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CARBONIZED STARCH MICROCELLULAR FOAM-CELLULOSE FIBER COMPOSITE STRUCTURES

Andrew R. Rutledge, Richard A. Venditti,* Joel J. Pawlak, Sameer Patel, and Janderson L. Cibils

The production of microporous carbon foams from renewable starch microcellular foam-fiber (SMCF-Fiber) composites is described. Carbon foams are used in applications such as thermal insulation, battery electrodes, filters, fuel cells, and medical devices. SMCF-Fiber composites were created from an aquagel. The water in the aquagel was exchanged with ethanol and then dried and carbonized. Higher amylose content starches and fiber contents of up to 4% improved the processability of the foam. The SMCF structure revealed agglomerates of swollen starch granules connected by a web of starch with pores in the 50-200 nanometer range. Heating the SMCF-fiber in a nitrogen atmosphere to temperatures between 350-700˚C produced carbon foams with a three-dimensional closed cell foam structure with cell diameters around 50 microns and pore walls around 1-3 microns. The stress versus strain compression data for carbonized samples displayed a linear elastic region and a plateau indicative of brittle crushing, typical of an elastic-brittle foam. The carbon foam products from these renewable precursors are promising carbon structures with moderate strength and low density.

Keywords: Microporous carbon foams; Foam; Starch; Fiber; Composites; Microcellular

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INTRODUCTION

Carbon Foams

Carbon foams are porous, low density materials with densities in the range of 0.3 to 0.5 g/cm^3 that contain high percentages of carbon. Production of these foams involves the heat treatment of organic polymer foams to produce a carbonized material. The final properties of the carbon foam depend greatly on the precursor material and the thermal history of the treatment. The major application of carbon foams is for thermal insulation (Klett 1975), but they have also been used in limited quantities for structural applications, battery electrodes, filters, fuel cells, medical devices, and radar adsorption (Touchstone 2004). The development of advanced precursor materials, such as non-combustible coals, have allowed for the production of lightweight and strong carbon foams, which have compressive moduli of 620-830 MPa and compressive strengths of 8.3-15 MPa (Touchstone 2004). These materials have been able to replace expensive woven materials and some honeycomb structural design materials (Hager et al. 2000). There is great interest in the development of new inexpensive precursor materials from renewable resources that produce advanced structures and properties.

Starch Microcellular Foams

Starch microcellular foams (SMCF) are foam structures based on starch that have a significant quantity of pores in the 10 micron range. The properties of these are very different from normal extruded starch foams, which contain much larger pores, greater than 1 mm, and are often used in the production of cereals, snacks, and recently starch-based packing foams. SMCF is created by cooking starch solutions and then cooling to produce stiff aquagels that are dried from a pore-preserving solvent of low surface tension. Upon removal of the solvent, a relatively hard, opaque microcellular foam material is produced (Glenn and Miller 2006).

Glenn and coworkers have developed several SMCF materials from corn, wheat, and high amylose starches and have found that harsh drying conditions of the aquagels are not suitable for the production of SMCF. The pore structures will collapse in simple air drying processes. In order to produce a SMCF structure, the high surface tension water must be replaced with a liquid of lower surface tension.

Glenn also notes that SMCF structure properties from starch are greatly affected by the amounts of amylose and amylopectin in the starch (Glenn and Irving 1995). Another paper by Glenn further reports on the effects of these polymers in starch on the SMCF structure. They have found that shrinking during drying, the viscosity of the aquagel, ethanol exchangeability, opacity, density, and compressive strength are all affected by the starch composition (Glenn and Miller 1996). Glenn et al. note in another paper that the addition of fiber improves the properties of the SMCF structure while calcium carbonate ($CaCO_3$) has no significant effect (Glenn et al. 2001).

Venditti, Pawlak, and coworkers have produced SMCF materials and have found that the properties can be improved by the addition of a cross-linking agent or an increase in starch molecular weight (El-Tahlawy et al. 2007). A cross-linking agent was found to increase the specific surface area, brightness, and water resistance. The pore diameter was found to be dependent on the crosslink concentration. In another study, lower density microcellular structures were correlated with improved brightness, suggesting more micropores in the microcellular structure, as in the example structure shown in Fig. 1 (Patel et al. 2008).

It was also reported that the addition of Alkyl Ketene Dimer (AKD) to the SMCF structure could aid in the water resistance of the SMCF (Bolivar et al. 2007; El-Tahlawy et al. 2008).

The SMCF structure is an interesting precursor for a carbon foam porous material that should have high surface area (180 m^2/g) and low density (Budarin et al. 2006). Carbonized SMCF structures pretreated with an organic acid to accelerate carbonization were prepared and the products were termed “Starbons”. With increased carbonization temperatures of up to 700°C the volume of micropores increased, the pore diameters increased, the C:O ratio increased, and the hydrophobicity increased (Budarin et al. 2006).

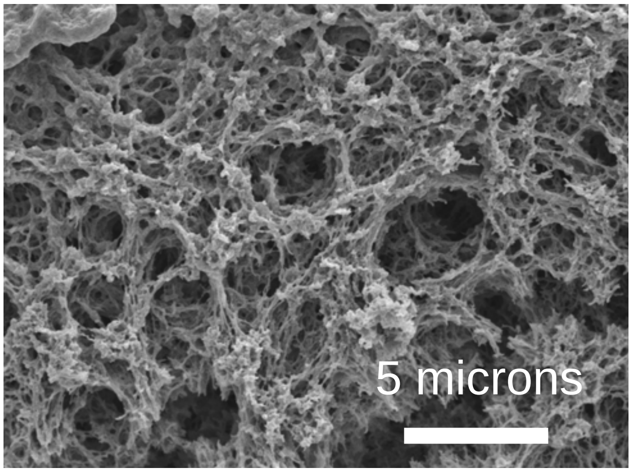

Fig. 1. Example of an SMCF foam structure. Dent corn starch as an 8% solids suspension was heated and stirred for 20 minutes at 90˚C, then cooled, followed by a slow ethanol exchange process at every 48 hr with 40, 70, 90, 100, 100, and 100% ethanol (three times the weight of the initial aquagel) and then air dried. Note that the sample was not carbonized (Patel et. al, 2008)

Khashoggi Industries has investigated the effect of some additive materials on SMCF structure (Anderson and Hodson 2006). They note that the inclusion of long fibers that are well dispersed prevents the need for further conditioning steps normally required to develop good foam structure. Increased water content in the aquagel was found to increase the amount of pores and the pore diameter. Inexpensive fillers such as $CaCO_3$ that do not absorb water improve process-ability by facilitating drying. Aggregate particles ranging from 0.05 microns to 2 mm can be included to improve compressive strength of SMCF and control density. Fatty acids such as stearate are noted in this patent to help the molding process of the aquagels while increasing flexibility. Thickening agents, such as polyethylene glycol, can be used to help control the dispersion of fiber and the settling of other solids in the aquagel before the SMCF structure can be dried. Also, cross-linkers were reported to improve the stability and strength of SMCF by controlling water absorption (Anderson and Hodson 2006). In that report materials were heated to 200 ˚C to remove water, but higher temperatures at which carbonization may occur were not explored.

