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Compressive behavior of cenosphere/epoxy syntactic foams in arctic conditions

Kiran Shahapurkar[a], Carlos D. Garcia[b], Mrityunjay Doddamani[a,*], G.C. Mohan Kumar[a], Pavana Prabhakar[c]

[a] Advanced Manufacturing Laboratory, Department of Mechanical Engineering, National Institute of Technology Karnataka, Surathkal, India
[b] Department of Mechanical Engineering, University of Texas at El Paso, El Paso, TX 79968, USA
[c] Department of Civil and Environmental Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA

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ABSTRACT

In this paper, the effects of arctic condition on the compressive response of ceno-sphere/epoxy syntactic foams are investigated. Understanding the behavior of such foams under extreme conditions is critical for exploring their suitability for constructing lightweight platforms used in arctic explorations, which are exposed to subzero temperatures for extended periods of time potentially degrading their mechanical properties. In the research study presented here, samples of cenosphere/epoxy syntactic foams were conditioned under arctic environment at a temperature of −60 °C for a period of 57 days. Compression tests were then conducted at room temperature as well as in-situ −60 °C on the conditioned samples and compared against unconditioned samples tested at room temperature. Combinations of surface modification and cenosphere volume fractions were considered. For the case of unconditioned samples, compressive strength decreased with increasing cenosphere volume fraction for both surface modified and unmodified cenospheres. For the arctic conditioned samples, cenospheres/epoxy foams did not present visible signs of degradation prior to testing, but manifested a reduction in compressive modulus in a range of 47–57% and 47–65% for untreated and treated cenospheres/epoxy syntactic foams as compared to their unconditioned counterparts. On the other hand, the compressive strength increased in a range between 32–68% for untreated and 59–80% for treated cenosphere foams in arctic environment, which can be attributed to the matrix hardening introduced by frigid in-situ environment. Also, under in-situ arctic compressive loading, the post peak response for all foam types have shifted from a progressive failure to a brittle type behavior.

1. Introduction

Sandwich composites have gained significant importance in recent years in the context of replacing conventional engineering materials for naval applications due to favorable properties such as lightweight and the ability to tailor mechanical properties. These sandwich composites typically consist of a lightweight core which is sandwiched between two fiber-reinforced laminated facesheets in order to provide the basis for a strong and stiff structure. Closed-cell low-density polymeric foams are targeted for naval crafts as they are ideal for such applications. Naval structural materials are typically exposed to critical conditions for extended periods of time, which can be detrimental to the mechanical properties. Few commonly experienced conditions are exposure to sea water, temperature changes in the water, wave impact, etc. Further, with increased interest in arctic exploration, these materials could be exposed to harsh conditions of the arctic region [1–5]. Therefore, it is of utmost importance to understand how such materials behave under these extreme conditions. The focus of the present work is on exploring the behavior of a foam core material, called syntactic foams, under arctic exposures.

Syntactic foams are closed cell composite foams, which consist of hollow microspheres dispersed in a matrix resin [6]. Given the advantage of syntactic foams over other materials due to their tailor made properties [6,7], these foams have been employed in distinct engineering structural applications like ribs, hulls and decks of ships for marine exploration. Researchers in recent past have investigated the behavior of syntactic foams with engineering glass microballons as the filler material [8–10]. Sodalime-borosilicate glass is a major constituent of these engineered glass particles. However, it has been shown that the degradation of such syntactic foams is due to dealkalization of glass [11]. In the present study, cenospheres are used as filler material in the foams. These are hollow particles of fly ash, which are an industrial

* Corresponding author.
E-mail address: mrdoddamani@nitk.edu.in (M. Doddamani).

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waste material and a potential environmental pollutant. Fly ash is a by-product of coal plants and is primarily comprised of alumina and silica. Use of cenospheres in syntactic foams can help the environment by minimizing waste, while creating foams with better properties [12–17].

Extensive studies have been performed in the past exploring their suitability for a wide range of applications [8,18–21]. For example, in the work presented by Gupta, Woldesenbet and Mensah [22], it was shown that the compressive strength and modulus of syntactic foams increased with reducing internal radius of cenospheres while keeping all other parameters at the same level. The relationship that exists between the fillers and matrix is rather complex and can pose issues while exploring the possibilities in tailor making the mechanical properties of syntactic foams. Thereby, different types of tests have been performed on syntactic foams, such as three-point bending tests in either flexural [23–26] or short beam shear tests [27–29] in order to determine their response under such types of loading. Other studies have been performed for capturing the response of syntactic foams under compressive [30–35], hygrothermal [36–38] and impact loading [39] as well. In many of these studies, only the effect of varying the filler content on the mechanical properties is reported. Other aspects such as particle wall thickness variations, interfacial bonding and the porosity of the walls of the hollow spheres in cenosphere/epoxy foams makes it challenging to establish structure-property correlations. Furthermore, studies have been performed in order to help reduce the time and effort that it takes to characterize the material behavior. In works presented by Zeltmann et al. [40,41], methods to predict strain rate sensitivity in the modulus of polymers and polymer matrix composites was developed using dynamic mechanical analysis data. The methods allowed obtaining the modulus of the specimen for various strain rates.

In many experimental investigations, it was observed that the mechanical properties are affected by water absorption by the syntactic foams [25,36,38,42]. A majority of these studies along with previously mentioned studies were carried out under room temperature conditions. In the case of marine vessels for Arctic or Antarctic exploration, understanding the behavior of syntactic foams at subzero temperatures is very important and crucial. Nevertheless, there is no literature that discusses the effect of arctic environment on the compressive properties of cenosphere/epoxy foams. The present study explores this case by investigating the change in compressive properties of syntactic foams due to change in external temperatures. Cenosphere materials, matrix resin, surface modification of filler and volume fractions are maintained between syntactic foams at room and arctic temperatures. Changes in the compressive response, failure and fracture patterns can be attributed to the operating temperature. The novelty of the present study include: (a) use of industrial waste fly ash cenospheres for developing eco-friendly syntactic foams and (b) structure-property correlations under arctic conditions. This paper is organized in the following sections: Section 2 presents a description of the material constituents, manufacturing process of the samples, the process to expose the samples to arctic environment and the procedure for compressive testing. This is followed by Section 3, where the results from material processing and compression tests with and without arctic exposure of cenosphere/epoxy foams are presented. Finally, the conclusions of this study are reported.

