Processing and Properties of Syntactic Foams Reinforced with Carbon Nanotubes

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ABSTRACT: This article presents synthesis and mechanical characterization of carbon nanotube (CNT)-reinforced syntactic foams. Following a dispersion approach (comprising ultrasonic, calendering, and vacuum centrifugal mixing), single- and multi-walled functionalized CNTs (FCNTs) were incorporated into two foam composites containing various commercially available microballoon grades (S38HS, S60HS, and H50 from 3M). The FCNT-reinforced composites were tested for compressive strength and apparent shear strength before and after hot/wet conditioning. The results showed that the FCNT-reinforced composites' mechanical properties depended on the vacuum pressure used during processing. Compared with pristine and commercially available syntactic foam (EC-3500 from 3M), the FCNT-reinforced composites processed at high vacuum (0.2 kPa) showed significant increase in compressive strength and apparent shear strength before and after hot/wet conditioning. Dynamic mechanical analysis showed an increase of about 22°C in glass transition temperature for composites processed at high vacuum with 0.5 wt % FCNT and 45 wt % S38HS–5 wt % S60HS microballoons. Thermogravimetric analysis indicated water absorption and lower decomposition temperature for the FCNT-reinforced composite mixed at atmospheric pressure, whereas no significant change was observed for the compound processed at high vacuum. Fracture analysis showed matrix failure for the composite processed at high vacuum and microballoon crushing for the composite mixed at atmospheric pressure. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2383–2394, 2012

Key words: foams; syntactic foams; composites; nanocomposites; carbon nanotubes

INTRODUCTION

Hollow particle filled composites—syntactic foams—are lightweight materials synthesized by incorporating large quantities of microballoons or microspheres into a polymer based resin. Due to their low density,[1,2] low coefficient of thermal expansion,[3] and high strength,[4] these foam composites are widely used in aerospace applications to reinforce the core section of sandwich laminates and make structures capable of sustaining high compressive load.

Syntactic foams possess a unique feature with respect to other conventional composites, as their physical and mechanical properties can be tailored to specific structural applications by changing the microballoon constituent. Despite this inherent benefit, performance is influenced by several factors such as microballoon volume fraction,[2] microballoon composition,[5–7] matrix, microballoon/matrix interface,[8] void content,[1] and processing.

Ideally, syntactic foams are considered as a two-phase system because they are formed by two constituents: binder (resin) and filler (microballoons). Due to processing, however, air entrapment is likely to occur leading to void formation within the structure. The presence of voids makes syntactic foams a three-phase system with lower mechanical properties[1] and higher susceptibility to moisture absorption when exposed to severe environments (e.g., hot/wet in which moisture uptake can lead to modifications of physical and mechanical properties that reduce the overall foam performance[8–10]).

In aerospace structural applications, syntactic foam use is limited by density and strength. Typically, higher strength is associated with heavier syntactic foams, which is concern in the design of advanced aerospace structures. In view of this challenge, several approaches have been proposed in an attempt to increase the performance of syntactic foams without compromising their weight substantially. Today, researchers have used short fibers[11–13] and nanoclay,[14,15] with nanoclay results offering promise for fracture toughness but remaining inconsistent for compressive strength.[14] Other authors[16] have shown enhancement in fracture toughness of 35% by addition of carbon fibers but did not report

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Additional Supporting Information may be found in the online version of this article.

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values of compressive strength. Although several studies in the literature address characterization of reinforced syntactic foam under dry conditions, little emphasis has been put on investigating the properties of reinforced foam composites after the exposure to hygrothermal conditions. Therefore, a need exists to design syntactic foams that can sustain high external load under different environmental conditions with minimum impact on density.

One possible way to overcome this issue is by incorporating fillers such as carbon nanotubes (CNTs) as reinforcement. Because of their resilience, large surface area, and outstanding physical and mechanical properties, CNTs are a potentially ideal reinforcement material for enhancing syntactic foam strength without significant effect on density. In recent years, many investigations have used CNTs to improve the electrical,[17] thermal,[18] and mechanical[19–21] properties of polymer composites. Although several approaches have been developed to improve the intrinsic incompatibility of CNTs with polymer and the dispersion of nanotubes in matrices, little attention has been placed on using CNTs as reinforcement material for syntactic foams. In this work, the effect of CNT addition on syntactic foam mechanical properties was investigated by testing CNT-reinforced specimens of varying concentration and type of microballoons. Following a design of experiment (DOE) approach, several factors were studied to identify variations in mechanical properties of CNT-reinforced composites with processing conditions. CNTs were carboxylic acid functionalized (FCNTs) and then dispersed into two foam composites through a dispersion approach comprising ultrasonic, calendering, and vacuum centrifugal mixing. Several FCNT-reinforced composites were manufactured and tested for compressive strength and lap shear strength before and after hot/wet conditioning. Results were then compared with pristine and commercially available compounds to evaluate the benefits of adding CNTs.

EXPERIMENTAL

Materials

The matrix system used for manufacturing pristine and CNT-reinforced composites was comprised of a phenolic-epoxy based resin and an alicyclic-anhydride accelerator (Cytec's product #70800902) supplied from Cytec Industries (Woodland Park, NJ). This system was chosen because it is the main constituent used in the production of Cytec's Corfil 625-1—a lightweight one-part foam composite containing the abovementioned matrix and silica glass microballoons. Both resin and accelerator were mixed at a ratio of 74 : 7 by weight, according to the vendor's recommendations.

TABLE I
Physical and Mechanical Properties of Corfil 625-1 and EC-3500

Material	Density (kg/m^3)	Compressive strength (MPa)	Lap shear strength (MPa)
Corfil 625	400–496.6	20.7	–
EC-3500	640.7	41.36–62.05	~ 6.5

Commercially available compounds, Corfil 625-1 and EC-3500—a high-strength two-part epoxy resin widely used in aerospace applications—were obtained from Cytec and 3M (St. Paul, MN), respectively. For the latter compound, the epoxy was mixed with the hardener at a ratio of 2 : 3 by weight, following the vendor's specifications. The physical and mechanical properties of both off-the-shell compounds are shown in Table I.

Three types of Scotchlite™ hollow glass microballoons supplied by 3M were used for synthesizing foam composites. Microballoons were used as received, and their properties are provided in Table II.

Single-walled CNT (SWCNT) and multi-walled CNT (SWCNT) produced by chemical vapor deposition were obtained from SES Research (Houston, TX) and Cheap Tubes (Brattleboro, VT), respectively. The SWCNTs had an outer diameter of less than 2 nm, a length range of 5–15 μm, purity of more than 90 weight percentage (wt %) of CNTs and 50 wt % SWCNTs, ash content of less than 2 wt %, and amorphous carbon content of less than 5 wt %, as provided by the manufacturer. The MWCNTs had an outer diameter of 20–30 nm, an inside diameter of 5–10 nm, a length range of 10–30 μm, purity of more than 95 wt %, ash content of less than 1.5 wt %, and specific surface area of 100 m^2/g, as provided by the vendor. All other chemicals were obtained from Fisher Scientific (Waltham, MA) and used as-received.