It is of interest to explore SMCF-Fiber composite materials as products themselves and as carbon foam precursors. In this research, the effect of the incorporation of wood based fibers on the processing and material properties of SMCF-Fiber composites, both carbonized and non-carbonized, are described.

EXPERIMENTAL

Materials

Starches were donated by Cargill (Minneapolis, MN) and were Cargill Corn Milling Industrial Pearl B Dent Starch Product # 1103, Cargill Amylogel 03001 (50% amylose), and Cargill Amylogel 03003 (70% amylose). Bleached softwood market pulp from a commercial source in the Southeast United States was used, as-received. The length weighted mean length of the pulp was 2.1 mm, the mean width was 25.0 micrometers, and the length weighted percent of fines (0.05-0.20 mm) was 9.63%, measured on 2000 fibers with a HiRes Fiber Quality Analyzer (OpTest Equipment, Ontario, Canada).

Preparation of SMCF-Fiber Aquagels

Starch aquagels can be created by heating the starch and water indirectly in a water or oil bath or directly with steam or other heating techniques. During cooking the opaque and white starch-water solution will transform into a clearer viscous aquagel. For this project a microwave (Sharp R-510CK 1100W 2450 MHz) was used for heating due to its ease and quickness. Each sample had about 125 ml of total volume. In each sample, 110 grams of a water-fiber suspension was used. The amount of fiber was based on the weight percentage of fiber in the fiber-water suspension. Starch (air dry) was added as a percentage of the weight of the total sample. As an example, 15 grams of starch was added to 110 grams of a water-fiber mixture with 3% fiber, resulting in 106.7 grams of water, 3.3 grams of fiber, and 15 grams of starch; a total of 125 grams. The starch concentration will be indicated by the weight of starch to total weight, which in this case is 12%=100%*15/(125).

The amounts of starch were varied in the sample from 8% to 14%, depending on the starch type. A viscosity of the suspension after cooking was targeted that allowed for easy pouring into the molds but provided adequate stiffness of the aquagel after cooling. Regular dent corn starch does not need as high of a percentage of starch due to the increased amount of amylopectin increasing the aquagels viscosity and was used at 8%. The highest amylose (70%) starch needed 12-14% starch in the sample to create the proper viscosity of the starch aquagel, as the viscosity was too low at 8%. The 50% amylose starch was used at 10% to create the proper viscosity.

A 125 ml sample with dent starch was processed in a microwave for 90 seconds in 15 second intervals with ten seconds of manual stirring applied between cooking intervals. High Amylose (50 and 70%) starches were cooked for 120 seconds with stirring in the same manner at 15 second intervals. Wood fiber was added to the starch before cooking in an attempt to strengthen, prevent cracking/wrinkling, and keep the shape and volume of the molded aquagels during drying and other processing steps. Fiber content between 3% and 4% in the water-fiber mixture was found to be optimal. In high amylose starches (50 and 70%) lower than three percent fiber, the SMCF-Fiber samples cracked extensively during drying.

The hot aquagels were immediately removed from the microwave and poured into a shallow silicone mold, with aquagel sizes being about 1 cm thick, 6 cm wide and 15 cm long. The samples were then put into a freezer uncovered for 30 minutes to cool to approximately 5˚C, at which their permanent shape was determined. The cooled samples were then removed from the molds, weighed, and placed into a closed plastic container. Then an amount twice the weight of the wet aquagel of ethanol was poured over the sample and was left for one day. This was repeated each day for a total of 7 days. Following this, the sample was allowed to dry for two days in a 50% RH and 23˚C conditioning room. During air drying the sample was placed under metal plates totaling 500 grams in weight to prevent warping during drying.

Density Measurements

The densities of the samples were measured by weighing the sample alone and then weighing the sample immersed in a bed of plastic beads (average diameter of 0.25 cm) in a graduated cylinder with a known total volume. The packing density of the beads was determined from a plot of the volume of beads (cm^3) versus mass of beads (grams) plot, which resulted in a straight line of the following equation:

$$\text{Volume} = 0.711 * \text{Mass} + 0.0\ ,$$

with an R^2 value of 0.999. The slope is the inverse of the packing density of the beads, determined to be 1.406 g/cm^3. The density of a sample was then determined by the following equation:

$$\text{Volume of sample plus beads (cc)} = \frac{\text{Mass of bead (g)}}{\text{Density of bead (g/cc)}} + \frac{\text{Mass of sample (g)}}{\text{Density of sample (g/cc)}}$$

For each sample the measurement was taken at least five times (repacking the sample in beads each time) and the average and standard deviation reported.

TGA Procedure

Thermogravimetric analysis was performed using a TGA-Q500 from TA Instruments on samples of less than 20 mg in pre-weighed platinum pans at atmospheric pressure in a nitrogen gas environment. The temperature was ramped to 700°C at 10°C/min and then cooled to 50°C at 30°C/min.

Carbonization of Samples

Heat treatment of samples ranging from 1 to 2 cm^3 in volume were performed at atmospheric pressure with approximately 50 ml N_2/min gas flow in a high temperature vacuum quartz tube furnace, MTI Corporation OTF-1200X. Inside the 3 inch diameter tube were placed high heat alumina crucible boats approximately 1 x 2 inches and ½ inch deep, containing two to three samples each. After sample loading, the caps on each end of the tube were sealed. Nitrogen gas was then allowed to flow through the glass tube at a desired rate and vent to atmosphere. Samples were heated at 0.5˚C/min to a set maximum temperature, held at that temperature for one hour, and then cooled to room temperature at an uncontrolled rate.

Physical Testing Procedure

Compression modulus of rupture (MOR) and modulus of elasticity (MOE) were measured with an MTS Model Alliance RF300 60,000 lb electromechanical UTF rated frame with a 259 lb Omega load cell. Samples were approximate cubes of 1 to 2 cm^3. The strain rate was 0.5 mm/min.

