Compressive Behaviour of Syntactic Foam Filled with Epoxy Hollow Spheres Having Different Wall Thickness

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Abstract

An innovative approach of producing epoxy syntactic foams was developed by incorporating single-coated and double-coated of epoxy hollow spheres within epoxy resin matrix. These syntactic foams were prepared by embedding epoxy hollow spheres into the epoxy resin matrix and were then cured for 24 hours in a mould using casting technique. Generally, both types of the produced hollow spheres have approximately 4 mm diameter mean size, but possess different wall thicknesses. The comparative compressive properties of these syntactic foams were evaluated and reported. It was observed that the measured peak compressive stress was higher for the syntactic foam filled with double-coated of hollow spheres compared to that of incorporated with single-coated hollow spheres since the shell of the double-coated hollow spheres were found to be thicker. Results also indicated that the double coated hollow spheres seemed to be able to retain their shape after compressive crushing. The present study illustrated that the compressive properties exhibit proportional increase in strength with increasing density of the resultant epoxy syntactic foam.

1.0 Introduction

Syntactic foams can be considered as composite materials which consist of hollow spheres embedded in a polymeric matrix. Over the past three decades, beginning as simple two-phase polymer matrix foams based upon hollow glass or polymer spheres, this material has primarily been used as a buoyancy material for applications in the marine and submarine industry [1,2]. Since that, because of its excellent properties, syntactic foams have developed rapidly and are widely utilized in aeronautical, space and marine applications [3].

These materials are classified as closed pore foams, since the porosity in syntactic foams exists in the form of discrete hollow particles. The closed pore structure gives advantages of higher strength, low density as well as lower moisture absorption compared to the open cell polymeric foams [4]. Suitable polymeric material for the foam matrix can be selected from a vast range of thermosetting resins such epoxy, polyimide, phenolic, cyanate esters, or thermoplastic resins such as polyethylene, polystyrene [5]. On the other hand, the hollow spheres may be made of various materials such as metals [6], polymers [7,8], or ceramics [9] but glass microballoons are by far the most common of all [1]. In several cases, additional reinforcement such as fibers can also be added to syntactic foams to obtain certain desired properties [10,11].

Syntactic foams have been gaining attractiveness as core materials in the sandwich-structured composites. A number of theoretical studies [12] and experimental [13,14] describing characterization of the syntactic foam core sandwich composites have been published. Most published studies investigate the effects of variation in microballoon volume fractions on the physical and the mechanical properties [15,16]. It is observed that increase in the microballoon volume fraction decreases the density and strength of the syntactic foams [4]. However, the idea of maintaining the volume fraction constant but still be able to vary the properties of the syntactic foams would seem to offer several benefits. One example of this approach is through utilization of microballoons of with different wall thickness which could also affect the density and the mechanical properties of syntactic foams and this method is explored in the present study.

In this study, a new and innovative syntactic foam system consisting of epoxy hollow spheres dispersed in the epoxy matrix have been produced. The idea to utilize epoxy hollow spheres instead of the common glass microballoons has not only reduced the cost of production but also offer equivalent properties when compared with other established hollow spheres. Epoxy resin was used as the matrix for the hollow spheres due to their higher thermal and chemical stability [17]. Essentially in this study, epoxy hollow spheres of two different wall thicknesses have been used to produce the syntactic foams. Both types of hollow spheres have more or less the same inner radius. However, there is a considerable difference in their densities, due to the differences in their outer radii. The composition of matrix resin, hollow spheres volume fractions, and processing parameters for all types of syntactic foams have been kept the same. Hence, the approach allows the observed difference in the mechanical properties of the syntactic foams to be directly related to the variation in the wall thickness of the hollow spheres.

2.0 Experimental

2.1 Materials

2.1.1 Matrix Resin

D.E.R. 331, a clear epoxy resin, manufactured by DOW Chemical Company was selected for the study. This is a diglycidyl ether of Bisphenol A (DGEBA) based resin. D.E.R 331 was chosen as the polymer matrix for the syntactic foam due to wide variety of curing agents available to cure the liquid epoxy resin at ambient conditions.