Processing of pristine syntactic foams

To obtain syntactic foams with properties similar to EC-3500, an initial study was performed to investigate variation in density and strength of foam composites with respect to microballoon type and concentration. Experiments were conducted following a full factorial DOE approach consisting of three variables: microballoon type (S38HS and H50), microballoon concentration (45 and 60 wt %), and supplemental microballoon type (5 wt % S60HS). This last variable was chosen to investigate the influence of high-density and high-strength microballoons on composites manufactured with only one kind of hollow spheres. Composites were formulated by mechanically stirring a mixture of phenolic-epoxy

TABLE II
Physical and Mechanical Properties of Microballoons

Microballoon	Density (kg/m^3)	Average diameter (μm)	Crush strength (MPa)
S38HS	379.96	44	37.92
S60HS	600.05	30	124.11
H50	499.94	37	68.95

resin and alicyclic-anhydride accelerator with the microballoons as described in the DOE. Tests were performed before and after hot/wet conditioning with the purpose of evaluating the composite performance in distinct environments and selecting two compounds with properties close to EC-3500. From the mechanical test results obtained before conditioning, it was noticed that all composites fabricated with H50 microballoons showed density and strength values higher than EC-3500, whereas composites containing 45 wt % S38HS microballoons showed density and strength results similar to EC-3500. A decrease in density and strength was observed by increasing the concentration of S38HS microballoons to 60 wt %, clearly indicating dependence of properties on the microballoon content. Interestingly, by adding 5 wt % S60HS microballoons to 45 wt % S38HS composites, the compressive strength increased from 68 to 75 MPa, and the apparent shear strength decreased from 15 to 13 MPa, whereas still maintaining a density close to EC-3500 (636 kg/m^3). After conditioning, a substantial decrease in compressive strength was noticed for all composites, whereas the apparent shear strength stayed significantly high for compounds with H50 microballoons. In that context, by comparing mechanical test results before conditioning and evaluating density values with EC-3500, the first compound to be modified with CNTs was chosen—the composite prepared with 45 wt % S38HS–5 wt % S60HS microballoons. This composite, hereafter referred to as BSS, was selected because it provided compressive strength and apparent shear strength values similar to those of EC-3500 with an equivalent density. After analyzing hot/wet strength results along with density values, it was concluded that the composite with 60 wt % H50–5 wt % S60HS microballoons was a good alternative to be modified with CNTs. This composite, henceforth referred to as BHS, provided a compressive strength close to EC-3500, apparent shear strength higher than EC-3500, and the lowest density among the compounds containing H50 microballoons. Although having a higher density than EC-3500, this formulation could be used to better understand the effect of nanotube addition on the syntactic foam properties. The DOE structure as well as the density and mechanical test results for these experiments can be found in the Supporting Information.

Processing of functionalized carbon nanotube-reinforced syntactic foams (FCNT-reinforced composites)

It has been well documented that syntactic foam physical and mechanical properties depend on the resin-microballoon ratio.[22] However, when CNTs are added into foams composites with the purpose of enhancing their mechanical properties, different variables need to be studied to identify the processing parameters required to attain reinforcement. Using a DOE approach with resolution four, the effect of CNT reinforcement on the physical and mechanical properties of syntactic foams was investigated. This approach is an effective technique for studying large number of variables that could affect the final CNT-reinforced composite properties, although trends are difficult to identify. Consisting of eight factors of three levels each—a high (1), a low (−1), and an intermediate (0) value—, the DOE was followed to fabricate 35 samples. Factors are provided in Table III, whereas a review of experimental configuration for each specimen type discussed in this article is presented in Table IV. A description of the 35 specimens manufactured following the DOE is shown in the Supporting Information. For each composite formulation, eight compression and ten lap shear specimens were prepared.

The DOE factors were defined to investigate the influence of different functionalized nanotube types and processing conditions on density and strength of foam composites (factor *h*). As reinforcement particles (factor *g*), SWCNTs and MWCNTs were chosen because of their outstanding performance in polymer composites.[19,20] Due to intrinsic van der Waals attractions between individual tubes in combination with large surface area and high aspect ratio, pristine CNTs tend to bundle together forming agglomerates that are difficult to disperse and do not interact well with the matrix system. To

TABLE III
Factors for the DOE

Factors	−1	1	0
a, nanotubes (wt%)	0.5	1.5	1
b, mixing time (min)	20	30	25
c, vacuum (kPa)	0.2	97.5	48.8
d, sonication power (W)	78	156	125
e, acid time (min)	60	240	120
f, acid temp (°C)	60	90	75
g, nanotube type	SW	MW	MW
h, microballoon type	BSS	BHS	BHS

Note: SW, single-walled; MW, multi-walled; BSS, 45 wt% S38HS–5 wt% S60HS; BHS, 60 wt% H50–5 wt% S60HS.

TABLE IV
Composition of Specimens Fabricated and Density Values

Specimen	DOE#	*a* (wt %)	*b* (min)	*c* (kPa)	*d* (W)	*e* (min)	*f* (°C)	*g*	*h*	Density (kg/m^3)
Corfil 625-1	–	–	–	–	–	–	–	–	–	536.41
EC-3500	–	–	–	–	–	–	–	–	–	654.25
BSS	–	–	–	–	–	–	–	–	S38HS-S60HS	635.77
SW1BSS	12	0.5	30	0.2	156	240	90	SW	BSS	692.71
SW2BSS	19	1.5	20	0.2	156	60	90	SW	BSS	697.03
MW1BSS	9	0.5	30	0.2	78	60	90	MW	BSS	687.35
MW2BSS	18	1.5	20	0.2	78	240	90	MW	BSS	699.65
BHS	–	–	–	–	–	–	–	–	H50-S60HS	701.64
SW1BHS	11	0.5	30	0.2	156	60	90	SW	BHS	771.83
SW2BHS	20	15	20	0.2	156	240	90	SW	BHS	770.52
MW1BHS	10	0.5	30	0.2	78	240	90	MW	BHS	769.4
MW2BHS	17	1.5	20	0.2	78	240	90	MW	BHS	763.83
MW-97.5 kPa	22	1.5	20	97.5	78	240	60	MW	BHS	659.67
MW-0.2 kPa	27	1.5	30	0.2	125	60	60	MW	BHS	768.75

suppress agglomeration and improve nanotube chemical affinity to polymer, chemical modification of the graphitic sidewalls and tips is necessary. This can be accomplished by enabling the formation of functional groups onto the CNT surface through oxidation reactions. It should be noted that introduction of functional groups produces defects on the CNT graphitic walls, reducing their strength and stiffness. Therefore, several functionalization profiles based on various times and temperatures (factors *e* and *f*) were used to study the effect of nanotube treatment on composite properties. Notice that in this work, the properties of foam composites reinforced with raw or as-received CNTs were not studied. Previous report showed a 15% increase in compressive strength and a 9% decrease in apparent shear strength after adding as-received MWCNTs of 20–30 nm in diameter to syntactic foams.[23] Hence, it was concluded that further increase in mechanical properties could be achieved by increasing nanotube/matrix interaction through covalent functionalization of CNTs. Two nanotube concentrations (0.5 and 1.5 wt %) were chosen to investigate changes in composite physical and mechanical properties with respect to nanotube content (factor *a*), whereas composite processing was studied by setting different parameters for sonication, mixing time, and pressure (factors *b*, *c*, and *d*).