Scanning Electron Microscopy (SEM)

Samples at room temperature were fractured by initiating a crack with a knife in the plane of largest dimension in the molded parts and then manually separating the sample into two parts in that same plane. The exposed fractured surface was then coated with an approximately 100 angstrom layer of gold/palladium (60/40) and then inspected using a cold field emission SEM, JEOL JSM-6400F.

RESULTS AND DISCUSSION

SMCF-Fiber Aquagel Preparation

Some characteristics of the microwave cooking procedure were investigated in order to understand whether the starch gelled or not. The temperature rose in the microwave heating rapidly and was recorded as 80˚C after one minute total heating time and 85˚C as the final heating temperature at two minutes of heating. A dramatic increase in the viscosity of the starch suspension during heating was in agreement with the gelation of the material. The swelling and gelation of the starch granules was further evaluated by inspecting cooled samples taken during stirring periods using light microscope images and cross polarized light images, Fig. 2.

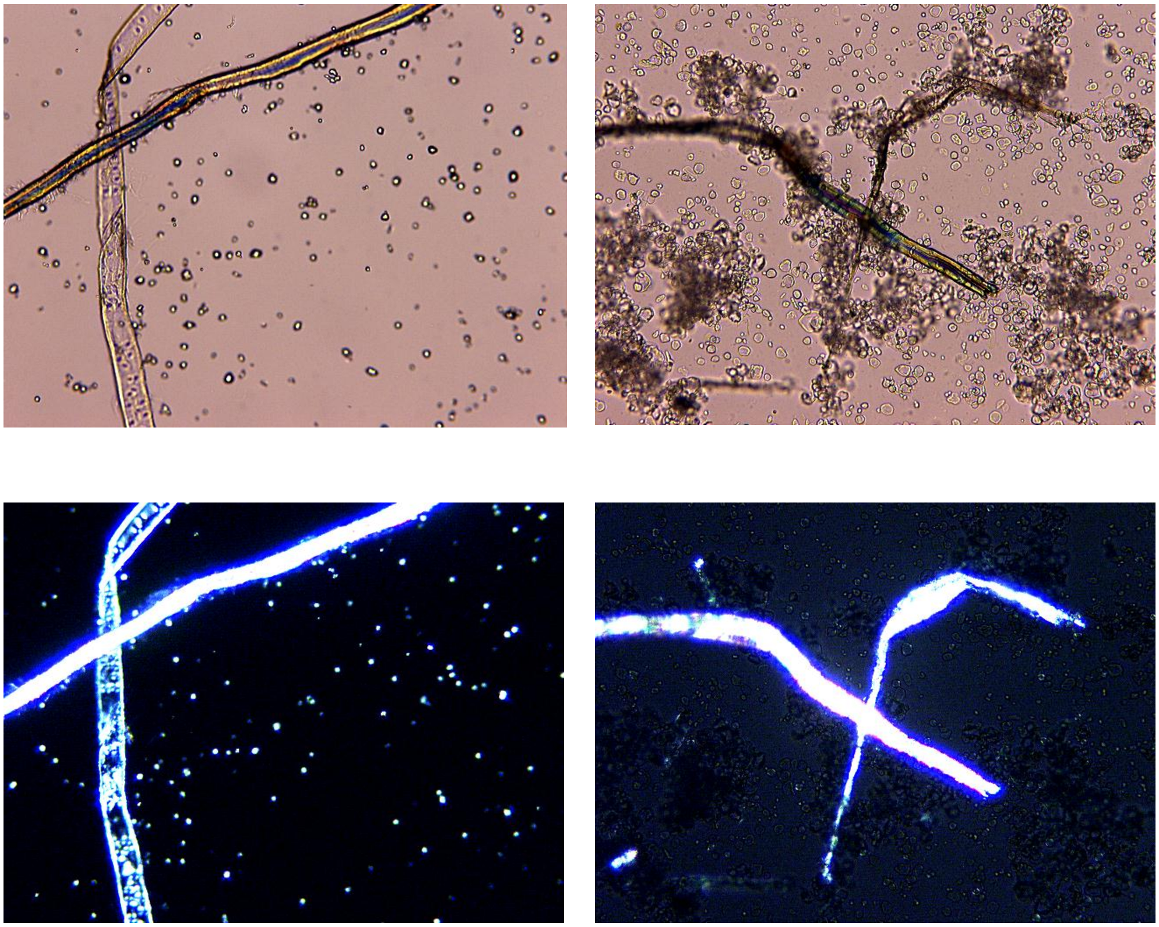

Fig. 2. Samples of starch-fiber on the left are uncooked; images on the right are after microwave heating for 120 seconds at 15 second intervals. Top images were taken with unpolarized light and the bottom images with cross-polarized light. Sample prepared from a 10% solution of 50% amylose starch with a fiber level of 3%. The width of images is approximately 400 microns.

The observed loss of birefringence was indicative of the starch gelatinization process, i.e., the swelling and hydration of granules or the melting of starch crystallites (Zobel 1984). There still remained a granular structure of the starch as can be observed in Figure 2, thus, the starch granules were not completely solubilized under these heating conditions. The viscous nature of the sample after heating was in agreement with gelatinization. This is commonly accepted as the amylose component extending out of the granule and bridging with other amylose polymers to form a gel (Austin 1984; Morris 1990). Further evidence of the formation of a gel is presented in this research via images of the starch matrix after solvent exchange, see later. This structure was different from previous research in this lab, Fig. 1, in which the heating and mixing conditions were more intense and the resulting structure shows no evidence of a residual granular structure.

SMCF-Fiber Materials

Qualitative characteristics of the samples with different starch type, starch percentage, and fiber percentage after solvent exchange and drying in the constant humidity and temperature room were determined. Increasing amylopectin content increased the strength of the SMCF material, whereas increasing amylose content improved the shaping and smoothness of the molded SMCF material. The addition of increased amount of fiber improved all qualitative features (shape and smoothness) of the foam up to 4% wt/wt fiber/(fiber+water), above which no benefits were observed. Increased fiber content in this range lowered the density of the foam, presumably due to the fibers resisting foam shrinkage upon drying. At levels of 5% fiber the material formed a discontinuous aquagel with uneven distribution of fibers. The materials with fiber content of 5% were weak, brittle, and abraded easily. All SMCF-Fiber composites had an approximate density of 0.35 to 0.45 g/cm^3, Table 1. Higher amylose (50-70%) content starches had an increase in density due to the high amylose starch foams shrinking more during drying. It may be possible to further the development of the microporous structure by adding an acetone exchange step to remove ethanol and lower the surface tension of the liquid from which the SMCF is dried (Budarin et al. 2006).