2. Materials and methods

2.1. Constituents

Fly ash cenospheres of CIL 150 grade used as filler are procured from Cenosphere India Ltd., Kolkata, West Bengal, India. Table 1 presents the physical, chemical and sieve analysis details in as received condition. Cenospheres primarily comprise of alumina, silica, calcium oxide and iron oxides as observed from this table. Lapox L-12 epoxy resin with K-6 hardener, supplied by Atul, Valsad, Gujarat, India is the matrix resin used. Syntactic foams are prepared with two configurations: 1) with as received cenospheres and 2) surface modified cenospheres. Silane coating on cenospheres is carried out using 3-Amino propyl triethoxy silane (APTS), procured from Sigma Aldrich, Bangalore, India. A minimum of five specimens are tested in compression under room temperature and in arctic conditions.

Table 1
Physical, chemical and sieve analysis details of cenospheres.[a]

Physical properties		Chemical analysis		Sieve analysis	
True particle density	920 kg/m^3	SiO_2	52-62%	+30# (500 μm)	Nil
Bulk density	400–450 kg/m^3	Al_2O_3	32-36%	+60# (250 μm)	Nil
Hardness (MOH)	5–6	CaO	0.1–0.5%	+100# (150 μm)	Nil
Compressive strength	180–280 kg/m^3	Fe_2O_3	1-3%	+150# (106 μm)	0-6%
Shape	Spherical	TiO_2	0.8–1.3%	+240# (63 μm)	70-95%
Packing factor	60-65%	MgO	1–2.5%	- 240#	0-30%
Wall thickness	5-10% of shell dia.	Na_2O	0.2–0.6%		
Color	Light grey – light buff	K_2O	1.2–3.2%		
Melting point	1200–1300 °C	CO_2	70%		
pH in water	6–7	N_2	30%		
Moisture	0.5% max.				
Loss on ignition	2% max.				
Sinkers	5% max.				
Oil absorption	16–18 g/100g				

[a] As specified by supplier.

2.2. Surface modification of cenospheres

In syntactic foams, the volume fraction and size of cenospheres can alter the overall mechanical properties. Apart from the volume fraction and size, the interaction between cenospheres and epoxy plays a major role in load transfer mechanism between the constituents [43]. Mechanical properties of cenosphere reinforced polymer composites are inferior owing to poor interfacial interactions between the hydrophilic cenosphere surface and hydrophobic polymer. Silane coupling agents are usually used as adhesion promoters between inorganic filler and organic matrix. In the present work, cenospheres are surface treated with silane by mixing 50 g of cenospheres into 100 ml solution of water/ethanol (20:80 wt %). Further, 2% by volume of APTS is added into the solution and continuously stirred for 30 min at 80 °C in a microwave reactor (Enerzi microwave systems, Bangalore, India). The resultant product is filtered, washed at least three times using a mix of water/ethanol and then dried in an oven to extract the coated cenospheres.

2.3. FTIR, XRD and particle size analysis

Cenospheres are analyzed by FTIR spectroscopy (JASCO 4200, Japan, Automated Total Reflection mode, wave number 4000 to 650 cm^{-1}) to confirm the silane coating. X-ray diffractograms are determined for 2Θ values using DX GE-2P, JEOL, Japan having Nickel filter material with scanning speed of 2°/min and Cu Kα (λ = 1.514A°) radiation. Particle size and shape analysis is conducted using a Sympatec (Pennington, NJ) QICPIC high speed image analysis system [44,45].

2.4. Sample preparation

Syntactic foams are fabricated by mixing desired volume fraction of cenospheres with Lapox L-12 epoxy resin and K-6 hardener at room temperature. The mixture is gently stirred to obtain a homogeneous and

uniform slurry, followed by adding 10 wt % hardener and finally degassing the mixture for 4 min prior to casting in aluminum molds. The cast slabs are cured at room temperature for 24 h and post cured at 90 °C for 3 h. Three different syntactic foams with varying cenosphere volume fraction of 20, 40 and 60 vol% in epoxy matrix are fabricated. This procedure is adopted for both as received and silane treated cenospheres. Additionally, neat resin specimens, i.e., without any filler in the matrix, are also prepared for comparison. Samples are named according to the convention EXX-Y, where E denotes epoxy resin, XX is the volume fraction of cenospheres and Y represents filler modification condition (U denotes untreated and T represents treated cenospheres). Cast slabs are trimmed using diamond saw cutter to confirm the dimensions as mentioned in ASTM D695 (compression). The densities of all the samples are measured using the procedure as outlined in ASTM D792-08. Theoretical density is computed using rule of mixture and is given by,

$$\rho_c = \rho_f V_f + \rho_m V_m \quad (1)$$

where, ρ and V are density and volume fraction, respectively. Subscripts *c*, *f* and *m* denote composite, filler and matrix, respectively. Furthermore, the void content (ϕ_V) is estimated using theoretical (ρ^{th}) and experimental (ρ^{exp}) densities and is given by Refs. [22,24],

$$\phi_V = \frac{\rho^{th} - \rho^{exp}}{\rho^{th}} \quad (2)$$

2.5. Arctic conditioning

There is no standard for arctic exposure studies to the best knowledge of the authors. Therefore, a procedure for specimen conditioning is developed in-house, which is similar to the initial conditioning for water intake measurements as mentioned in ASTM C272 and D5229 standards. Prior to any type of conditioning and testing, the syntactic foams are oven dried for 24 h to eliminate moisture content absorbed during processing, if any. Further, five samples for each volume fraction for both untreated and treated categories are placed in a freezer, which is maintained at −60 °C. All specimens are then conditioned for 57 days, after which the specimens are mechanically tested under in-situ arctic conditions (−60 °C). The procedure followed to obtain the mechanical properties for the syntactic foam samples is discussed in the following section.