The functionalization of SWCNTs and MWCNTs was performed using a three-step process: purification, thermal oxidation, and carboxylation. Purification involved an oxidation reaction with nitric acid (HNO_3) at 126°C for 120 min. A 2.0 g of as-received CNTs (AR-SWCNTs/AR-MWCNTs) was added to a concentrated solution of HNO_3 and sonicated at a constant cycle (156 W) for 30 min in a cup-horn. The suspension was refluxed, diluted in deionized (DI) water, and collected by vacuum filtration. The purified CNTs were washed with DI water, until the excess acid was removed (filtrate pH $\sim$ 7) and then dried overnight in a vacuum oven at 75°C. After finishing the purification treatment, the CNTs were air oxidized at 550°C for 30 min to remove remaining amorphous carbons. The oxidized CNTs were functionalized using a 3 : 1 (v/v) mixture of sulfuric acid (H_2SO_4) and HNO_3 under vigorous stirring at the temperatures and times shown in the DOE (factors *e* and *f*). The resulting carboxylic acid nanotubes [functionalized single-walled carbon nanotubes (FSWCNTs)/functionalized multi-walled carbon nanotubes (FMWCNTs)] were washed with DI water, until the pH reached $\sim$ 7 and then dried overnight in a vacuum oven at 75°C. The FCNTs were stored inside a desiccant box until further use.

The FCNT-reinforced composites were processed by combining three methods: ultrasonic, calendering, and vacuum centrifugal mixing. First, 40 mL of acetone and 30 g of resin were mixed with FCNTs (factors *a* and *g*) by ultrasonic mixing (factor *d*) for 10 min. After the sonication period elapsed, the excess acetone was removed by placing the mixture inside an oven and heating it up to the acetone boiling point (57°C) for 60 min. The mixture was then allowed to cool to room temperature before degassing. The degassing step was performed by vacuum centrifugal mixing. This nonintrusive mixing technique uses centrifugal and revolving forces to mix a compound in vacuum atmosphere removing air and/or solvent from it. The mixture revolves and rotates at a speed of 2000 rpm while it is contained in a vacuum chamber that applies vacuum pressure (0.2 kPa). The mixture was vacuum centrifuged for 5 min to yield a nanotube-polymer paste free of acetone. Next, high shear mixing was applied by passing the nanotube-polymer paste through a three-roll-mill. This helped to disperse and disentangle remaining nanotube aggregates and create a uniform distribution of CNTs in the polymer. The parameters for the three-roll-mill are described in Table V. Once collected from the mill, the nanotube-

TABLE V
Three-Roll-Mill Set-Up

Pass through the mill	Feed roller (μm)	Center roller (μm)	Speed (RPM)
1	20	10	150
2	10	5	300

polymer paste was mixed with the accelerator, and one of the two sets of microballoons (factor *h*) using the vacuum centrifugal mixer. The process parameters used to perform this final mixing step were adjusted as presented in factors *b* and *c* of Table IV and Supporting Information.

Mechanical characterization and hot/wet conditioning

Prepared mixtures of BSS, BHS, FCNT-reinforced composites, Corfil 625-1, and EC-3500 were cast to make both compression and lap shear test specimens. Compression specimens were prepared and tested according to ASTM D 695-02a.[24] Mixtures were potted in a stainless steel mold containing cylindrical holes of 12.7 mm in diameter and 50.8 mm in height, as shown in Figure 1a. The samples were cured at 177°C for 60 min in a hot press set to 276 kPa. After curing, they were removed from the mold, ground down to a height of 25.4 mm, and tested for end loading compression.

Lap shear specimens were prepared using aluminum coupons according to ASTM 1002-05.[25] Two coupons were bonded together with foam composite creating an overlap of 12 mm, which was enough to induce failure in the material of interest and not in the aluminum substrates. The sample's thickness was controlled by placing shims of 101.6 μm thick on each side. Two stainless steel plates were then placed on the prepared specimens to create a uniform pressure along the contact area. The assembly was put inside a hot press (also set to 276 kPa) and cured as mentioned above. A schematic of the sample preparation is shown in Figure 1b. Finally, specimens were tested using a universal testing machine.