Table 1. Densities of SMCF-Fiber Composites after Ethanol Exchange and Drying

SMCF-Fiber Composite Description	**Avg. Density (g/cm^3)**	**Standard Deviation (g/cm^3)**
10% (50% Amylose) starch solution - 3% fiber	0.395	0.032
10% (50% Amylose) starch solution - 4% fiber	0.337	0.033
12% (70% Amylose) starch solution - 3% fiber	0.423	0.040
12% (70% Amylose) starch solution - 4% fiber	0.359	0.044
14% (70% Amylose) starch solution - 3% fiber	0.434	0.049
14% (70% Amylose) starch solution - 4% fiber	0.430	0.054

The production of SMCF fiber foams depended greatly on the type of starch used. The regular dent corn starch, which has 20% amylose by weight, did not maintain its shape during drying; curling and surface wrinkling were significant. The addition of fibers to dent starch decreased only slightly this undesirable shape instability. Starch containing 50% amylose did not wrinkle like the dent starch, but it needed fiber to prevent cracking and maintain strength. The same was true for the high amylose starch, which contains 70% amylose. The high amylose starches (50-70%) also maintained the smoothness of the surface of the original aquagel without wrinkling. Light restraint of the samples to prevent warping was performed by simply placing 500 gram metal plates on top of the parts during drying. The main advantage of adding fibers to the foams was that processability (maintenance of sample without cracking or warping during solvent exchange and drying) was improved.

TGA Carbonization Experiments.

Six samples were carbonized in a TGA furnace at a 10˚C/min heat ramp in a nitrogen environment: dent starch, dent starch with fiber, 50% amylose starch with fiber, high amylose starch with fiber, bleached softwood market fiber, and a softwood pine chip. Fiber contents were 4% fiber to starch wt/wt. The TGA data for the 50% amylose starch with fiber sample are shown in Fig. 3, and the yield and peaks in the 1st derivative of weight loss versus temperature for all of the samples are listed in Table 2. The TGA data clearly show a mass loss due to fiber decomposition in the 1st derivative curves with peaks at around 325-350˚C and for starch at around 305˚C (Fig. 3).

The yield calculation was based on an initial weight at 105 ºC, assuming that the moisture had been removed at that temperature. The yields varied from 25% to 7.6%, Table 2. The softwood pine wood chip had the highest yield (25%), presumably due to the presence of lignin in the untreated wood; a typical lignin content for pine is 28%. The onset of mass loss was lower for the pine chip, presumably due to extractives and volatiles in the wood. In contrast, the bleached softwood market fiber had a lower yield, 14%, due to it’s near-zero lignin content. Dent starch had a very low yield of around 8%. The onset of mass loss was at higher temperatures than the pine chip, due to the absence of extractives/volatiles, in agreement with previous research which reported for 10˚C/min heating that both cellulose and starch began to degrade at 250˚C (Aggarwal et. al, 1997). Furthermore, the dent starch dramatically expanded (about 2-3 times its original volume) during heat treatment, unlike the other samples in the TGA. The presence of fibers in the dent starch SMCF-Fiber sample prevented this dramatic expansion. Higher amylose content starches had higher yields than the dent starch.

Table 2. Carbonization of Starch and Wood at 10˚C/min to 700˚C, nitrogen atmosphere in the TGA furnace. Onset of mass loss was determined as 1% mass loss of dry material.

Sample:	**Yield (%)**	**Onset of Mass Loss (°C)**	**1st derivative peaks (°C)**
Softwood pine chip	25%	205	325
Bleached SW market fiber	14%	265	350
70% amylose starch with fiber	14%	264	305, 335
50% amylose starch with fiber	14%	281	305, 335
Dent starch SMCF (20% amylose) no fiber	7.6%	261	305
Dent starch SMCF (20% amylose) with fiber	8.0%	260	305, 335

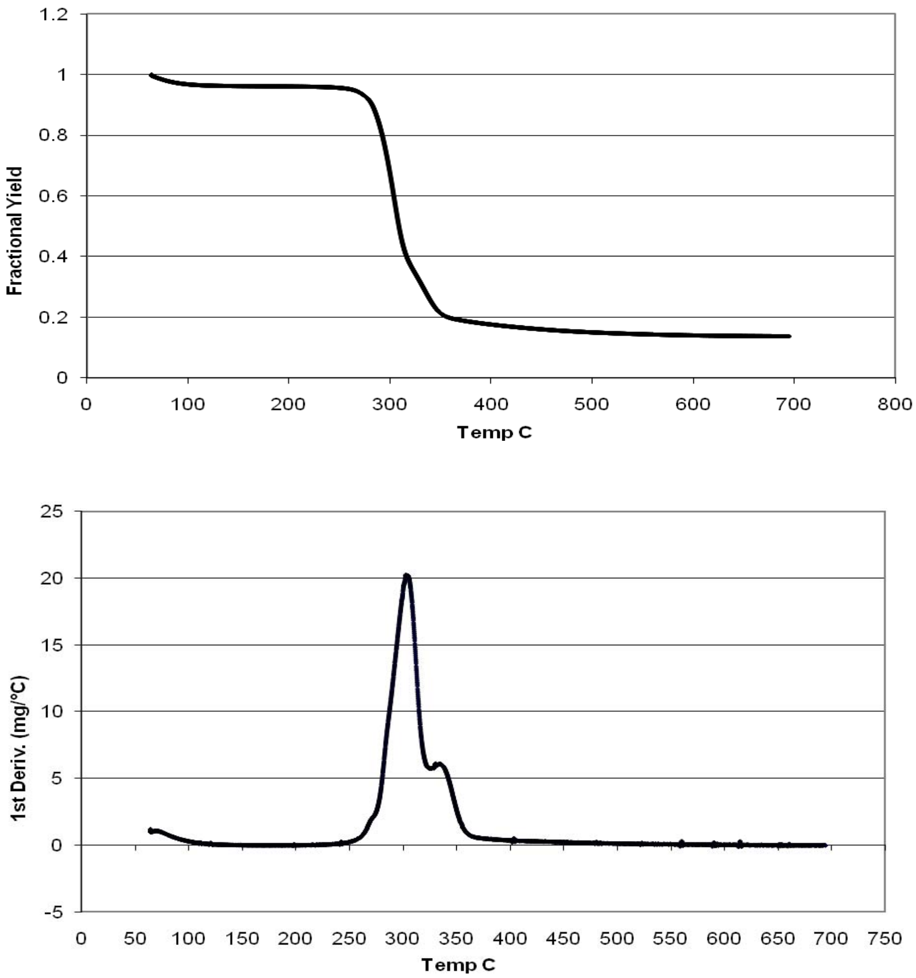

Fig. 3. TGA results (fractional yield and the 1st derivative of mass versus temperature in mg/˚C) for a high amylose starch (50% amylose) and fiber at 10°C/min in nitrogen. This first peak at about 305˚C is attributed to starch, and the second peak at about 335˚C is attributed to the cellulose fiber.