2.1.2 Hardener

The above mentioned epoxy pre-polymer is an epoxy resin system which is supplied in liquid state and can be hardened by a curing agent when they are mixed in stoichiometric ratio. Ancamide A062 curing agent or hardener (a liquid polyamide) was utilized and this chemical was supplied by Euro-Chemo Trading Sdn. Bhd.

2.1.3 Diluent

It is difficult to mix large volumes of hollow spheres in the resin if the viscosity is high. Hence, a diluent was added to reduce the viscosity of the resin mix. To obtain this, Potassium Hydroxide (KOH) aqueous solution with a concentration 3% (w/w), was added to the mix to bring down the viscosity of the resin. The amount of KOH solution was fixed at 40% by weight with respect to the resin mix. Besides being the diluent for the system, the KOH solution also function as an emulsifier that could be utilized to stabilize another foaming activity (i.e. physical frothing) which was initiated by extensive mixing during the preparation of the resin mix.

2.2 Preparation of Epoxy Hollow Spheres

A resin mixture comprising of clear epoxy resin (D.E.R 331) and polyamide hardener (Ancamide A062) with 2:1 ratio was formulated and mixed to produce the epoxy system. The EPS beads were later added into the prepared epoxy system in apportioned quantities and were ensured to be fully coated with the epoxy system. After that, the epoxy-coated EPS were transferred onto a tray filled with sufficient amount of $CaCO_3$ powder. This step is to ensure that the stickiness problem of the uncured epoxy-coated beads was addressed thus preventing the beads from clumping to each other. These coated EPS beads were then cured in an oven for 15 minutes at 80°C and post-cured at 120°C for 90 minutes to shrink the EPS beads with the intention to produce epoxy hollow spheres.

2.3 Preparation of Syntactic Foam

In order to form the epoxy syntactic foams, the mixture for the matrix were prepared by mixing the epoxy resin with the hardener continuously with combination of 3% KOH solution for 15 minutes. The prepared cured epoxy hollow spheres were then added at regular intervals into the mixture subsequently after the matrix system's preparation process was completed within the duration of 15 minutes. Using such procedure, the uncured matrix compound consisting of epoxy hollow spheres dispersed in the epoxy matrix was achieved. The mixture was then poured evenly into a polypropylene mould and after the mixture has been transferred into the mould successfully, a constant load was placed on top of the mould lid. The mixture was left at room temperature to complete the curing process for 24 hours. The cured composites were then demoulded and cut according to standard dimension for respective testing. The samples were then post-cured in an oven with 100°C temperature. This post-curing procedure helps in ensuring that the relatively thick foams were fully cured and the remaining entrapped water was removed.

2.4 Characterisation

ASTM standard D 3574 was adopted to measure the density of the epoxy syntactic foams. Image analysis was carried out to determine the wall thickness of the epoxy hollow spheres shell in the matrix using optical microscopy and the digital images were then analyzed using Dino Capture image analysis software. ASTM standard D 3575 was followed in the determination of compressive strength of the foams. The compression tests were carried out using Shimadzu UMH-50 universal testing machine. A crosshead speed of 5 mm/min was used during the compression test.