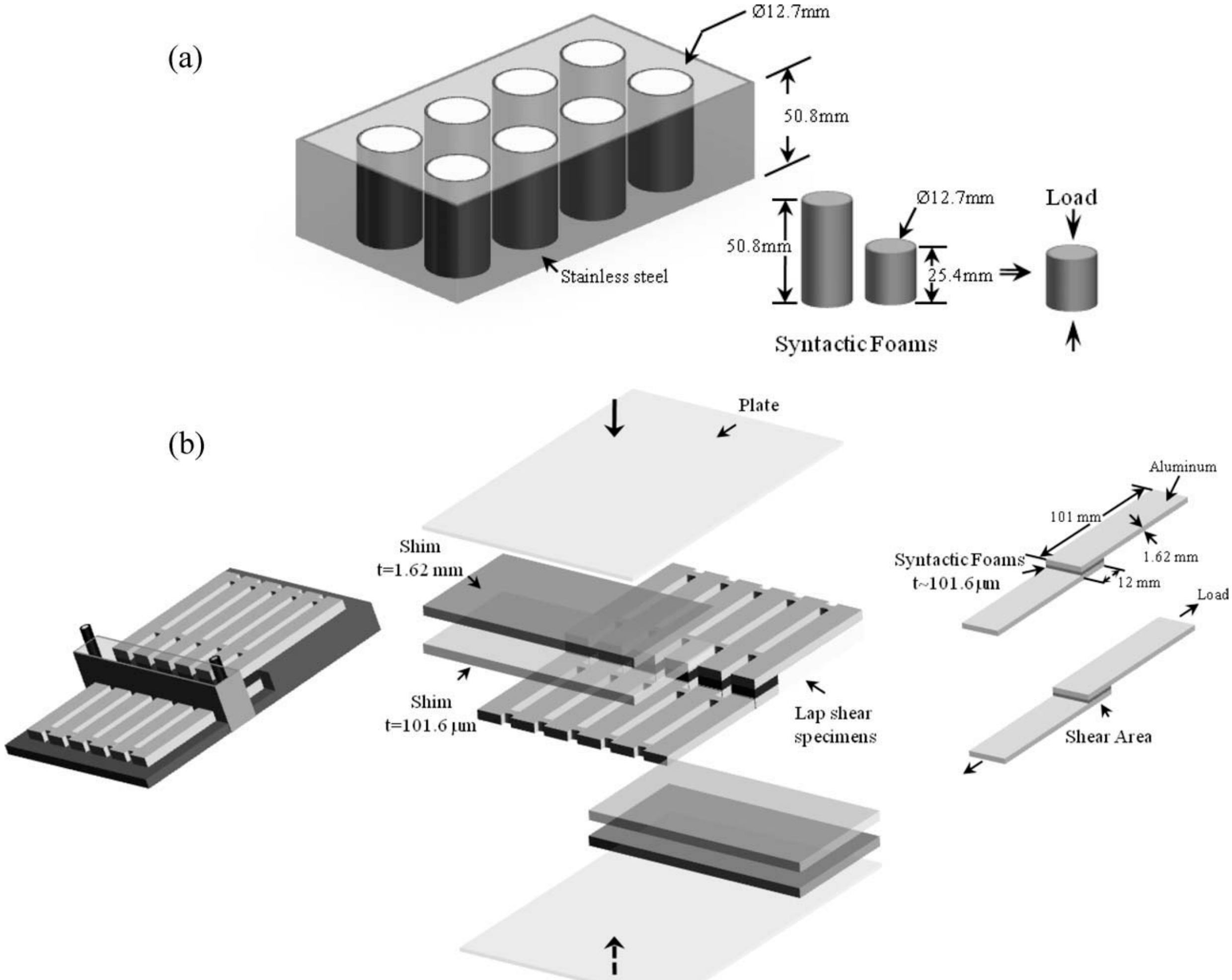

Figure 1 (a) Compression and (b) lap shear mold for sample preparation.

For each composition, eight compression and 10 lap shear specimens were prepared. Compression specimens were used for density measurements before mechanical testing. The density of each specimen was calculated by dividing mass by volume, and the values are provided in Table IV. The specimens were separated into two sets: the first set—4 compression and 5 lap shear specimens—was tested under dry conditions at room temperature. Tests were performed immediately after curing (grinding in the case of compression samples) and measuring dimension and mass to reduce the impact of possible moisture absorption over time. The average strength and the standard deviation were calculated. The second set of specimens was subjected to hot/wet conditioning for 30 days at 71°C and 85% relative humidity. Moisture uptake was determined according to weight changes measured by briefly taking specimens out of the hot/wet chamber, weighing them, and putting them back inside the chamber in under two min so desorption of water would be minimalized. After the conditioning period, specimens were removed from the hygrothermal atmosphere and placed into an environmental testing box heated to 82°C. Specimens were kept inside the test box for 5 min to reach thermal equilibrium and were tested for strength.

RESULTS AND DISCUSSIONS

Fourier transform infrared spectroscopy (FTIR) and TGA characterizations of CNTs

The presence of functional groups on the SWCNT and MWCNT surface was investigated by FTIR spectroscopy and thermogravimetric analysis (TGA). Spectra and plots for CNTs functionalized by varying times and temperatures (DOE factors *e* and *f*) are shown in Figures 1s and 2s of the Supporting Information. Results confirmed the present of carboxylic acid (–COOH) groups on the surfaces of both CNTs after functionalization treatment.

Compressive strength and lap shear strength

As mentioned in the Experimental section, a DOE approach was followed to manufacture different FCNT-reinforced composites and identify factors affecting the compressive strength and apparent shear strength of syntactic foams. In general, test results indicated that the mechanical properties of the FCNT-reinforced composites depended primarily on the vacuum pressure used during synthesis (factor *b* and *c*). Figure 2, for instance, shows how the FCNT-reinforced composite mechanical properties before and after hot/wet conditioning change with respect to the applied pressure during processing. These results correspond to BHS composites with the same weight percentage (1.5 wt %) of FMWCNTs mixed under different vacuum pressures: 97.5 kPa and 0.2 kPa—atmospheric pressure and high vacuum, respectively. Testing before hot/wet conditioning indicated an increase of 25% and 50% in compressive strength and apparent shear strength when the FMWCNT-reinforced composite was mixed at high vacuum, respectively. Although the apparent shear strength increased insignificantly, a decrease of 30% in compressive strength was observed after synthesizing the FMWCNT-reinforced composite at atmospheric pressure.

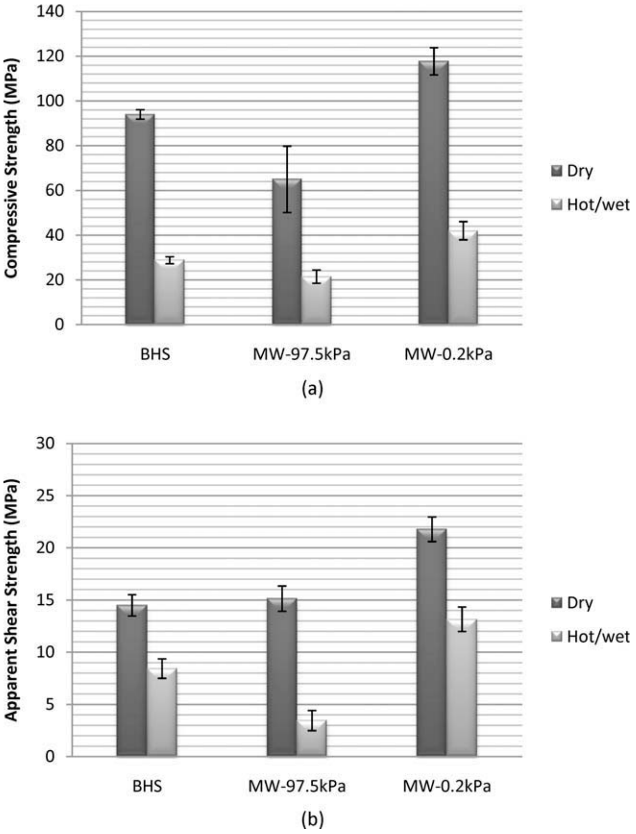

Figure 2 Effect of vacuum on (a) compressive strength and (b) apparent shear strength of syntactic foams reinforced with FMWCNTs.

To further understand the effect of processing condition on the mechanical properties of the FCNT-reinforced composites, dynamic mechanical analysis (DMA) was performed. A DMA instrument (TA Q800) equipped with a compression clamp was used to measure the glass transition temperature (T_g). Dry specimens were run at 5°C/min under 0.02% strain at 1 Hz. The specimen geometry and temperature range were 12.7 mm in diameter ×3 mm in thickness and 50–180°C. The T_g was determined by intersecting two tangent lines from a logarithmic plot of the storage modulus versus temperature, and the values are listed in Tables VI and VII.