The TGA results, combined with the qualitative molding characteristics of the samples, were used to determine which starch fiber foams to carbonize for further analysis and what temperatures to carbonize the foams. The 50% amylose and the 70% amylose starches did not show uncontrolled expansion as did the dent starch in the TGA, and for this reason they were chosen for further study at the 3% and 4% fiber content in water and with the 12% and 14 % starch to fiber/water composition. The temperatures chosen for heat treatment under inert atmosphere were: 200, 350, 450, and 700 ºC, which included temperatures before and after the weight loss peaks observed in the TGA.

Properties of Carbonized SMCF-Fiber Foams

Samples of various formulations were heat-treated in a tube furnace to investigate their properties when carbonized. The samples were cubes in the range of 10 to 15 mm on edge and had mass in the range of 0.5 to 1.0 grams. Initially, a 10˚C/min heating rate was used, which resulted in a 21% yield at 700˚C. However, it was found that the samples greatly expanded in an uncontrolled and irreproducible manner, resulting in an extremely low density (0.006 g/cm^3). The visual observations of these materials suggest that trapped gasses inside the materials expanded and caused the thermoplastic samples to foam. This material was extremely brittle and could not be evaluated for physical properties.

Due to the irreproducible expansion of the SMCF-Fiber composites at 10°C/min our preferred heat treatment procedure utilized a 0.5˚C/min heating ramp, cf. Table 3. The samples no longer expanded in an irreproducible manner but instead decreased in volume and in density, and were not as brittle. The density and reduced density (density/cell wall density) decreased with increased heating temperature (an estimate of cell wall density of 1.5032 g/cm^3 was used, i.e., the measured density of maize starch granules (Fortuna and Juszczak 1997)) up to a heating temperature of 350˚C, but remained approximately constant up to 700˚C. It must be stated that the cell wall density changes due to compositional variations are not accounted for in this calculation. The relative density indicates that the material transitions from a solid with isolated pores (relative density greater than 0.3) to a fully developed cellular solid (relative density less than 0.3) at a temperature between 200˚C and 350˚C (Gibson and Ashby 1997). The yields dramatically decreased between 200°C and 350˚C treatment temperatures, in agreement with the TGA results, despite the different heating rates used in TGA and in the tube furnace. The carbon content increased to 90% at 700˚C, and the hydrogen decreased to less than 1% at 700˚C. The calculated oxygen content (total mass minus C and H) decreased to less than 10% at 700˚C. This may not be the true oxygen content as it may include other atoms not detected in the elemental analysis procedure. The changes in carbon/hydrogen/oxygen composition of the foams with increased treatment temperature can be correlated with increased hydrophobicity, as observed in the water contact angle values, cf. Table 3.

Micro-Structure of the SMCF-Fiber Composites

The Scanning Electron Microscope images show the micro-structural features of the SMCF-Fiber composites, Figs. 4-6. These images were taken for fracture surfaces of the bulk of the material. For the untreated SMCF-Fiber composites the fibers and starch matrix were easily distinguished, Fig. 4. A random orientation of the embedded fibers in the starch matrix in Fig 4 was representative of several additional areas inspected using the SEM, data not shown. Further evidence of random orientation was observed in SEM images of the surface of the SMCF-Fiber composites molded parts, data not shown. The starch matrix material is an extremely complicated porous structure, revealing a variety of features over several orders of magnitude length scales. The largest structural feature of the starch matrix was revealed as agglomerates of swollen starch granules. The remnants of starch granules are connected by a web of starch with fibril widths of about 1 micron. This web-like net of starch strands is expected to be from leaching amylose molecules that diffuse out of the swollen granule and form a gel at temperatures from 57-100˚C (Young 1984; Morris 1990).

Table 3. Effects of Temperature on SMCF-Fiber at 0.5˚C/min Heating Rates.

	Treatment Temperature (˚C)				
Properties	**25**	**200**	**350**	**450**	**700**
Yield (%)	100.0	74.2	25.5	22.5	20.9
Density (g/cm^3)	0.508	0.437	0.167	0.151	0.169
Relative Density	0.338	0.291	0.111	0.100	0.112
% Reduction	N/A	16%	205%	236%	201%
Volume (cm^3)	0.487	0.476	0.398	0.381	0.307
% Reduction	N/A	2.3%	18.7%	26.7%	47.2%
Cross Sectional Area (cm^2)	0.648	0.648	0.497	0.461	0.408
% Reduction	N/A	-0.12%	23.2%	37.6%	52.1%
Thickness (cm)	0.752	0.730	0.802	0.826	0.750
% Reduction	N/A	2.87%	-6.90%	-9.18%	0.18%
Elem. Analysis - % C	43.2	44.6	76.8	83.7	90.2
% H	3.61	2.51	2.55	2.11	0.91
Theoretical - % O	53.2	52.9	20.7	14.2	8.89
Contact Angle - 0 min	77°	77°	115°	115°	113°
1 min	45°	61°	115°	115°	113°
5 min	0°	0°	115°	115°	113°

Inspection of the surfaces of the starch granules and of the web material show an abundance of pores on the surfaces, with pore diameters around the 50-200 nanometer range. These fine features are to be expected with the pore-preserving solvent exchange process with drying from ethanol (Glenn et. al, 1995; El-Tahlawy et al. 2007). (If these materials are dried from water, a clear, dense, brittle solid is produced). Note that the SMCF structure in Figure 1 lacks the appearance of granule remnants due to the more intense thermal treatment and shear conditions used to produce the starch aquagel in that study (Patel, et. al, 2008).

Samples treated at 200˚C with a 0.5˚C/min heating rate, Fig. 5, also displayed the fibers in a random orientation on the fracture surfaces. However, the appearance of the starch had changed, losing most of the porous nature of the web and granules. The starch particles had somewhat flowed and coalesced. The images of these somewhat smooth starch areas display many recessed voids, indicative of either starch granules that had been displaced during fracture or voids produced by expanding gasses.