3.0 Results and Discussion

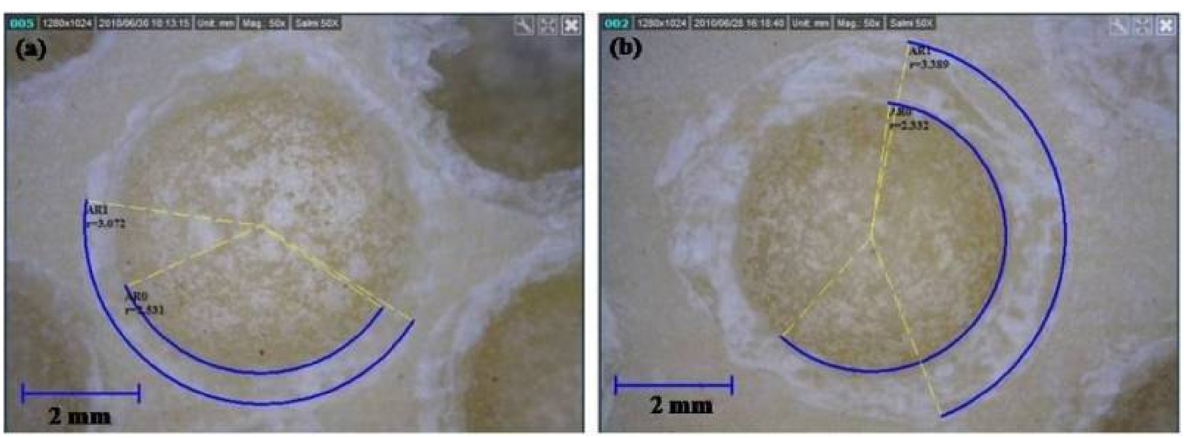


Figure 1: Optical micrographs of (a) single coated of hollow spheres and (b) double coated of hollow spheres at 50X magnification

The optical micrographs in Figure 1 present the wall thickness of single coated hollow spheres and double coated hollow spheres, respectively. The measurement was implemented using

Dino Capture image analysis software and it was determined that the average wall thickness of the single coated hollow spheres was 0.54 mm while 1.10 mm for the double coated samples. The micrographs clearly revealed that the shell wall of the double coated hollow spheres was thicker than that of the single coated spheres.

3.1 Effect of wall thickness of hollow spheres on density

Figure 2 display densities of syntactic foam produced with hollow spheres having different wall thicknesses and the control system. From the experimental determination, the produced epoxy syntactic foams densities yielded experimental values of 636.1 kg/m^3 for single coated hollow spheres and 804.2 kg/m^3 for double coated hollow spheres respectively, while the control system (without hollow spheres) recorded a density value of 920 kg/m^3.

It was discovered that the density of syntactic foam with single coated hollow spheres was lower than that of syntactic foam with double coated hollow spheres and the control system. Logically, according to the equation (1), at the same volume, the mass of single coated and double coated epoxy hollow spheres contribute to the variation in density of the epoxy syntactic foam.

