed blade at 15 to 20 × 10^3 r.p.m. The foams are held in place under a partial vacuum during machining. It is also possible to machine the carbon-coated salt bars just prior to leaching.

Mechanical properties will be reported separately [7]. Briefly, the foams are brittle and exhibit considerable statistical variations in their fracture. Fracture strain in bending is 1 to 2%. Young's modulus and fracture stress vary in a linear fashion with density over the range of 35 to 70 $\mathrm{mg\,cm^{-3}}$. At ~ 50 $\mathrm{mg\,cm^{-3}}$, Young's modulus is ~ 55 MPa and compressive strength is ~ 110 Pa. As a measure of hardness, it was found that a metal cone of half-angle 60° penetrated to a depth of ~ 0.5 mm under a 10 g load. It was also observed that carbon foams made from unsintered salt substrates are somewhat stiffer and stronger than otherwise identical foams made from sintered salt substrates [7]. Thermal expansivity of the foams is $\sim 3.5 \times 10^{-6}\,{}^\circ\mathrm{C}^{-1}$ over the temperature range of 20 to 300° C.

A principal attraction of the process described is that it is a generic one allowing many possible variations of substrate, polymer and cure cycle. In particular, the process was also used to make well-crosslinked but undegraded phenolic foams by simply curing to 300° C. It is also worth emphasizing that the process variables controlling properties are substantially decoupled from one another. For example, cell size is determined by the size distribution of the salt powder, while density (for a given cure cycle) is controlled by adjusting the concentration of the prepolymer solution.

4. Conclusion

The production of low-density carbon foams with small cell sizes is a difficult task. In this paper, a substrate replication procedure has been used to pyrolyse a phenolic polymer into a carbon foam. Foam densities ranging from 35 to 70 $\mathrm{mg\,cm^{-3}}$ are readily achieved. SEM examination of these carbon foams reveals an interconnected web structure. Mercury porosimetry of the foams reveals a median cell size of approximately 8 μm, but some cells of a diameter greater than 35 μm exist. Future work is being directed at using finer sodium chloride in the substrate to produce an even smaller cell-size distribution in the foams.

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