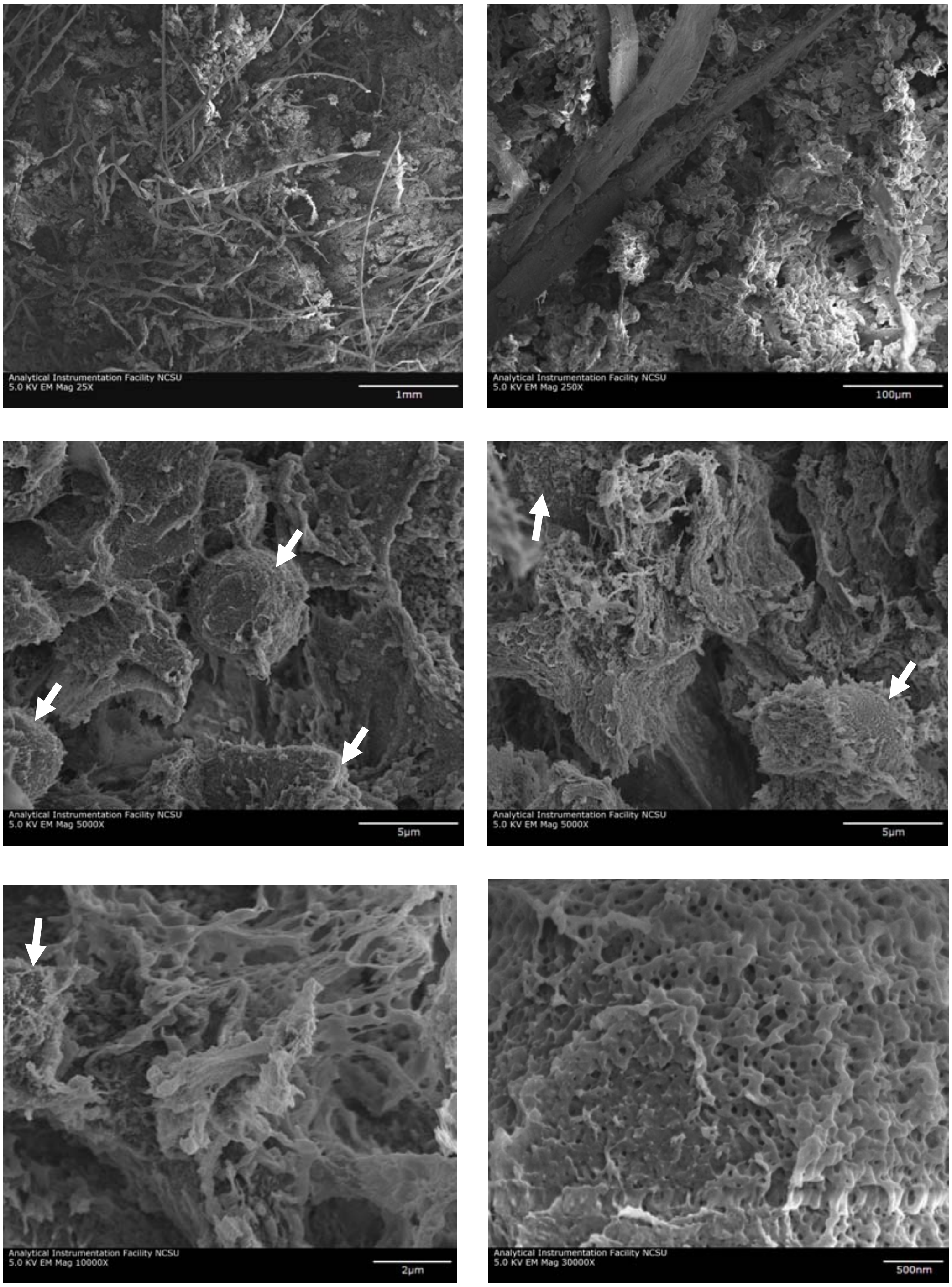

Fig. 4. Images of a fractured surface of an untreated SMCF-Fiber composite structures at several magnifications. White arrows point to swollen starch granules. Sample prepared from a 10% solution of 50% amylose starch with a fiber level of 3%. Bottom right: image of surface of starch granule.

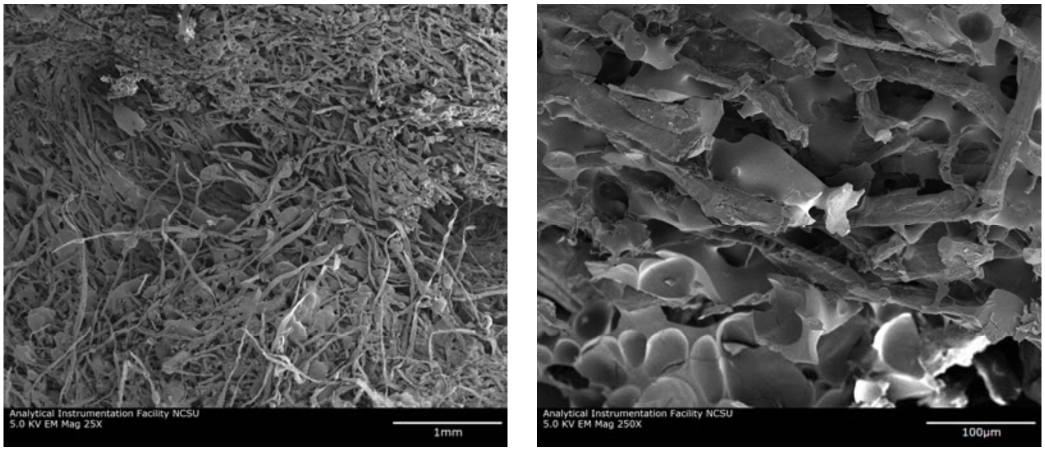

Fig. 5. Images of a fractured surface of an SMCF-Fiber composite after heat treatment of 200°C at 1 mm (left) and 100 micrometer (right) length scales. Sample prepared from a 10% solution of 50% amylose starch with a fiber level of 3%.