$$\rho = \frac{M}{V} \tag{1}$$

where, M = mass of specimen, in kilogram V = volume of specimen, m^3

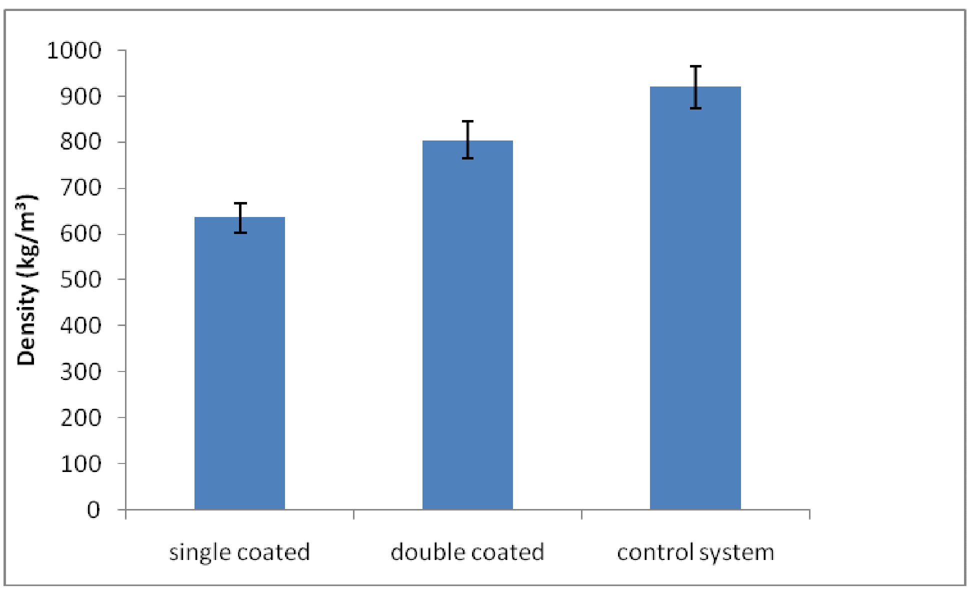


Figure 2: Effect of wall thickness on density

Assuming a uniform pore size and same volume of syntactic foam are produced, the mass of single and double coated of hollow spheres are obviously different. The double coating of the hollow spheres contribute to the increasing density which is attributed to the thicker shell of the double coated hollow spheres compared to that of the single coated hollow spheres. Therefore, it is projected that the mass of syntactic foam with double coated hollow spheres at the same volume is higher than that of the single coated hollow spheres. The above experimental result confirmed the projection and from this argument, wall thickness certainly one of the parameter that can be varied to alter the density of syntactic foam.

3.2 Effect of wall thickness of on compressive behavior.

Representative stress-strain curves for all types of specimens tested in this study are shown in Figure 3. It is observed that the compressive strengths of the foams are lower compared to the control system. Obviously, the incorporation of hollow spheres led to significant effect to the overall properties of the epoxy matrix.

Referring to Figure 3, all of the curves showed a yield stress, which corresponds to the point of crack initiation. The syntactic foam with double coated hollow spheres shows evidence for higher compressive strength compared to syntactic foam with single coated hollow spheres. In addition, the former exhibits a stress-strain curve which is more or less similar to the control system at low compressive strain. However, above 10% strain, the foam system deviates and this is a clear indication of the initiation of epoxy hollow spheres shell collapse. For particulate composites comprising solid or hollow particle of the same material, shape and size, the effective compressive strength are quite different. In the case of hollow particles, the effective Young's modulus depends on the wall thickness of the particles and, more specifically, on the wall thickness to particle size ratio [17]. In this study, this claim was confirmed when the experimental result showed that the double coated of hollow spheres gives higher compressive strength than the single coated hollow sphere.