2.6. Compression tests

All the specimens are mechanically tested in compression at room (30 °C) and arctic temperatures (−60 °C) using Instron 5969 Tabletop Universal Testing system. A crosshead displacement rate of 1.3 mm/min is applied on 12.7 × 12.7 mm face of each specimen following the ASTM D695 standard. Compressive modulus and ultimate strength are calculated using the following equations:

$$E_z^c = \frac{(P_{0.00x2} - P_{0.00x1})h}{(\delta_{0.00x2} - P_{0.00x1})A}; \quad F_z^c = \frac{P_{max}}{A} \quad (3)$$

where, E_z^c is the compressive modulus, $P_{0.00x}$ is the applied force at a given deflection, h is the specimen mean height, $\delta_{0.00x}$ is the recorded deflection value, A is the cross-sectional area, F_z^c is the ultimate compressive strength and P_{max} is the ultimate force prior to failure.

3. Results and discussions

3.1. Fabrication and material processing

Fly ash cenospheres used in the present study are used in as received (untreated) and silane modified (treated) conditions. FTIR results for untreated and silane treated cenospheres are presented in Fig. 1a. The spectrum confirms the presence of a silane surface layer and the –C–H– stretching of propyl group is observed at 2929 cm^{-1}. XRD diffraction results of as received and silane modified cenospheres is exhibited in Fig. 1b. Untreated and treated fly ash cenospheres has a main peak at 2θ value of 26.6 and 26.04 and other numerous small peaks manifesting mainly metal oxides, predominantly SiO_2 and $3Al_2O_3$ respectively.

Fig. 2 presents micrographs of untreated and treated cenospheres respectively. The coating layer is not visibly identifiable in the micrographs due to its small thickness, despite, FTIR results confirm the silane presence on cenospheres. Surface morphology is not uniform for fly ash cenospheres due to variations in sphericity and presence of numerous defects as seen from these micrographs. One such broken cenospheres is micrographed at higher magnification and is presented in Fig. 2c. Porosity in the cenosphere walls and irregular wall thickness is clearly evident from the micrograph, which might lead to lower mechanical properties as compared to non-porous ones. Such variations lead to deviation of the experimental investigation from that predicted by empirical and/or mathematical models.

Untreated and treated cenospheres are subjected to particle size analysis and the results are presented in Fig. 3. It can be observed that the volume weighted mean particle size for untreated and treated particles are 99.5 and 110.2 μm respectively. Broader peak is seen in case of treated particles. Untreated and treated cenospheres registered X_{50} median particle sizes of 76.3 and 98.1 μm, respectively confirming an increase in average diameter owing to silane treatment. Densities of as received and treated cenospheres are measured to be 0.92 and 1.0 g/cc. Sphericity of cenospheres is observed to be in the range of 0.6–0.85 [44]. Deviation from '1', a perfectly spherical particle, might be due to surface defects as observed in Fig. 2a. Shift in the curve of treated particles in the plot (Fig. 3) can also be attributed to particle coating. From Fig. 3, considerable extension is seen at the tail end of the curve for the treated particle indicating a small amount of cluster formation. Shear forces induced during manual stirring is expected to disperse some of these clusters formed, if any.

Synthesizing syntactic foam composites with uniform dispersion of cenospheres, minimum cluster formation and particle failure in the matrix during processing is a challenging task. Manual stirring approach is used in the present work to prepare cenosphere/epoxy foams. Micrographs of as cast cenospheres/epoxy foams are presented in Fig. 4. Uniform dispersion of hollow cenospheres both, untreated and treated in the matrix is observed in Fig. 4a–b demonstrating the feasibility of using manual stirring for developing such syntactic foam composites. Further, clusters are not seen to be formed for the foams with treated cenospheres (Fig. 4b) as anticipated from Fig. 3. Clusters are expected to be broken effectively due to shear forces induced due to stirring of the cenospheres/epoxy slurry as mentioned earlier. Interfacial adhesion between the epoxy resin and the as received cenospheres is seen to be poor as seen in Fig. 4c. Silane modification of cenospheres shows good adhesion between the constituents (Fig. 4d). Improvement in the interfacial bonding is expected to improve the load transfer from the matrix to the particle and improve the properties of syntactic foams. Load transfer between filler and the matrix along with failure mechanism are governed by interface topology. Flexural and tensile properties are strongly affected by the interfacial bonding strength [44–47] as interfacial cracks tend to form under such conditions. However, in compression, the mechanical properties are less sensitive to interfacial adhesion [48,49]. Nevertheless, non-uniform layer of coating makes comparison of mechanical properties to be a challenging [24], and is beyond the scope of the present work.

Quality and the mechanical properties of the syntactic foam samples depend on the survival of the hollow cenospheres and the void content due to entrapped air during processing. Thereby, it's necessary to quantify and correlate these parameters with the properties being investigated. Table 2 presents density and void content estimations. Theoretical densities are computed using Equation (1), which are higher compared to experimental ones as seen from Table 2. Reduction in the density of composites determined experimentally as compared to

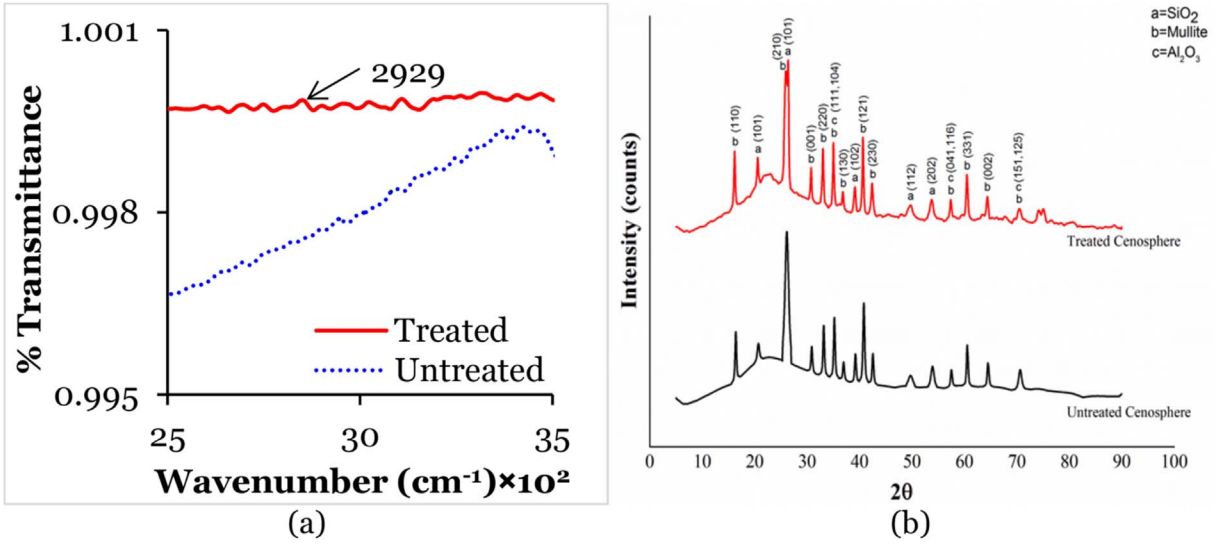

Fig. 1. (a) A section of the FTIR spectra of untreated and silane treated cenospheres [44] and (b) X-ray difftractogram of cenospheres.