Table VI shows the T_g results for the pristine (BHS) and the FCNT-reinforced composites mixed at

TABLE VI
Glass Transition Temperature (T_g) as a Function of Vacuum Pressure

Composite	T_g (°C)
BHS	133
MW-97.5 kPa	107
MW-0.2 kPa	125

atmospheric pressure (MW-97.5kPa) and high vacuum (MW-0.2kPa). It was noticed from the decrease in T_g values of the FCNT-reinforced composites compared with the T_g of BHS that plasticization[9] occurs in both compounds but at greater scale for the specimen processed at atmospheric pressure (T_g = 107°C). This intensified plasticization effect is potentially attributed to moisture absorption within the specimen pores, which might actually generate more free volume in the matrix and decrease T_g. The drop in T_g observed for the compound mixed at high vacuum is possibly ascribed to agglomeration of nanotubes in the matrix.[26] When not properly dispersed, the high concentration of nanotubes used to reinforce the foams can create clusters in the polymer that when embedded in between polymer chains create an additional space which increases matrix flexibility and so lower T_g.

Due to the presence of polar groups on their walls, FCNTs attract water molecules when exposed to air. Water uptake in the FCNT-reinforced composites affects the T_g and compromises the integrity of the structure. To obtain a measurement of the water absorbed by the FCNTs in the composites, TGA was performed. The analysis was applied to dry specimens to identify if moisture had been absorbed by the foam composites after being mixed with FCNTs. Tests were performed at a 10°C/min heating ramp under nitrogen flow of 25 mL/min. The sample weight and temperature range were 20 mg and 40–1000°C. A plot of weight loss as a function of temperature for the pristine and the FCNT-reinforced composites is shown in Figure 3. Only one transition step is seen between 310 and 500°C for the pristine and the FCNT-reinforced composite processed at high vacuum, whereas two transitions are observed for the FCNT-reinforced composite processed at atmospheric pressure. The first transition between 101 and 310°C represents a complex process involving evaporation of water absorbed by the composite.[27] As shown in the TGA plots of FCNTs (Fig. 2s), FCNTs attract water after being chemically modified increasing the composite's affinity to moisture and thus the water content in the compound once in contact with the humid environment. Another factor that influences water absorption is the distribution of voids within the composite. Voids can be formed by agglomeration of FCNTs in the matrix and by other processing conditions. Defects created by FCNT aggregates in the matrix produce localized points of moisture uptake within the composites accelerating matrix decomposition. Processing, on the other hand, could cause imperfections in the composite, as seen in Figure 4. From this image, it is clear that defects are larger for the FCNT-reinforced composite processed at atmospheric pressure than at high vacuum. It is also apparent that some microballoons are exposed to the environment when the FCNT-reinforced composite is processed at atmospheric pressure. Therefore, higher moisture uptake and lower decomposition temperature are expected in the nonvacuum sample due to higher flaws in the material, as confirmed in the first step of the TGA curve (Fig. 3). The final transition after 310°C indicates degradation of the polymeric foam.

Moisture absorption curves as a function of time for the pristine and the FCNT-reinforced composites processed at different vacuum pressures are shown in Figure 5. The values, given in wt %, correspond to the measurements taken from the compression specimens. In general, moisture uptake is less that 1% for all composites fabricated. An obvious difference was noted by changing the pressure during processing; the FCNT-reinforced composite mixed at atmospheric pressure absorbs more water than the FCNT-reinforced composite mixed at high vacuum. This indicates that higher porosity within the structure (as seen in Fig. 4) allows water to diffuse more easily and accumulate in the pores of composites mixed at atmospheric pressure, which leads to morphological disruption and premature failure of the material.[10,28]

Hot/wet results showed a decrease of ∼ 60% in compressive strength and apparent shear strength compared with the same dry composites. This, as expected, is clear due to water ingression into the composite. Nevertheless, specimens tested after hot/wet conditioning exhibited similar behavior to that

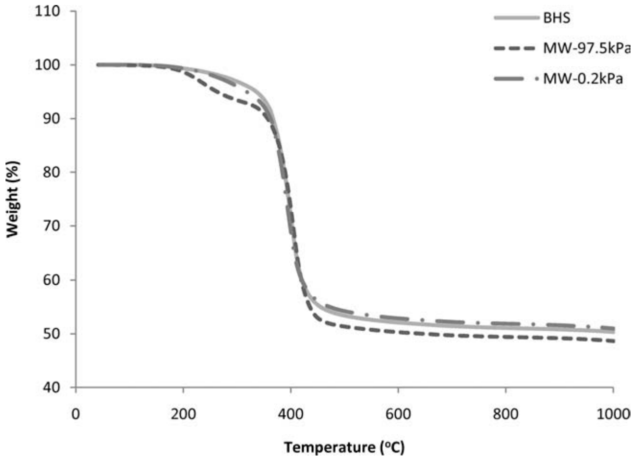

Figure 3 Thermogravimetric results for the FCNT-reinforced composites processed at different vacuum pressures.

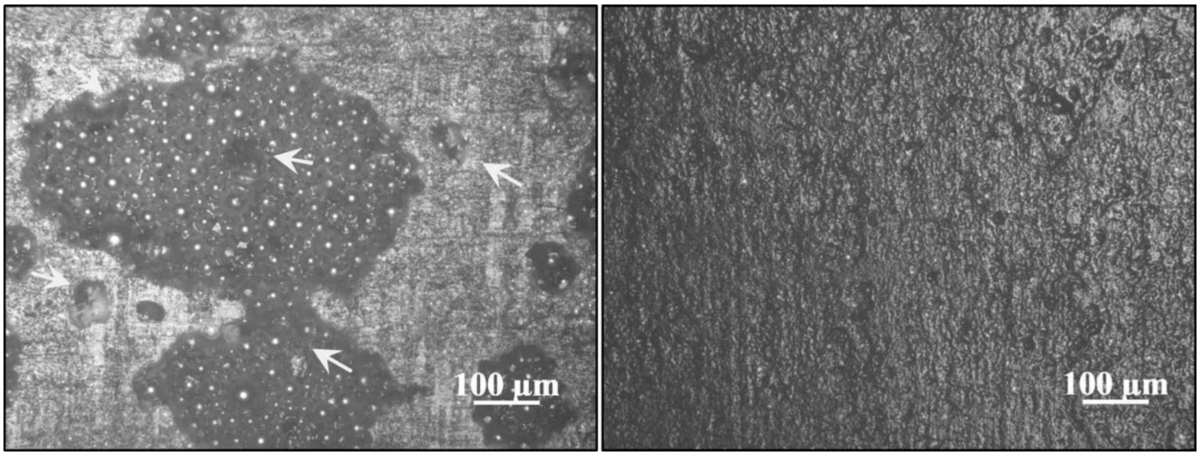

Figure 4 Effect of vacuum mixing on the FCNT-reinforced composites. Microscopic images at 100× show specimens mixed with vacuum (MW-0.2kPa) shown on right and without vacuum (MW-97.5 kPa) shown on left. Arrows indicate exposed microballoons and voids due to low resin impregnation.

observed for dry specimen; mechanical properties of specimen processed at high vacuum were higher than mechanical properties of specimen processed at atmospheric pressure, as shown in Figure 2. Compressive strength of the high-vacuum (MW-0.2kPa) composite increased by 46%, whereas apparent shear strength increased by 56% after hot/wet treatment in comparison to the pristine composite. On the contrary, a decrease of 25% and 60% in compressive strength and apparent shear strength, respectively, was observed for the no-vacuum (MW-97.5 kPa) composite with respect to the pristine composite. Therefore, compounds with significantly higher mechanical properties can be obtained by incorporating FCNTs into composites provided that high vacuum is applied during the manufacturing process.