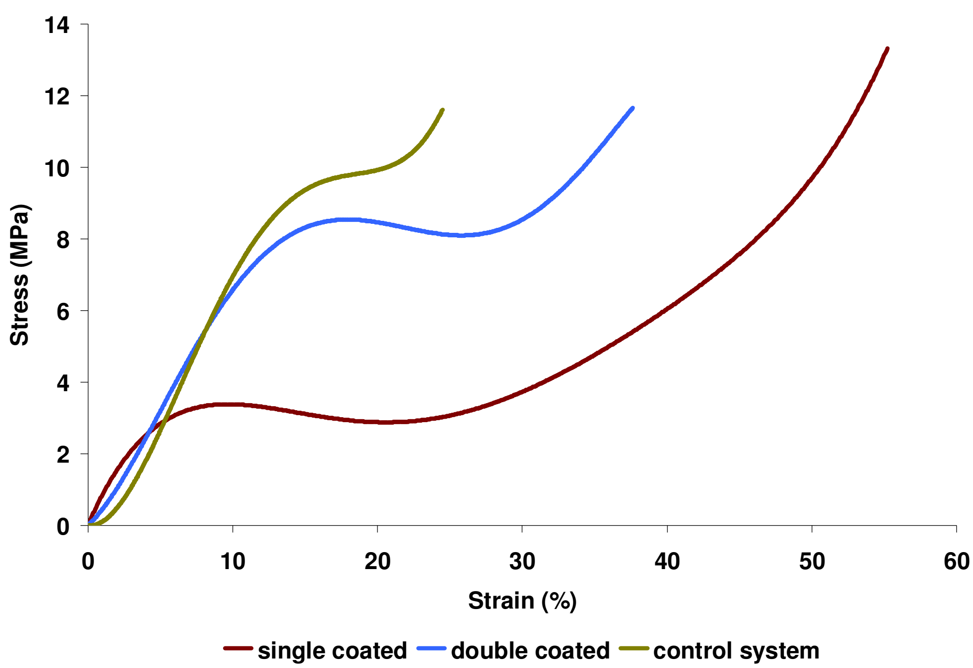


Figure 3: Stress-strain curve of different wall thickness

The shape of the obtained stress-strain curves describes several occurrences during the compression test. The region before the peak stress corresponds to the linear-elastic deformation of the syntactic foams. It occurs at small strains and it is characterized by elastic bending of the spheres' shell. The region ends when the material starts to yield and reaches its compressive yield strength. Upon yielding, the hollow spheres become crushed under the compression load and severe damage occurs. After reaching the maximum, the stress value decreased and become nearly constant during further compression. This region is referred to as the plateau region. The plateau region corresponds to energy absorption in the process of crushing all the available hollow spheres. In this stage, the hollow spheres are crushed, exposing their internal hollow feature. Due to the thicker wall thickness of double coated hollow spheres, at 10% of strain, this syntactic foam showed drastically higher compression strength than that of single coated hollow spheres. As for the plateau region, it is said to be attributed to the implosion of the hollow spheres under the increasing compression load.

At the end of the plateau region, stress again starts to increase. This third region is characterized as densification, where the slope of the stress-strain curves increases rapidly. The steep increase is due to the act that almost all the hollow spheres have been crushed and compacted, and a higher density of the matrix is being reached. The point where region of densification starts is considered to be the point of failure for the syntactic foam.

Following this further, Figure 4 shows that the hollow spheres of single coated exhibited complete crushing and collapse after the compression test. It is evident from the Figure 4 that the hollow space exposed by the fracture of hollow spheres was due to the incapability of wall thickness of hollow spheres to withstand the applied load.

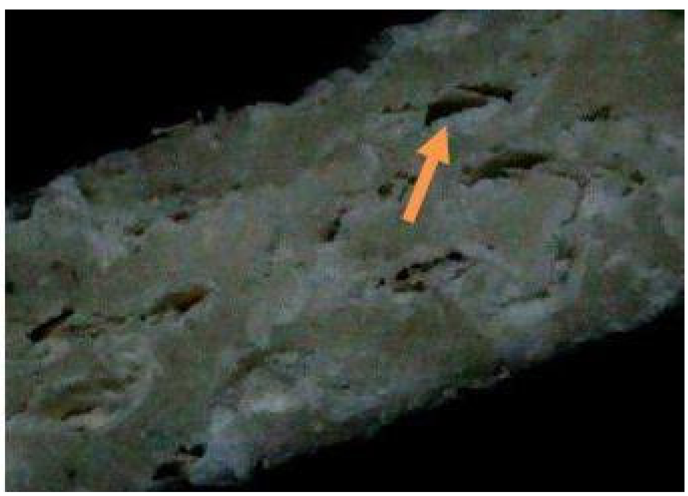


Figure 4: Cross section of single coated epoxy syntactic foam after compression

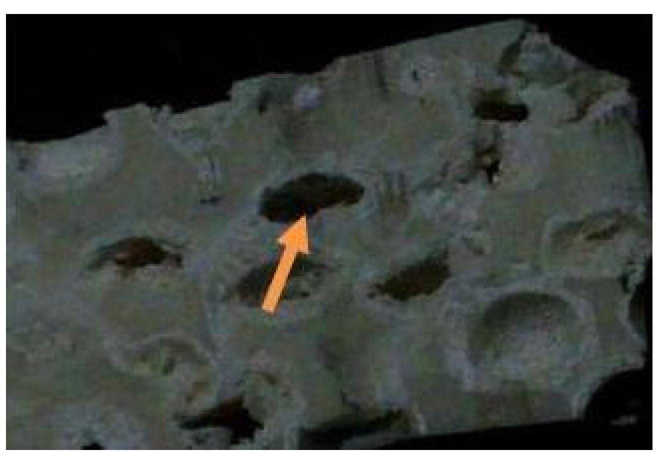
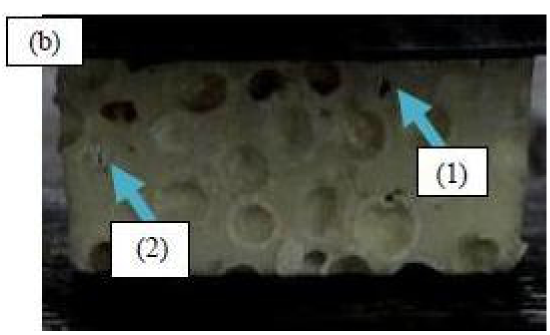