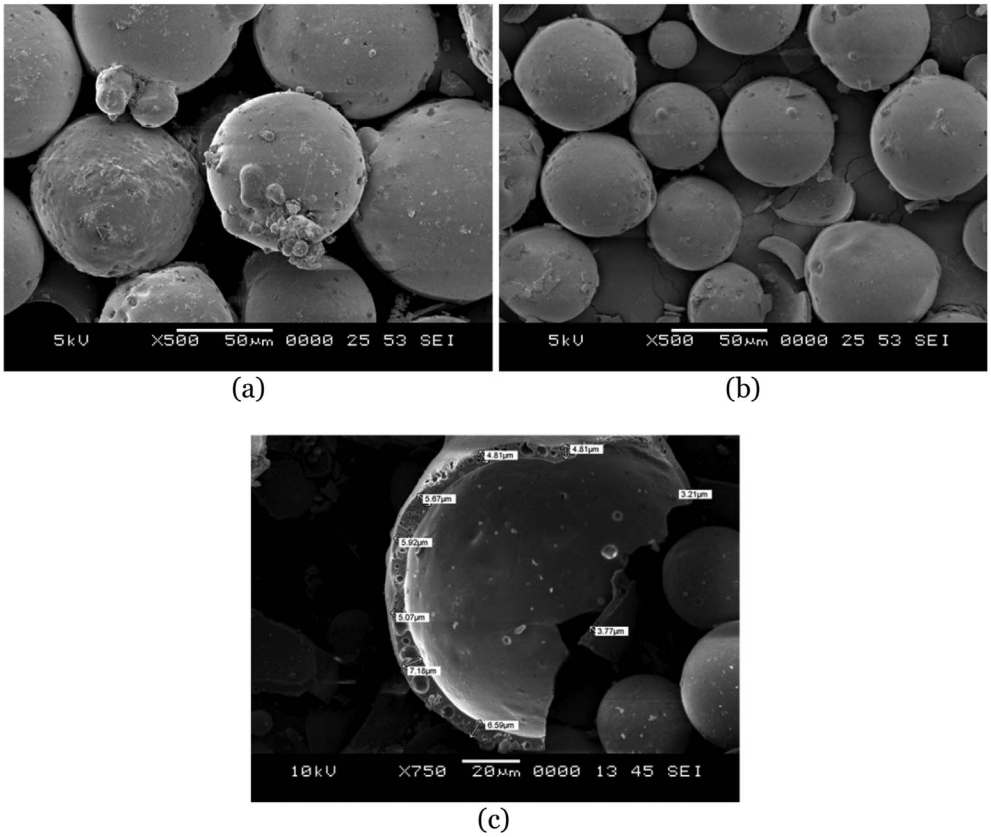

Fig. 2. Cenosphere micrographs of (a) untreated (b) treated and (c) one such broken treated particle.Wall thickness variations and built-in porosity in fly ash cenospheres are clearly evident from the micrograph.

the theoretical ones is attributed to the air entrapment in matrix during the process of mechanical mixing of cenospheres in the resin. The presence of very few entrapped air pockets is observed in representative samples as presented in Fig. 4a–b, which are characteristic of typical syntactic foams. Such entrapped air is undesired as it adversely affects the mechanical properties and is referred as voids. The void content (Φ_v) is calculated using Equation (2). As seen from Table 2, the void content appears to increase with increase in filler content except at highest filler loading. The presence of such voids further reduces the matrix content. The amount of matrix present at 60 vol % filler loading is much lesser compared to other compositions resulting in much lower void content. Density of foams with treated cenospheres registered higher density values for all the compositions prepared. Silane coating on as received cenospheres increases the effective mean diameter, thereby increasing their density. Narrow variations in standard deviations are observed affirming consistency in specimen processing. Further, weight saving potential is estimated as compared to neat epoxy samples, and values are listed in Table 2. Lower densities of syntactic foams with untreated cenospheres noted to have better weight saving. Specific mechanical properties are worth investigating for exploiting these lightweight cenosphere/epoxy foams in naval applications. It would be an interesting task to understand and analyze the effect of arctic environment on such abundantly available untreated/treated hollow fly ash cenospheres to propose suitable applications.

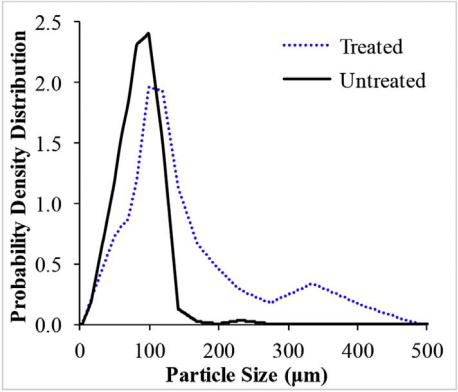

Fig. 3. Particle size analysis of untreated and treated cenospheres [44,45].

3.2. Compressive modulus and strength

Fig. 5 presents representative compressive stress–strain curves for all types of cenosphere/epoxy syntactic foams including neat epoxy samples prepared. The unconditioned (dry) neat resin and the syntactic foams show similar stress–strain profiles until peak stress, which consists of a linear elastic region followed by a strain softening region that is characterized by a drop in stress carrying capacity. Upon further loading the specimens in compression, the stress starts rising again in neat epoxy samples upto around 15% strain value after which it starts to drop until final fracture. The post peak increase in stress is faster and significantly higher in the case of neat resin, whereas for syntactic foams it depends on the volume fraction and surface modification of hollow fillers. In both treated and untreated syntactic foams, the strain at final fracture decreases with increasing cenosphere volume fraction.