Because the FCNT-reinforced composites processed at high vacuum yield the highest mechanical properties thus far, results discussed subsequently correspond to specimens prepared at high vacuum only. The FCNT-reinforced composites prepared at atmospheric pressure did not show any enhancement in properties compared with pristine compounds. Therefore, they will not be mentioned in the rest of the article.

Compressive strength is a critical property for applications in which honeycomb cores are used to fabricate sandwich composites. Results for compression tests of syntactic foams reinforced with FCNTs

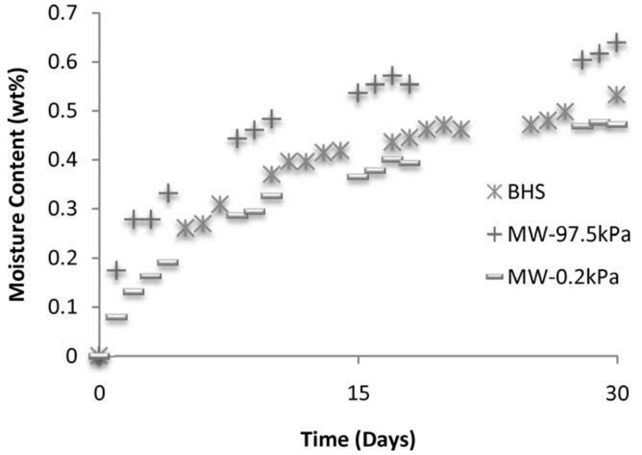

Figure 5 Moisture absorption of the pristine and the FCNT-reinforced composites subjected to hot/wet conditioning.

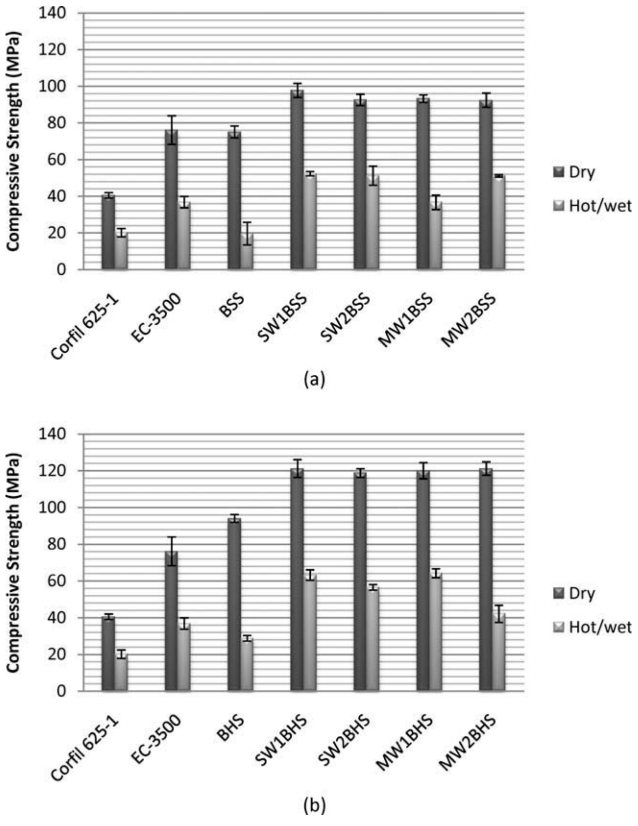

Figure 6 Compressive strength of reinforced syntactic foams with FCNTs and (a) BSS or (b) BHS.

TABLE VII
Glass Transition Temperature (T_g) for the FCNT-Reinforced Composites

Composite	T_g (°C)
BSS	**112**
SW1BSS	131
SW2BSS	122
MW1BSS	137
MW2BSS	124
BHS	**133**
SW1BHS	137
SW2BHS	120
MW1BHS	122
MW2BHS	121

Note: The boldface values correspond to the T_g of the pristine composites.

are shown in Figure 6. Also, values for two commercially available compounds, Corfil 625-1, EC-3500, are included in these figures for comparison. Generally, compression properties of nonreinforced syntactic foams are controlled by the type of microballoons used during synthesis. As observed in Figure 6, compounds with strength equivalent or superior to that of EC-3500 can be obtained by changing the concentration and type of microballoons (BSS and BHS) in agreement with findings observed by other investigators[29] regarding the mechanical properties of foam composites.

Addition of nanotubes has a remarkable effect on the compression properties of foam composites, as indicated in Figure 6. Significant enhancement in strength is observed compared with nonreinforced and commercially available compounds with an increase in density of 9%. A 20–60% increase in strength is shown when composites—BSS and BHS—are reinforced with FCNTs. As previously noted, this only occurs when the FCNT-reinforced composites are synthesized at high vacuum.

By reviewing the DMA results (Table VII), a considerable change in T_g is noticed for all composites fabricated with FCNTs. Addition of 0.5 wt % FCNTs in BSS caused T_g to increase to higher temperatures (~ 134°C), indicating a constraint of polymer molecular mobility caused by interaction with FCNTs. As suggested by Gunes et al.,[30] polar–polar interaction between polymer chains and CNTs can be stronger than nonpolar interaction. Accordingly, the increase in T_g and strength observed in this work for BSS composites reinforced with 0.5 wt % nanotubes could be attributed to polar interaction between carboxylic acid functional groups on the CNT surface and matrix. Although processing at high vacuum, a lower T_g was observed for compounds containing 1.5 wt % FCNTs. This could be due to poor distribution or agglomeration of nanotubes that weakens nanotube–matrix interaction and create plasticization effects.

It is well known that the properties of foam composites—particularly the mechanical properties—are affected by extreme humid environments.[10] As observed in Figure 6, compounds subjected to hot/wet treatment showed a decrease of ~ 50% in compressive strength with respect to those without conditioning. Nonetheless, results also showed a substantial improvement in strength for hot/wet specimens reinforced with FCNTs in comparison to nonreinforced and commercially available compounds exposed to the same treatment. An increase of 30–140% in strength was obtained by reinforcing composites with FCNTs compared with nonreinforced and EC-3500 compounds.

Lap shear strength is another property of interest for weight-sensitive applications in the aerospace industry. This represents the interfacial strength between core materials and adhesive/facesheets of sandwich laminates, which is equal to the polymer strength when no adhesive is used to bond the facesheet to the structure. The apparent shear strength results for the FCNT-reinforced composites, Corfil 625-1, and EC-3500 are provided in Figure 7. Strength values for composites subjected to hot/wet conditioning are also presented in this figure.

