INVESTIGATIONS ON PROCESSING OF CARBON FOAMS FROM SUCROSE AND REINFORCING CARBON ADDITIVES

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by

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ABSTRACT

Carbon foams are advanced carbon materials with excellent properties like low density, ablative properties, tunable thermal conductivities, low thermal expansion coefficient, good electrical conductivity and relatively high mechanical strength. They find applications in thermal protection systems, light-weight fire resistant structures, heat exchangers, radiators, battery electrodes, electromagnetic interference (EMI) shielding and acoustic absorption. The carbon foams are mainly prepared from the fossil fuel-based pitches and synthetic organic polymers which leave large carbon residue on pyrolysis. The depletion of fossil fuels and other environmental concerns necessitate a shift to alternate and naturally renewable precursors for carbon foams. Sucrose is a widely available naturally renewable precursor studied for the preparation of carbon foam. However, the density and mechanical strength of the carbon foam prepared from sucrose is low due to the low carbon yield. The main objectives of the thesis are to prepare carbon foams from sucrose by easy and energy efficient alternative methods and to study the effect of various reinforcing carbon additives on the foaming characteristics of sucrose and properties of carbon foams.

Thermo-foaming of molten sucrose using an aluminium nitrate blowing agent followed by dehydration and carbonization was used for the preparation of carbon foams. The aluminium nitrate catalyzed the –OH to –OH condensation reactions responsible for the nucleation, growth and stabilization of bubbles which enabled the faster foaming and setting of molten sucrose. The carbon foams obtained had an interconnected cellular structure. The density and cell size obtained were in the ranges of 0.15 to 0.05 g/cm^3 and 1.62 to 0.83 mm, respectively, at aluminium nitrate concentrations in the range of 0 to 4 wt.%. The carbon foams showed a turbostratic graphitic structure. The alumina (~ 0.2 to 1.58 wt. %) produced from the aluminium nitrate concentrated more on the surfaces of cell walls, ligaments, and struts. The compressive strength (0.06 to 0.64 MPa), Young's modulus (2.9 to 22 MPa) and thermal conductivity (0.04 to 0.07 W/m/K) of the carbon foams depended on the aluminium nitrate concentration. The surface area and pore volume of the carbon foams increased with an increase in aluminum nitrate concentration. The mechanism of formation of micropore due to *in situ* activation and alumina pillaring was established. The CO_2 adsorption capacity (2.87 to 3.37 mmol/g at 0 ^{o}C and 760 mmHg) of the carbon foams increased with an increase in aluminium nitrate concentration due to the interaction of quadrupole of carbon dioxide with the alumina. The alumina formed from the aluminum nitrate blowing agent catalyzed the carbon oxidation due to its Lewis acid character.

The oxidation resistance of carbon foams was improved by using boric acid as blowing agent. The H^+ generated from boric acid due to the formation of sucrose-boric acid complex catalyzed the -OH to -OH condensation reactions leading to the faster foaming and setting of the molten sucrose. The char yield increased from 24 to 39 wt.% when the boric acid concentration increased from 0 to 8 wt.% due to the formation of the B-O-C cross-links between sucrose polymer by B-OH to C-OH condensation. The density (0.103–0.16 g/cm^3) and compressive strength (0.2-1.1 MPa) decreased and cell size (0.67-1.17 mm)

increased with an increase in boric acid concentration. The thermal conductivity of the boron-doped carbon foams obtained was in the range of 0.057 to 0.043 W/m/K at 25 °C. The surface area and pore volume increased with an increase in the boric acid concentration up to 6 wt.% and then decreased. The boron present (0.44 to 3.4 wt.%) retarded the oxidation of carbon foams as evidenced from the increase in the oxidation onset temperature and char residue at 900 °C with an increase in boric acid concentration.

Various reinforcing agents such as activated carbon powder (AC), carbon fiber, multi-walled carbon nanotube (MWNT) and graphene were incorporated in sucrose to increase the carbon yield and to improve the mechanical properties of the carbon foams. The carbon composite foams were prepared by thermo-foaming of dispersions of the reinforcing carbon additives in molten sucrose to form solid organic foams followed by dehydration and carbonization.

The dispersed AC powder induced the foaming of molten sucrose by stabilizing the bubbles by adsorbing on the molten sucrose-gas interface, accelerated the foaming and foam setting by catalyzing the –OH to –OH condensation and increased the char yield. The density, cell size, compressive strength and thermal conductivity of the carbon composite foams depended on the AC powder to sucrose weight ratio. The maximum compressive strength of the carbon composite foam achieved was 1.36 MPa at an AC powder to sucrose weight ratio of 0.05. The foams had a hierarchical pore structure with interconnected cells made up of carbon-containing micropores. The carbon composite foams showed relatively high (2.59 to 3.04 mmol/g) CO_2 adsorption capacity with very good CO_2/N_2 selectivity and excellent recyclability. The carbon composite foams selectively absorbed oil phase from oil-water mixtures and surfactant stabilized oil-in-water emulsion.