For the case of arctic exposed samples, both treated and untreated cenospheres/epoxy foams demonstrated a brittle behavior. Upon reaching a maximum load carrying capacity, a slight decrease in stress is observed before complete failure of the samples. The compression rate is held constant in this experimental study at the ASTM standard recommended value, as the stress–strain behavior can potentially be a strain rate dependent phenomena [50,51]. In Fig. 5, it can be noted that all syntactic foam compositions do not show a stress plateau, which is seen as a typical feature for most types of syntactic foams, including epoxy and aluminum matrix syntactic foams [52,53]. In case of epoxy syntactic foams with relatively brittle microballoons, once the maximum load carrying is reached, the stress value decreases without much deformation till the final fracture [54]. Further, lower temperatures induce behavioral changes in the matrix making them more stiff and strong. In the presence of stiffer cenospheres, such an effect of matrix hardening when exposed to arctic conditions affects plateau stress to a greater extent [55,56]. In the current study, the syntactic foams tested under in-situ arctic conditions failed catastrophically after reaching the maximum compressive stress value. Therefore, the samples were not subject to further compressive loading beyond this point.

Compressive modulus is determined as the slope of the initial linear region of the stress–strain response and is presented in Fig. 6a–b. It is observed that compressive modulus increases with increasing filler content, for both untreated and treated fillers. Significant rise is observed for EXX-T foams with higher filler content. Also, the compressive modulus values are significantly higher in syntactic foams as compared to that of the neat resin. Further, the specific moduli (modulus divided by the foam density) for EXX-T composites are 26–81% higher than the neat resin as exhibited in Fig. 6b. Significant advantage over the neat resin in terms of weight saving can be achieved if EXX-T foams are used in compressive loading conditions. Compressive strength is defined as

Table 2
Density and void volume fraction of syntactic foams.

Material	ρ^{th} (kg/m^3)	ρ^{exp} (kg/m^3)	Φ_V (%)	Weight saving potential (%) compared to 'E'
E	–	1192.00 ± 23.84	0.34	–
E20-U	1137.60	1129.63 ± 22.59	0.70	5.23
E40-U	1083.20	1064.72 ± 21.29	1.71	10.68
E60-U	1028.80	1028.36 ± 20.56	0.05	13.73
E20-T	1153.60	1133.14 ± 22.66	1.78	4.94
E40-T	1115.20	1073.92 ± 21.47	3.70	9.91
E60-T	1076.80	1055.65 ± 21.11	1.98	11.44

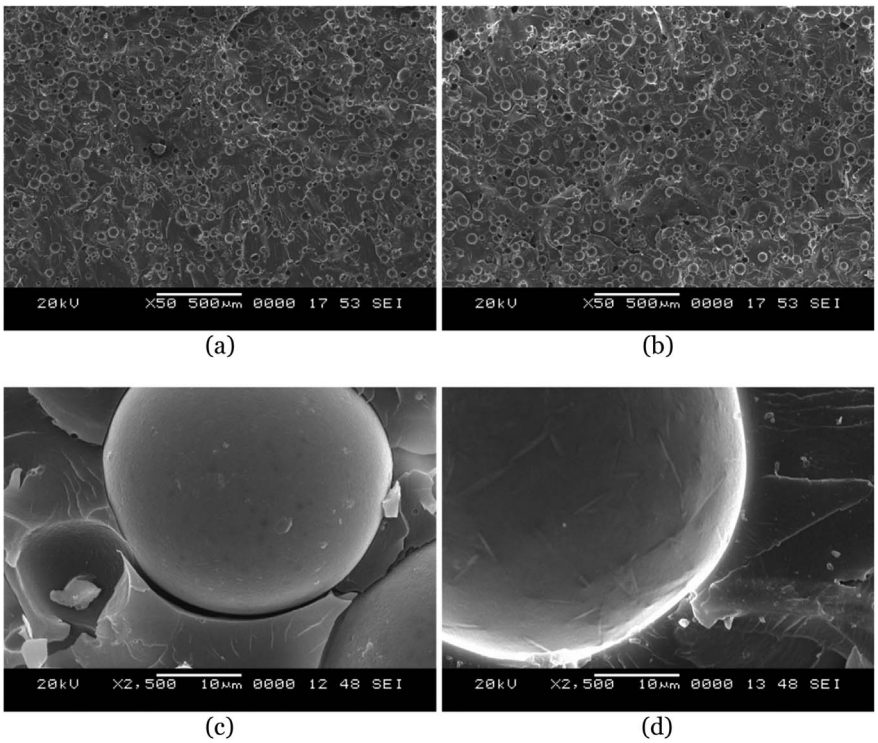

Fig. 4. Micrograph of as cast(a) E20-U (b) E20-T foams showing uniform dispersion of cenospheres. Lack of bonding for E20-U is seen in (c) while good interfacial bonding is evident from (d) due to silane treatment in E20-T.

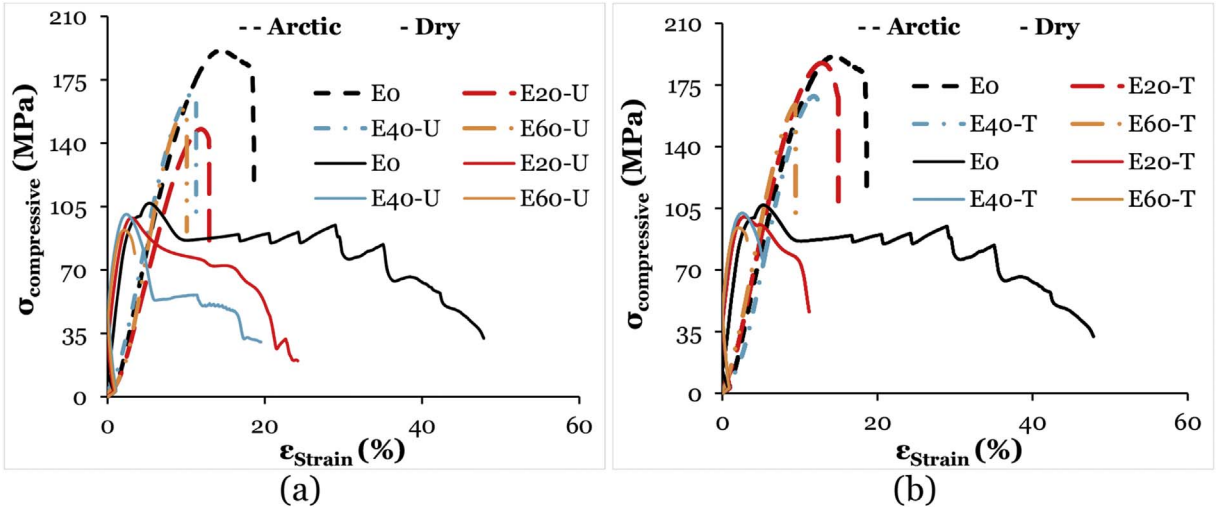

Fig. 5. Representative stress–strain curves obtained in compressive testing of syntactic foams containing 20, 40 and 60 vol % (a) untreated and (b) treated cenospheres.