Similar to the compressive strength results, syntactic foams reinforced with FCNTs showed significant enhancement in apparent shear strength with respect

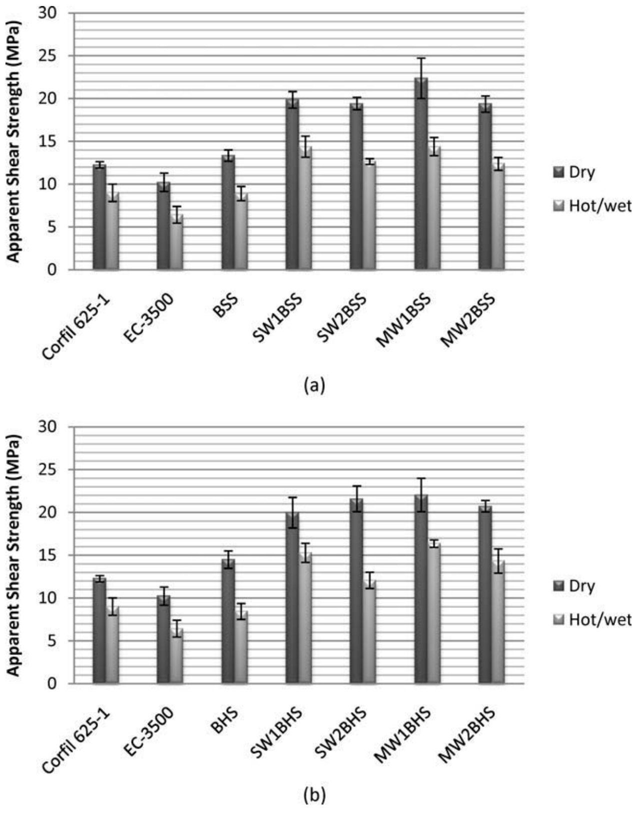

Figure 7 Apparent shear strength of reinforced syntactic foams with FCNTs and (a) BSS or (b) BHS.

to both pristine and commercially available compounds. Compared with nonreinforced composites (BSS and BHS), an increase of more than 38% in strength was achieved by adding 0.5 wt % FSWCNTs to BSS and BHS (SW1BSS and SW1BHS), whereas an increase of ∼ 47% was obtained by mixing 1.5 wt % FSWCNTs with the same pristine compounds (SW2BSS and SW2BHS). Likewise, addition of 0.5 wt % FMWCNTs to BSS and BHS (MW1BSS and MW1BHS) showed a 68% and 52% strength increase, whereas incorporation of 1.5 wt % FMWCNTs to pristine compounds (MW2BSS and MW2BHS) showed a 45% and 43% strength increase, respectively. Compared with EC-3500, a 100% increase in strength was observed for all the FCNT-reinforced composites.

After hot/wet conditioning, the apparent shear strength decreased by 30% with respect to the dry specimens. Results also indicated a behavior close to that observed for specimens tested under dry conditions. Hot/wet properties of FCNT composite increased provided that the sample was processed at

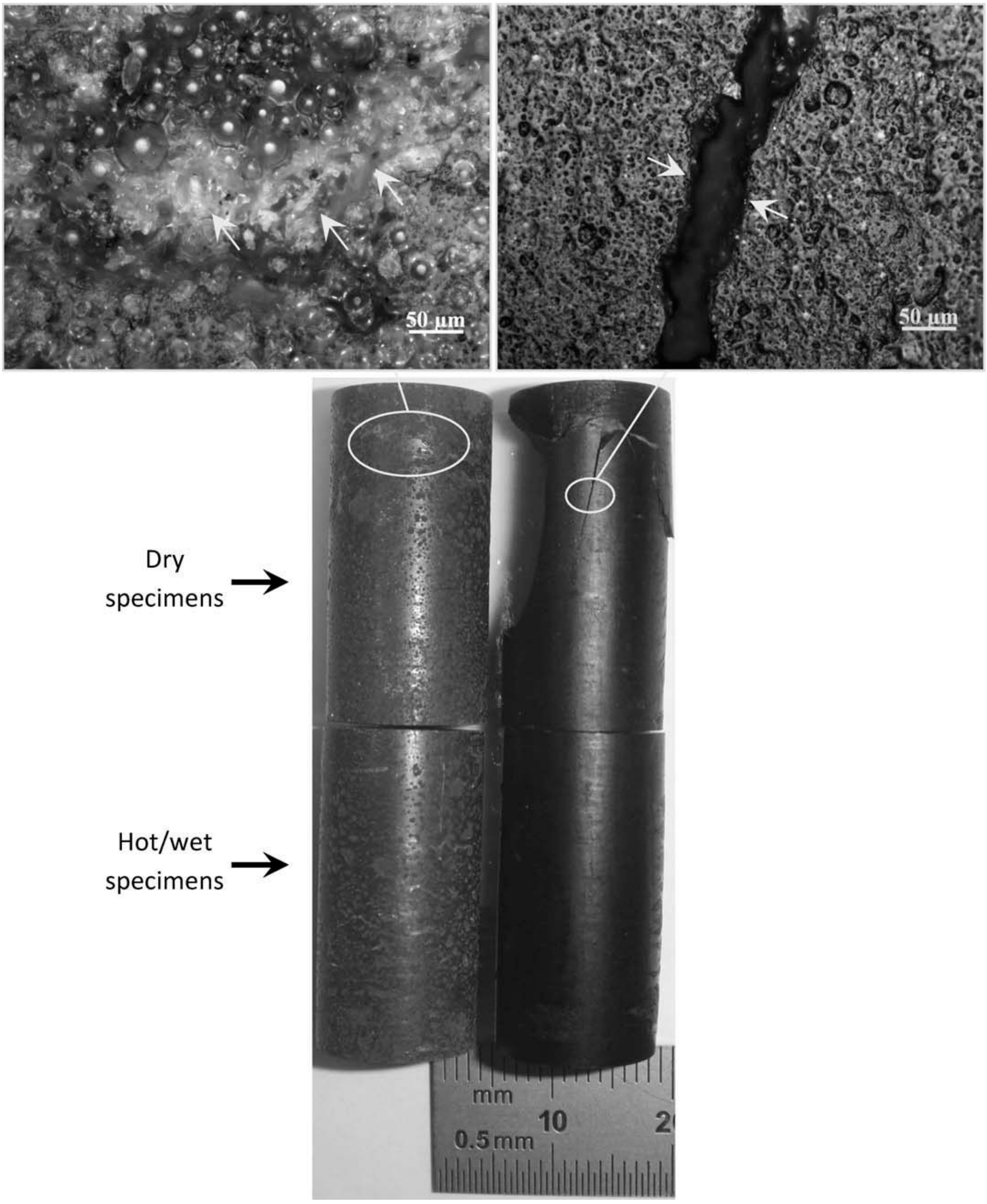

Figure 8 Failure mode of the FCNT-reinforced composites manufactured with vacuum (MW-0.2kPa) and without vacuum (97.5 kPa). Top specimens represent composites tested before hot/wet conditioning and bottom specimens correspond to those tested after hot/wet treatment. Macroscopic and microscopic images on the right show vertical cracking due to matrix failure, whereas those on the left indicate compressive failure due to microballoon crushing. Microscopic imaging was performed at 200×.

high vacuum. An increase of 40–150% in apparent shear strength was obtained for composites reinforced with FCNTs compared with pristine and EC-3500 compounds, respectively.