As the heat treatment temperatures increased above 200˚C, the individual fibers were observed with less frequency, and the entire sample began to produce a more regular three-dimensional closed cell foam structure, Figs. 6-8. It appears that some of the cells had openings in the wall, but this may have been due to the fracturing of the material. For the 700°C treatment the samples showed a well developed isotropic, closed-pore structure with pore diameters around 50 microns and pore walls around 1-3 microns. Fibers and starch were not identifiable after the heat treatment at 700°C. These images, with starch changes occurring at lower temperatures than the cellulose fibers, are in agreement with the TGA results, Table 2, indicating maximum mass loss rates for the starch and fibers at 305-335˚C and 350˚C, respectively. These results suggest that the untreated samples microstructure might be retained using a cross-linking agent to stabilize the starch foam structure (Budarin et al. 2006). However, the produced structure is of interest in itself, more so for applications requiring a closed pore structure, such as insulation, than for applications requiring open cell structure, such as filter media.

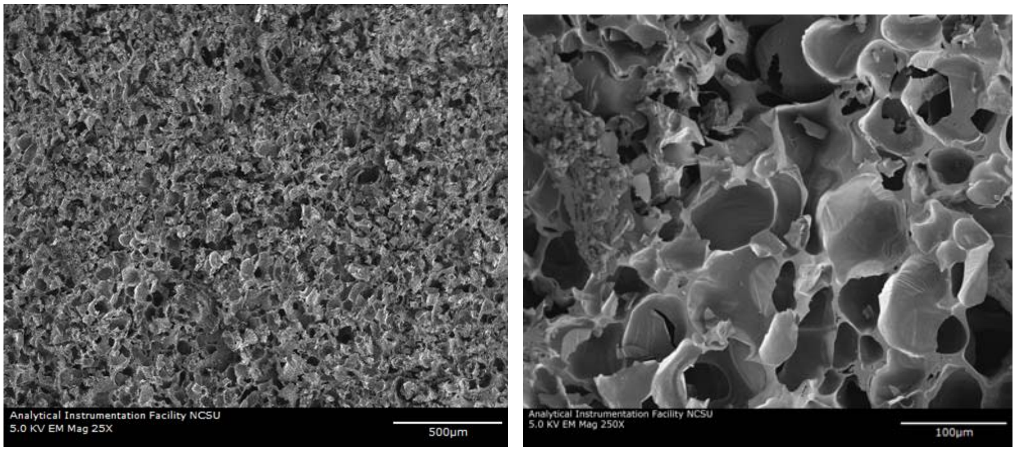

Fig. 6. Images of a fractured surface of an SMCF-Fiber composite after heat treatment of 350°C at 500 micron (left) and 100 micron (right) length scales; Sample prepared from a 10% solution of 50% amylose starch with a fiber level of 3%.

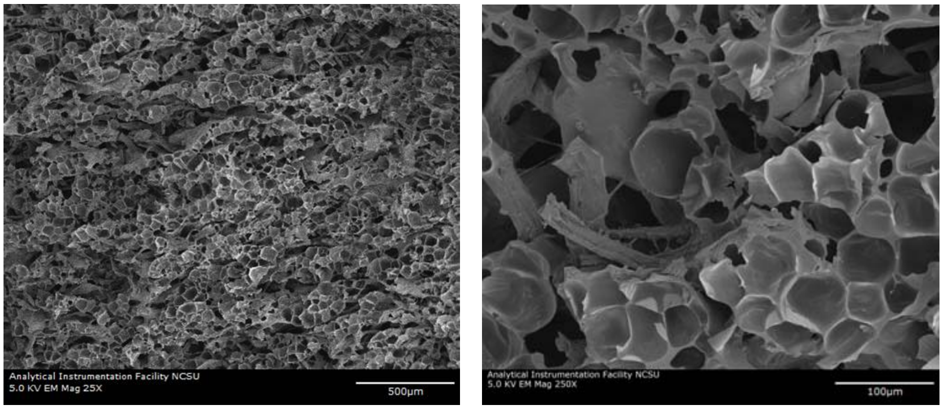

Fig. 7. Images of a fractured surface of an SMCF-Fiber composite after heat treatment of 450°C at 500 micron (left) and 100 micron (right) length scales; Sample prepared from a 10% solution of 50% amylose starch with a fiber level of 3%.

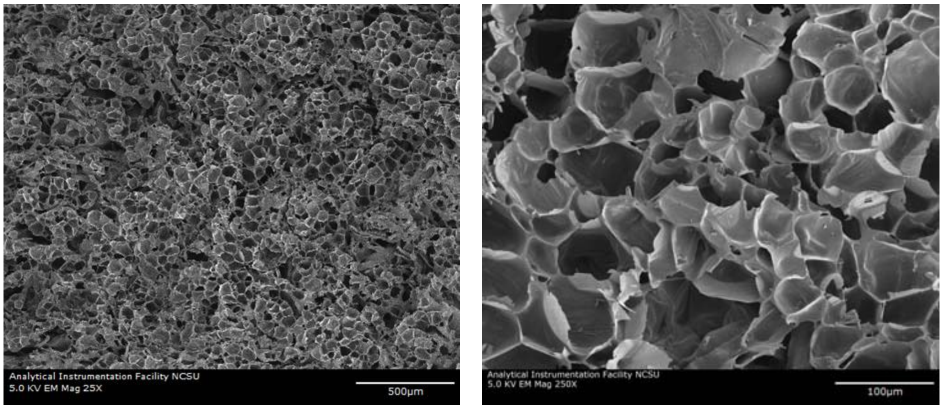

Fig. 8. Images of a fractured surface of an SMCF-Fiber composite after heat treatment of 700°C at 500 micron (left) and 100 micron (right) length scales; Sample prepared from a 10% solution of 50% amylose starch with a fiber level of 3%.

Mechanical Properties

The mechanical testing results on the pre-carbonized foams indicated that the 50 percent amylose starch foams had higher modulus of elasticity (MOE) and modulus of rupture (MOR) at 10% strain than the 70% amylose foams, Table 4. For the 70% amylose materials, 14% starch in water had improved properties over the 12% starch in water samples, suggesting that increased starch levels improved compressive strength. Increased fiber content, from 3 to 4%, actually decreased the strength properties of the pre-carbonized materials. This was not to be expected, as fiber content was initially predicted to have increased strength in the foams, but could possibly be the result of increased fiber samples having lower densities (Table 1), affecting the strength. The non-carbonized foams never reached a peak load modulus of rupture (MOR), but instead kept deforming under stress and never catastrophically failed. The modulus of rupture at 10% strain and modulus of elasticity were similar to those of SMCF produced from corn, high amylose corn, and wheat starches (Glenn and Irving 1995).