the first peak in the stress–strain response. Fig. 6c–d shows the compressive strength values, where it is observed that an increase cenosphere volume fraction in both EXX-U and EXX-T configurations decreases compressive strength value. Compressive strength values of all the foams tested are lower compared to neat epoxy samples. Nevertheless, results for specific compressive strengths (compressive

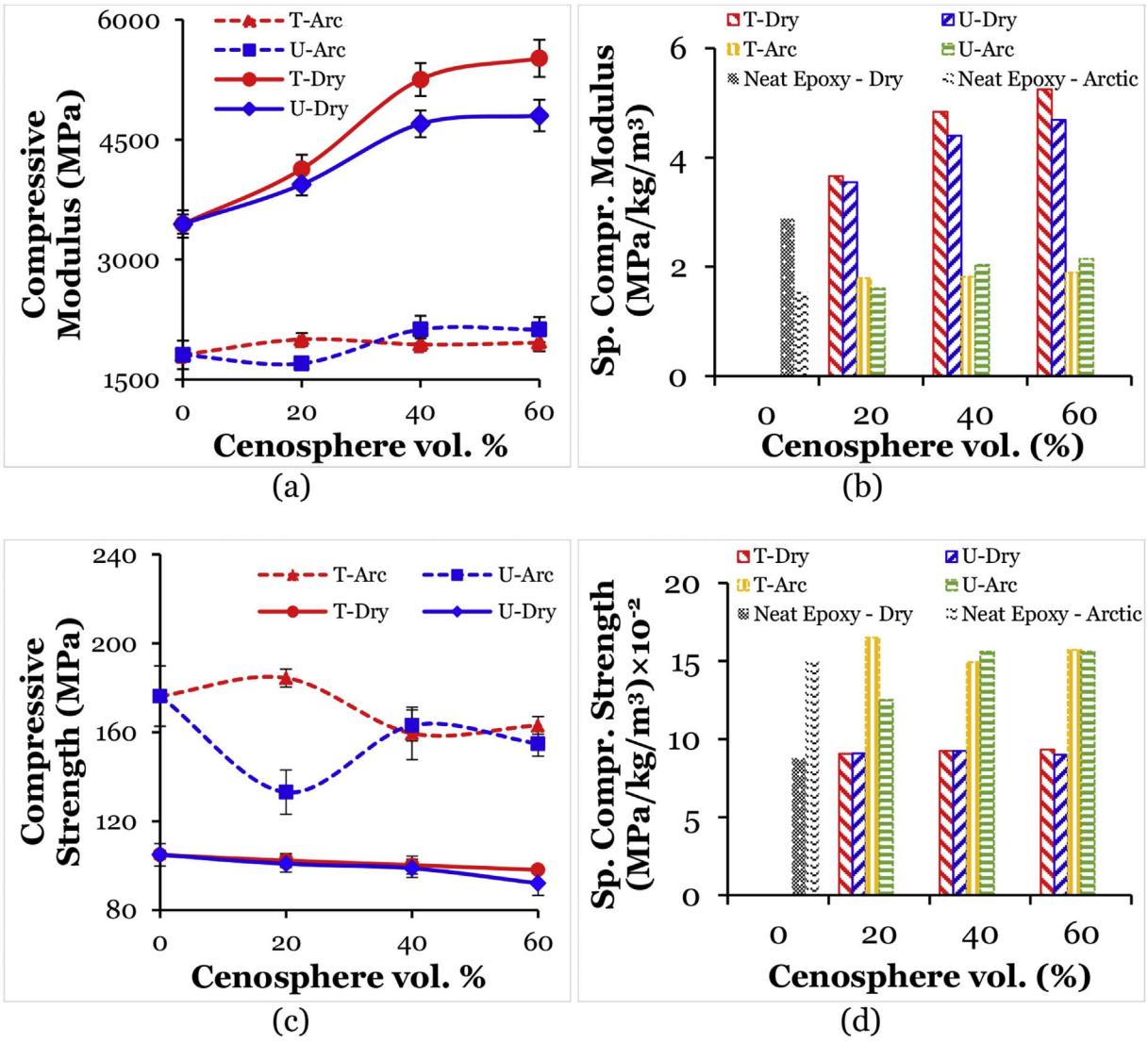

Fig. 6. Experimentally measured compressive (a) modulus (b) specific modulus (c) strength and (d) specific strength of syntactic foams.

Table 3
Modulus and Strength properties of syntactic foams.

Material	Compressive (MPa)			
	30 °C		−60 °C	
	Modulus	Strength	Modulus	Strength
E	3443.46 ± 119.78	104.88 ± 2.01	1807.48 ± 179.13	176.26 ± 13.-57
E20-U	3939.28 ± 137.03	100.79 ± 3.79	1701.09 ± 50.92	133.01 ± 9.98
E40-U	4697.47 ± 165.68	98.79 ± 4.1	2125.45 ± 171.09	163.03 ± 6.96
E60-U	4800.71 ± 197.21	92.06 ± 5.53	2124.40 ± 156.44	154.87 ± 5.67
E20-T	4132.08 ± 179.78	102.29 ± 3.14	2001.20 ± 80.54	184.41 ± 4.01
E40-T	5253.51 ± 206.85	100.26 ± 4.03	1937.16 ± 76.13	159.48 ± 11.-82
E60-T	5518.09 ± 231.88	98.11 ± 0.62	1959.14 ± 107.00	163.10 ± 3.91

strength divided by density) for all the foam compositions are comparable or marginally higher than that of the neat resin.