Interestingly, the highest performance observed corresponds to the MW1BSS specimen. This particular composite with a lower density (11% lower than FCNT composite with BHS) showed an apparent shear strength value similar to those obtained for composites with FCNTs and BHS. This suggests that low-density (635.77 kg/m^3) and low-strength composites (BSS) reinforced by FCNTs can achieve interfacial strength comparable to high-density (701.64 kg/m^3) and high-strength FCNT-reinforced composites. Further, it indicates that the applied load could be transferred from the matrix to the nanotubes, because the strength of the composite was increased without using microballoons of higher density and strength.

Because the load transfer mechanism from matrix to nanotubes is highly dependent on the nanoparticle aspect ratio,[19,31] it is presumed that SWCNTs would have better mechanical properties than MWCNTs when incorporated into polymer composites. However, the mechanical test results described herein showed that foam composites with FMWCNTs performed better than with FSWCNTs. A possible explanation for this behavior can be given due to nanotube dispersion in the matrix. As described in their work, Gojny et al.[19] suggested that dispersion of SWCNTs in polymer represents a challenge due to their high aspect ratio, indicating that composites with CNTs of two or more concentric tubes could exhibit higher mechanical properties than composites containing SWCNTs because of their lower aspect ratio and less pronounced nanotube agglomeration effect. In that context, it is believed that the poor dispersion of nanotubes in the matrix was the determinant factor for lower performance of foam composites with FSWCNTs. Furthermore, the high strength obtained with 0.5 wt % FMWCNTs in the composite implies that better dispersion quality and less nanotube aggregates—which act as imperfections and induce early composite failure during loading—were obtained with FMWCNTs than with FSWCNTs, justifying the superior performance achieved with FMWCNTs in apparent shear strength.

Failure analysis

The failure mechanism for the FCNT-reinforced composites under compression loading was determined from macroscopic and microscopic examinations of tested specimens (Fig. 8). A significant change in failure mode was observed with respect to the processing method used. The FCNT composite processed at high vacuum showed catastrophic failure after compressive loading, which could be caused by secondary stresses in the transverse direction.[32,33] This indicates matrix failure due to the brittle nature of the material after processing the FCNT-reinforced composite at high vacuum. The reinforced foam composite mixed at atmospheric pressure did not show failure due to vertical cracking, but instead showed compressive failure at the top/bottom of the specimen. This means that the microballoons were compressed after loading, thereby withstanding the load and preventing the catastrophic failure of the composite, as shown in the microscopic image of Figure 8. After hot/wet conditioning, macroscopic examination did not show signs of either matrix or compressive failure on the specimens' surface. This suggests that moisture has permeated the composites leading to their plasticization. Due to plasticization, the foam composites can compress without crack generation; hence, their morphology and their failure mechanism are modified.

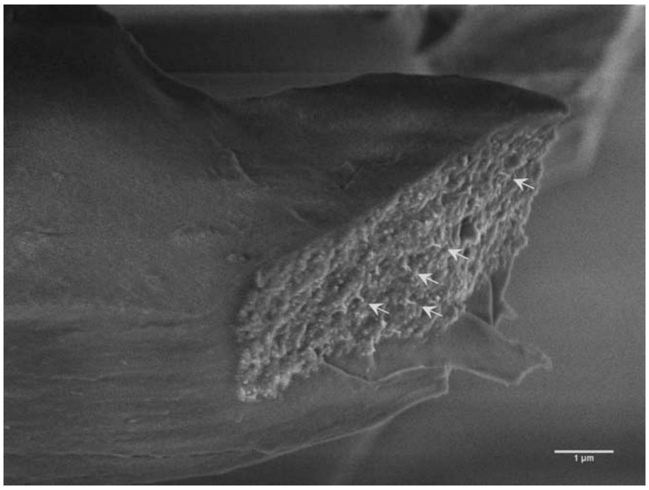

Figure 9 Fracture surface of syntactic foams reinforced with FMWCNTs. Arrows indicate how the FMWCNTs are pulled out of the matrix after matrix failure.

Further examination of the fracture surface at higher magnification was performed using field-emission scanning electron microscopy. Specimen was coated with gold because of inherently low conductivity. Figure 9 corresponds to the failure of the MW1BSS specimen after compressive loading. Even though it is difficult to characterize the dispersion quality from this image, it appears that the FMWCNTs are pulled out of the matrix after fracture, indicating the absence of covalent bonding with the polymer system. On the basis of the results observed by other authors, the carboxylic acid FCNTs could interact with the matrix through hydrogen bonding,[34] which is consistent with other findings.[30] Thus, it is suggested, according to this image and DMA results, that the enhancement in mechanical properties of the FCNT-reinforced composite could be attributed to hydrogen bonding between FCNTs and matrix.

CONCLUSIONS

A technique—comprising ultrasonic, calendering, and vacuum centrifugal mixing—was used to disperse FSWCNTs and FMWCNTs into two pristine syntactic foams (BSS and BHS). The fabricated FCNT-reinforced composites were characterized for compressive strength and lap shear strength before and after hot/wet conditioning. The results showed that the properties before and after conditioning depended on the vacuum pressure applied during processing: the strengths increased when the composites were mixed at high vacuum (0.2 kPa). Before hot/wet conditioning, an increase of 20–60% in compressive strength and 38–100% in apparent shear strength was observed for the FCNT-reinforced composites processed at high vacuum compared with the pristine and the EC-3500 compounds. After hot/wet treatment, an increase of 30–140% in compressive strength and 40–150% in apparent shear strength was observed for the same FCNT-reinforced composites (processed at high vacuum) in comparison to the pristine and the EC-3500 composites. It was also shown that the low-density (635.77 kg/m^3) and low-strength (BSS) composites can achieve apparent shear strengths similar to that of the high-density (701.64 kg/m^3) and high-strength (BHS) composites by adding FCNTs.

Macroscopic and microscopic examinations of the FCNT-reinforced composites showed different failure modes with respect to the vacuum pressure used during processing. Before hot/wet conditioning, the specimen mixed at high vacuum showed catastrophic fragmentation due to matrix failure, whereas the one mixed at atmospheric pressure showed signs of compressive failure attributed to microballoon crushing. No sign of either matrix or compressive failure on the specimen surface was identified after hot/wet treatment, indicating that moisture has permeated the composites leading to their plasticization. Furthermore, results indicate that porosity plays a critical part in the properties of syntactic foams reinforced with FCNTs. It is therefore essential to have control over voids when incorporating nanotubes into foam composites to achieve higher mechanical properties. In general, addition of FCNTs improved the properties of foam composites before and after hot/wet conditioning with an increase in density of 9% provided that the processing was performed under high vacuum, thereby making the reinforced composite a better core material for sandwich structures commonly used in the aerospace industry.

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