Figure 5: Cross section of double coated epoxy syntactic foam after compression

On the other hand, for the syntactic foam with the double coated hollow spheres, the thicker shell wall of the hollow spheres seems able to retain their shape after crushing as shown in Figure 5. This emphasis on the effect of shell wall thickness in controlling failure properties corresponds well with previous studies [18]. The study proved that the uniaxial compressive failure load of glass micro balloons was independent of its diameter and only related to the average strength and wall thickness. It is also evident from the referred study that syntactic foam composed of polymerized resin encapsulating glass hollow spheres with thicker wall thickness yielded higher hydrostatic compressive strength because their air holes are spherical and they are surrounded with more resin. It can be explained that compression strength of syntactic foams with hollow spheres having thinner shell layer is lower than that of the matrix material, while hollow spheres with thicker shell could stiffen the matrix system. These researchers [18] also found that variation of compressive strength with shell thickness can be associated with the different interaction of the hollow spheres to the externally applied stress. Carlisle et al have noted that when the weakest hollow spheres failed, their loads are transferred to neighboring hollow spheres and the binder or matrix, thus propagating the compressive failure [19].

3.3 General pattern of deformation under compression loading condition

The specimen fracture behavior was closely monitored in real-time during the process of compression. The fracture sequence of the syntactic foam samples are shown in Figure 6 (a)-(d), which were captured for syntactic foam with double coated hollow spheres sample. It is observed that the initial fracture took place with the generation of shear cracks from the corner of the specimen under the effect of compression forces. This is evident in Figure 6 (b) where shear cracks can be observed labeled as 1 and 2. The shear cracks grow to a substantial length to form a wedge-shaped fragment at the bottom or top of the specimen. The vertical crack can be observed in Figure 6 (c) and this vertical crack grows further, and finally develops up to the full height of the specimen leading to complete splitting and failure of the specimen. The cracks start to propagate when the load applied are increased. Meanwhile, at Figure 6 (d), it shows that the hollow spheres have collapsed completely.



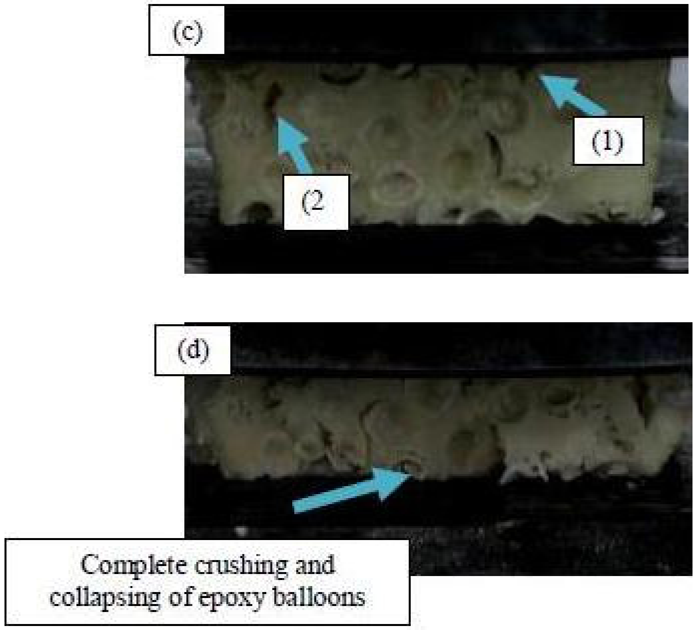


Figure 6: Fracture pattern of syntactic foam under compressive loading conditions (a) specimen before compression; (b) shear crack formation; (c) growth of vertical crack; and (d) failure of the specimen