For the arctic conditioned samples, both treated and untreated cenospheres/epoxy foams manifest a brittle behavior in their stress-strain response. By comparing the arctic conditioned samples to the unconditioned (dry) samples, a decrease in compressive modulus of elasticity by 47–57% and 47–65% is observed for untreated and treated cenosphere/epoxy foams as observed from Table 3. On the other hand, the compressive strength value increased by a range between 32–68% for untreated cenospheres and 59–80% for treated cenospheres. Exposure to arctic condition increases the strength due to the matrix hardening [54,55]. Lower temperatures induce a change in matrix strength and stiffness making them more stiff and strong as they are cooled [55]. Pre-conditioning of samples to arctic temperature appears to have degraded the foams due to cyclic change in temperature, thereby, causing a reduction in the compressive modulus. However, in-situ arctic condition introduced more strength into the syntactic foams due to matrix hardening. On the other hand, hygrothermal studies on syntactic foams by Gupta and Woldesenbet [36] reveal considerable decrease in modulus without significant change in the compressive strength at lower temperature owing to plasticization resulting from moisture infusion.

Fracture features of neat epoxy and syntactic foams with two volume fractions of cenospheres are compared in Fig. 7. Prominent shear crack and excessive plastic deformation marks are observed in neat epoxy sample (Fig. 7a). Syntactic foams containing 20 vol% cenospheres deform with fewer cracks than those containing 60 vol% ones for EXX-U and EXX-T configurations. The failure features of these specimens are similar to those observed in the work presented by Gupta et al. [30]. Shear cracks forms and propagates with fragment formation from the sidewalls. Brittleness of the foams increases at higher filler loadings due to inclusion of relatively brittle cenospheres in epoxy matrix. At E60, excessive crushing of constituents and specimen cracking are observed for foams with untreated and treated cenospheres respectively as seen from Fig. 7b–e. In addition, the stress–strain curves of unconditioned EXX-T type syntactic foams show lower fracture strain values compared to unconditioned EXX-U. Relatively higher brittleness owing to silane coating on cenospheres increases overall brittleness of composite foams reducing the fracture strain for EXX-T. Nevertheless, in the case of coated cenospheres, mean particle diameter appears to influence the higher stiffness of the composites resulting in earlier crack initiation in the direction of compression. This might lead to formation of relatively larger fragments in EXX-T. Such situations are preferred while designing core for sandwich structures. In case of arctic exposed samples, fracture strain values are similar between EXX-T and EXX-U type syntactic foams.

Fracture surfaces of representative syntactic foams are shown in Fig. 8 and Fig. 9, where extensive cenosphere damage is observed during compressive fracture of the EXX-U material. Such extensive fracture of brittle reinforcing media, similar to microballoons, has also been observed in epoxy matrix syntactic foams [31]. On the other hand, EXX-T foams manifest lesser cenosphere damage in combination with matrix damage at both lower and higher cenosphere volume fractions. This shift in failure mechanism is an indication of effective transfer of stresses between cenospheres and the matrix, which is attributed to good interfacial bonding between the constituents due to silane treatment. Though the interfacial strength has not been explicitly measured at the microscale for these samples, the existence of silane coating has been determined through FTIR as shown in Fig. 1a. At E60-T, majority of the cenospheres are partially fractured retaining their original locations resulting in higher strength values compared to E60-U foam. Though the compressive strength shows decreasing trend with increasing filler content, specific values are comparable or marginally better than the neat resin counterparts. Such situations are highly desirable in structural components used in marine applications.

4. Conclusions

Compressive properties of untreated and treated cenosphere/epoxy foams under room and arctic temperatures are analyzed in the present work. It is observed that the cenosphere/epoxy foams with untreated and treated fillers manifest lower strains to failure under compressive loading at room temperature conditions as compared to neat epoxy samples. All foam compositions show an increase in compressive modulus compared to that of the neat resin. The results show that epoxy matrix syntactic foams with treated cenospheres have promise for structural application at room temperatures. Significantly higher specific compressive moduli and marginally higher specific strength make treated cenosphere/epoxy (EXX-T) foams a viable material for marine applications.

Further, these foams were subjected to compressive loading at −60 °C to explore the feasibility of using them in arctic environment. Similar to room temperature tested samples, all cenosphere/epoxy foams with treated and untreated fillers exposed to arctic conditions demonstrated lower failure strains compared to neat epoxy, but also compared to its unconditioned counterpart. It was observed that for the compression specimens, the modulus of elasticity decreased for arctic specimens compared to the unconditioned (dry) specimens. However, an overall increase in compressive strength was observed when tested under in-situ arctic condition. After examining the behavior of all samples, it was observed that the conditioning of specimens under extreme low temperatures caused the material to reduce their compressive modulus. Also, the syntactic foams behaved in a brittle manner causing drastic failure under in-stiu compression testing. This can represent a challenge when using this type of foams since no signs of deterioration/damage can be observed before failure occurs.