The density and compressive strength of the carbon fiber reinforced carbon composite foams at an average fiber length of 300 μm decreased with an increase in fiber concentration due to the agglomerations by bridging of longer fibers. The average fiber length was decreased by planetary ball milling of sucrose-carbon fiber mixtures. The compressive strength of carbon composite foams increased with a decrease in fiber length, reached a maximum at an average fiber length of 33 μm and then decreased. The maximum compressive strength of 3.86 MPa was achieved at an average fiber length of 33 μm and a fiber concentration of 2 wt.%. The maximum improvement in compressive strength and specific compressive strength obtained as a result of reinforcement with the carbon fiber was 125 % and 92 %, respectively.

The foaming time and foam setting time of molten sucrose were decreased with an increase in MWNT concentration due to the catalytic effect of MWNT towards –OH to –OH condensation. The density of the MWNT reinforced carbon composite foam obtained was in the range of 0.23 to 0.26 g/cm^3. The maximum compressive strength and specific compressive strength of 4.9 MPa and 21 MPa/g/cm^3, respectively, were obtained at an MWNT concentration of 0.5 wt.%. Beyond 0.5 wt.% MWNT, the compressive strength and specific strength were decreased due to the agglomeration of MWNT. The d-spacing of (002) plane decreased from 3.614 to 3.472 Å when the MWNT concentration increased from 0 to 2.5 wt.% due to the development of crystal structure parallel to MWNT axis. The electrical conductivity increased with an increase in the MWNT concentration up to 1 wt.% and then marginally decreased due to MWNT agglomeration. The EMI shielding effectiveness (SE) of the carbon composite foams in the X-band region increased gradually with an increase in the MWNT concentration up to 1.5 wt.% and then rapidly. The pores created by the local shrinkage of sucrose polymer within the MWNT agglomerates contributed to the SE by acting as new interfaces for internal reflections which are responsible for rapid increase in EM absorption at MWNT concentrations higher than 2 wt.%. The highest SE achieved was 39 dB at an MWNT concentration of 2.5 wt.%. The highest specific shielding effectiveness (SSE) of the MWNT reinforced carbon composite foam obtained was 166 dB/g/cm^3.

The melting point of the sucrose decreased from 190 to 120 ^{o}C when the GO GO concentration increased from 0 to 1.25 wt.%. The viscosity of GO dispersions in molten sucrose increased gradually with GO concentration up to 0.75 wt.% and then rapidly with further increase in GO concentrations. The foaming time and foam setting time decreased drastically from 6 to 1 h and 34 to 9 h, respectively, when the GO concentration increased from 0.25 to 1.25 wt.% due to the catalytic effect of GO towards –OH to –OH condensation reactions. The density and cell size of the graphene-reinforced carbon composite foams depended on the GO concentrations. A maximum compressive strength and specific compressive strength of 5.2 MPa and 21.3 MPa/g/cm^3, respectively, were achieved at a very low GO concentration of 0.25 wt.%. The electrical conductivity and EMI SE of the graphene reinforced carbon composite foams increased with an increase in the GO concentration up to 0.15 wt.% and then decreased due to graphene agglomeration. The maximum SE achieved was 38.6 dB at a GO concentration of 0.15 wt.%. The maximum SSE of the graphene reinforced carbon composite foam obtained was 160 dB/g/cm^3.

Thermo-foaming of dispersions of various reinforcing carbon additives (AC powder, carbon fiber, MWNT, and graphene) in an aqueous resin prepared by acid-catalyzed polymerization of sucrose solution was studied for the preparation of carbon foams. Among the various reinforcing carbon additives, AC powder only produced solid organic foam with homogeneous foam structure. The dispersion of AC powder in the aqueous sucrose resin was due to the adsorption of sucrose polymer molecules on the AC powder. The dispersed AC powder retarded the –OH to –OH condensation reactions responsible for the cross-linking of the sucrose polymer. The mechanism of foaming of aqueous sucrose resin by stabilization of the bubbles by the adsorption of AC particles on the gas-resin interface was established. The foam volume increased with a decrease in the AC particle size due to the better stabilization of bubbles by the finer particles. The AC particle size had a marginal effect on the density and thermal conductivity of the carbon composite foams. The maximum compressive strength of 2.8 MPa was achieved at the AC powder to sucrose weight ratio of 0.05 and at an average particle size of 15 μm. The carbon composite foams showed low thermal conductivity in the range of 0.026 to 0.063 W/m/K. The carbon composite foams showed very good machinability characteristics and fire resistance.