3.4 Types of failure under compression loading

Several failure mechanisms were able to be followed through real-time monitoring of the compression test. One of them is shell debonding of the hollow spheres which is marked by an arrow in Figure 7. This shell debonding process could have its origin in the earlier stated incomplete wetting problem between hollow spheres and epoxy matrix. Meanwhile, Figure 8 shows a completely crushed, collapsed and caved-in of hollow spheres that were pointed by the arrow. These findings indicate that due to the large volume of hollow spheres and the intended load-bearing ability of the system being affected, the sample exhibits the least strength.

Figure 7: Shell debonding of hollow spheres after compression

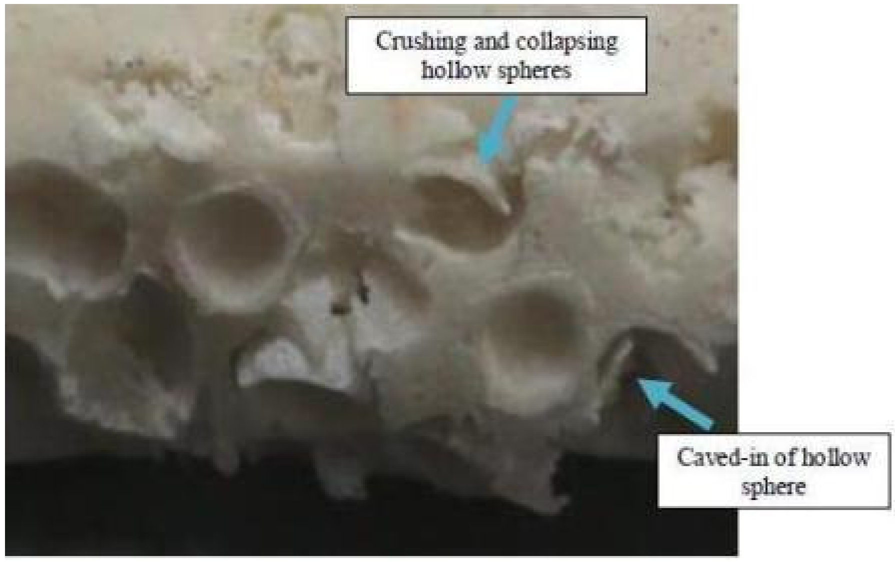


Figure 8: Failure of hollow spheres crushing after compression

4.0 Conclusion

Increase in the density and compressive strength of syntactic foams can be achieved by incorporating hollow spheres with different shell wall thickness into the syntactic foam system. Syntactic foam embedded with hollow spheres having thinner shell wall exhibits complete crushing and collapse after the compression test while foams with hollow spheres having thicker shell wall seems able to retain their shape after crushing. It can also be concluded that the fracture features for all types of syntactic foams are more or less similar. It is observed that the initial fracture mode is shear cracking followed by the vertical splitting of the specimens in the direction of applied load until the hollow spheres have collapsed completely.

The compression test results of syntactic foams also presented familiar trends of the stress-strain curves for other established syntactic foams. It is also can be concluded that the incorporation of hollow spheres led to significant effect to the overall properties of the epoxy matrix when results showed that the compressive strengths of the foams are lower compared to the control system. Based on the experimental results, it is evident that the innovative approach adopted in this study is reasonably effective because increase in the compressive strength is achievable with small change in density. Hence, the specific strength of the syntactic foams was increased considerably.