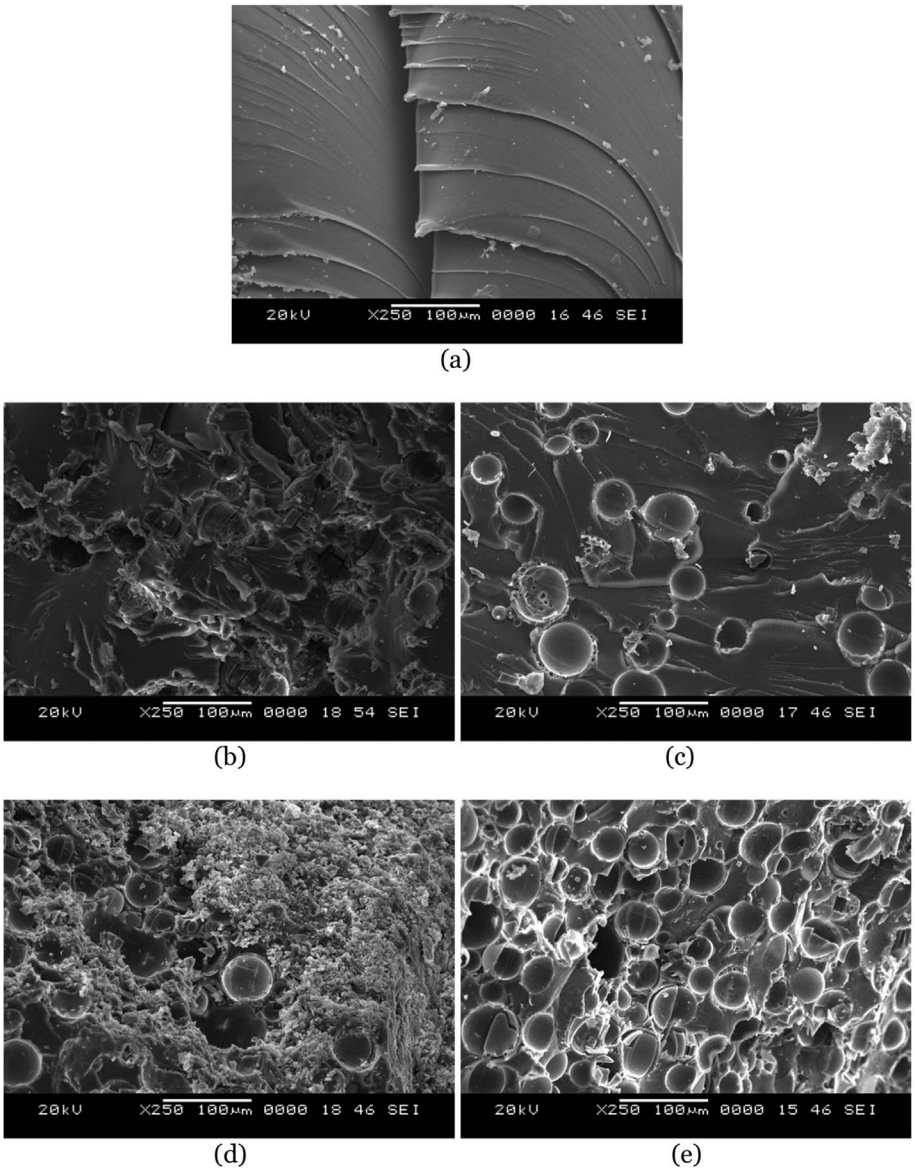

Fig. 7. Micrographs of (a) Neat epoxy resin (b) E20-U (c) E20-T (d) E60-U and (e) E60-T post compression room temperature tests.

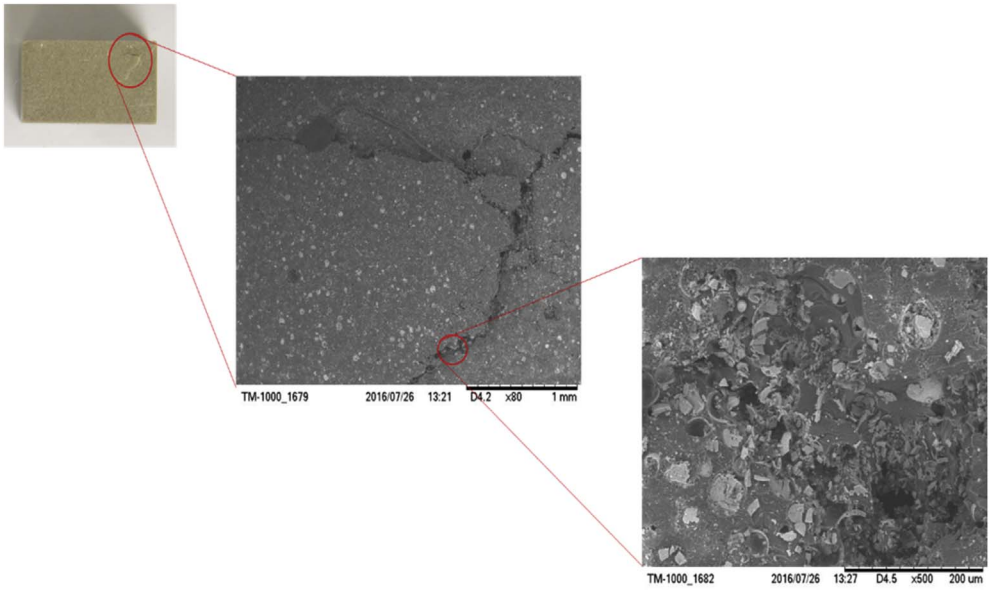

Fig. 8. E40-U compression specimen schematic post arctic condition test.

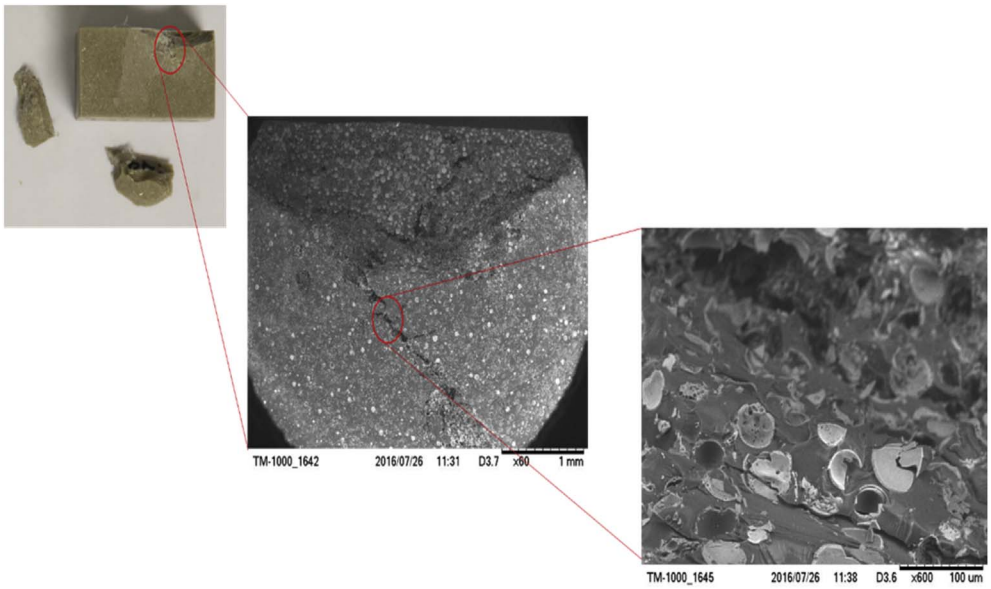

Fig. 9. E40-T compression specimen schematic post arctic condition tests.

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