Table 4. Compression Results for SMCF-Fiber (non-carbonized)

Non-Carbonized Foams	Density	MOE Avg. and Range	Stress at 10% strain Avg. and Range
	g/cm^3	MPa	MPa
10% (50% Amylose) - 3% Fiber	0.40	121.1 ± 20	2.51 ± 0.50
10% (50% Amylose) - 4% Fiber	0.34	79.4 ± 15	1.70 ± 0.20
12% (70% Amylose) - 3% Fiber	0.42	44.6 ± 20	1.14 ± 0.15
12% (70% Amylose) - 4% Fiber	0.36	24.8 ± 10	0.72 ± 0.07
14% (70% Amylose) - 3% Fiber	0.43	54.2 ± 8	1.74 ± 0.10
14% (70% Amylose) - 4% Fiber	0.44	66.6 ± 10	1.39 ± 0.10

Initial experiments with heat treatments utilized 10˚C/min, but as stated, irreproducible expansions occurred at higher temperatures, resulting in materials with densities in the neighborhood of 0.005 g/cm^3. However, results at 10˚C/min heating rate to 200˚C did not suffer from this, and the results are reported in Table 5. A heat treatment at 200˚C was found generally to increase the MOE (Table 5) relative to the untreated foams (Table 4). The heat-treated materials showed a peak load (Table 5), not detected with the untreated samples. An increase in fiber content improved the stress at a strain of 10%, but at peak load the foams with less fiber had improved strength. The MOE results did not show a correlation between fiber content and strength.

Table 5. Compression Results for SMCF-Fiber Heat Treated at 200°C at a Heating Rate of 10°C/min

Carbonized Foams at 10°C/min to 200°C	Density	MOE	Stress at 10% Strain	MOR at peak load
	g/cm^3	MPa	MPa	MPa
10% (50% Amylose) - 3% Fiber	0.40	135.3	1.11	2.24
10% (50% Amylose) - 4% Fiber	0.35	162.2	1.64	2.04
12% (70% Amylose) - 3% Fiber	0.35	91.2	0.72	1.81
12% (70% Amylose) - 4% Fiber	0.34	74.5	1.14	1.69
14% (70% Amylose) - 3% Fiber	0.48	55.4	0.91	1.28
14% (70% Amylose) - 4% Fiber	0.45	38.7	0.92	1.01

Like the untreated foams, the increased amylopectin content in the 50% amylose starch relative to the 70% amylose starch for 200˚C treatment produced higher moduli in the SMCF-Fiber composites. The increased starch content from 12% to 14% in the high amylose starch (70% amylose) generally decreased the strength of the 200˚C heat treated SMCF-Fiber composites, the opposite effect of the non-treated foams, Table 4. The density was decreased with increased fiber content for five out of the six formulations evaluated, Tables 4 and 5, indicating that the fibers decreased shrinkage during solvent exchange and drying. No strong trends between physical properties and density were observed for the limited density range, Tables 4 and 5.

Further heat treatments (but with the preferred 0.5˚C/min heating rate) were conducted with the composition of 10% (50% amylose) starch with 3% fiber, which showed the highest strength values for the untreated samples, Table 4. The results at 25°C and 200°C treatments for 0.5˚C/min in Table 6 are in agreement with previous experiments shown in Tables 4 and 5, showing a small increase in stress at 10% strain from 25°C to 200°C. There was a 50-60% decrease in modulus at 10% strain of the samples treated at 350°C and 450°C relative to the 200˚C treatment samples; this is the temperature range in which most mass loss occurred. However, samples treated at 700°C displayed an increased modulus at 10% strain relative to the 350°C and 450°C treated samples. The samples treated at 700°C showed promising modulus of elasticity at a significantly reduced density. Similarly, the modulus of elasticity also passed through a minimum with heat treatment.

The stress versus strain compression data for samples untreated or treated to 200˚C displayed a linear elastic region and a densification region, results typical of an elastomeric foam, but did not exhibit a significant plateau with elastic buckling (Gibson and Ashby 1997). The lack of the stress-strain plateau in these samples is to be expected, as the relative density of these samples was near 0.3, indicative of largely a solid with pores. For samples treated at 350˚C, 450˚C, or 700˚C the stress versus strain compression data displayed a linear elastic region and a plateau, indicative of brittle crushing, which is typical of an elastic-brittle foam (Gibson and Ashby 1997). A typical densification region for an elastic-brittle foam was not achieved in these tests due to the catastrophic failure of the samples (samples leaving the test contact area).

The modulus of elasticity to density ratio, Table 6, increased with increased treatment temperature, with a significant increase between 450°C and 700°C. Further, the MOR at peak load to density ratio was also increased between 450°C and 700°C. The results suggest that improvement in compression properties with higher heat treatments may reflect the more regular closed pore structure (Figs. 5-8, SEM images) and more extensively carbonized wall composition (Table 3, elemental analysis data) for the higher temperature treatments.

Table 6. Effect of Treatment Temperature on SMCF-Fiber Compression Properties at Heating Rate of 0.5˚C/min. Sample prepared from a 10% solution of 50% amylose starch with a fiber level of 3%.

Temp	MOE Avg. and Range	MOE/Density Avg. MOE / Density	Stress at 10% Strain Avg. and Range	MOR Avg. and range	MOR at peak load/Density
(°C)	MPa	MPa / (g/cm^3)	MPa	MPa (peak load)	MPa / (g/cm^3)
25	14.1 ± 4	27.7	1.35 ± 0.35	10.7 ± 6	21.0
200	18.7 ± 7	42.9	1.63 ± 0.40	5.72 ± 4	13.2
350	8.00 ± 3	48.0	0.64 ± 0.05	0.83 ± 0.1	5.0
450	7.35 ± 2	48.6	0.61 ± 0.12	0.90 ± 0.1	6.0
700	17.8 ± 7	105.7	1.63 ± 0.35	2.55 ± 0.4	15.1

CONCLUSIONS

1. The use of higher amylose content starches as well as up to a 4% fiber suspension content of the precursor aquagel improved the uniformity and the preservation of the foam structure upon solvent exchange and drying.
2. Increased amylopectin content improved compression strength of the starch microcellular-fiber foams, but caused defects during the drying process.
3. Carbonization of the starch microcellular-fiber foams transformed the materials from a structurally complex solid with pores into an elastic-brittle foam (displaying an elastic region followed by a plateau indicative of brittle crushing) with a closed pore structure.
4. The heating rate had an important effect on the structures of the foams.
5. The modulus of elasticity to density ratio increased with increased carbonization temperature up to 700°C.

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