5.0 Acknowledgements

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6.0 References

1. Gladysz, G.M.; Chawla, K.K., *Preface Syntactic and Composite Foams: Proceedings of Engineering Conferences International (ECI) Conference*, Journal Material Science, 41 (2006) 3959-3960
2. Choqueuse, D.; Davies, P., *Ageing of Composites in Underwater Applications*, Woodhead Publishing (2008)
3. Woldesenbet, E.; Peter, S., *Volume Fraction Effect on High Strain Rate Properties of Syntactic Foam Composites*, Journal Material Science, 44 (2009) 1528-1539
4. Gupta, N.; Woldesenbet, E., *Microballoon Wall Thickness Effects on Properties of Syntactic Foams*, Journal of Cellular Plastics, 40 (2004), 461-482
5. Devi, K.A.; John, B.; Nair, R.C.P.; Ninan, K.N., *Syntactic Foam Composites of Epoxy-Allyl Phenol-Bismaleimide Ternary Blend-Processing and Properties*, Journal of Applied Polymer Science, 105 (2007) 3715-3722
6. Banhart, J., *Manufacture, Characterization and Application of Cellular Metals and Metal Foams*, Prog. in Meters Sci., 46 (2001) 559-632
7. Lawrence, E.,; Wulfshon, D.; Pyrz, R., *Microstructural Characterization of Syntactic Foam,* Polymers and Polymer Composites, 9 (2001) 449-457
8. Lawrence, E.; Pyrz, R., *Viscoelastic Properties of Polyethylene Syntactic Foam with Polymer Microballoons*, Polymers and Polymer Composites, 9 (2001) 227-237
9. Bardella, L.; Genna, F., *On the Elastic Behavior or Syntactic Foams*, International Journal Solids and Structures, 38 (2001) 7235-7260
10. Gupta, N.; Karthikeyan, C.S.; Sankaran, S.; Kishore, *Correlation and Processing Methodology to the Physical and Mechanical Properties of Syntactic Foams with and without Fibers*, Materials Characterization, 43 (1999) 271-277
11. Karthikeyan, C.S.; Sankaran, S.; Kumar, M.N.J.; Kishore, *Processing and Compressive Strengths of Syntactic Foams with and without Fibrous Reinforcement,* Journal Applied Polymer Science, 81 (2001) 405-411
12. Bardella, L.; Genna, F., *Elastic Design of Syntactic Foamed Sandwiches obtained by filling of Three-dimensional Sandwich Fabric Panels*, International Journal Solids and Structures, 38 (2001) 307-333
13. Gupta, N.; Sankaran, S.; Kishore, *On the Characterization of Syntactic Foam Core Sandwich Composites for Compressive Properties*, Journal Reinforced Plastic Composite, 18 (1999) 1347-1357
14. Corigliano, A.; Rizzi, E.; Papa, E., *Experimental Characterization and Numerical Simulations of a Syntactic Foam/Glass-fibre Composite Sandwich*, Composites Science Technology, 60 (200) 2169-2180
15. D'Almeida, J.R.M., *An Analysis of the Effect of the Diameter or Glass Microspheres on the Mechanical Behavior of Glass Microsphere/Epoxy-resin Composites*, Composites Science Technology, 59 (1999) 2087-2091
16. Kim, H.S.; Khamis, M.A., *Fracture and Impact Behaviors of Hollow Micro-sphere/Epoxy Resin Composites*, Composites Part A, 32 (2001) 1311-1317
17. Klempner, D.; Frish, K.C., *Handbook of Polymeric Foam and Foam Technology*, Hanser Publications (1991)
18. John, B.; Nair, R.C.P.; Devi, K.A.; Ninan, K.N., *Effect of Low-Density Filler on Mechanical Properties of Syntactic Foams of Cyanate Ester*, Journal Material Science, 42 (2007) 5398-5405
19. Carlisle, K.B.; Koopman, M.; Chawla, K.K.; Kulkarrni, R., *Microstructure and Compressive Properties of Carbon Micro Balloons*, Journal Material Science, 41 (2006) 3987-3997