

Hydrostatic strength of hollow glass microspheres composites: Influencing factors and modelling

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ABSTRACT

This study deals with the hydrostatic strength of hollow glass microspheres composites, commonly known as syntactic foams, using model materials made of 0.15 g/cm³ microspheres with 3 types of matrix, two epoxies and one paraffin. More than 100 model material samples are characterized for that work. The hydrostatic strength of these composite materials is determined in a pressure vessel, which can go up to 100 MPa. Two major parameters are studied: stiffness of the matrix and microsphere volume content within the composite material. The results clearly show that the hydrostatic strength of the syntactic foam can be improved by an increase in matrix stiffness or a reduction in microspheres content. Based on experimental data an empirical model with two parameters is proposed to describe the hydrostatic strength of syntactic foam. The relevance of the model is discussed.

1. Introduction

The oceans represent 70% of our planet surface, however it is the largest unexplored place on Earth. Indeed, less than 5% of the oceans have been explored. [1]. The oceans are a complex and aggressive environment, limiting their exploration and exploitation. Marine exploration systems must resist to sea water, withstand the pressure induced by the water column, support storms and winds, have as low perturbation as possible to the marine environment and should require little maintenance. This leads to major technological challenges.

One of those challenges is related to buoyancy systems. On one hand submarines and Remotely Operated Vehicles (ROV) need to be buoyant to be able to go back to the surface. On the other hand, for fixed marine structures, buoyancy is needed to reduce their apparent weight in water to reduce the mechanical loads, the most relevant example being the riser tower in the oil industry [2].

Systems buoyancy can be increased through the use of low-density materials, which are mainly syntactic foams [3]. These are composite materials made of a polymer matrix and hollow glass microspheres with a diameter range of 1 to 150 μm and thickness of around 1 μm [3,4]. Those hollow inclusions allow significant reductions in the material density while resisting the environmental hydrostatic pressure [3,4].

Since their first use in the 1960's, syntactic foams have been widely studied [2,5-18]. Their mechanical behaviour was mainly studied under uniaxial compressive loading or tensile loading [19-23]. However, those approaches are not representative of the loading conditions in marine applications. But the study of syntactic foams mechanical behaviour under hydrostatic loading requires specific equipments [5,6]. Those apparatus are not easily accessible, leading to few relevant studies for that specific case studied in the present paper.

Syntactic foams for marine applications are defined by their density and crush pressure (i.e. hydrostatic strength), the latter being the pressure at which the material starts losing volume and buoyancy [6]. The composite density depends on the matrix density, microspheres density and the proportion of microspheres in the material [24]. Based on the available literature, the crush pressure depends on the matrix nature [5] and on the microspheres density [17]. Indeed, the heavier the microspheres are, the thicker they are, the stronger they get [25]. Therefore, there is a compromise to between the syntactic foam density and its crush pressure.

Despite being widely used in a marine environment since several decades, syntactic foams are still empirically designed. In fact, their design is based on feedback from the manufacturer and users, and on the use of high security factors. This study aims to define the parameters

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Table 1
Syntactic foams studied.

Syntactic foam name	Matrix	HGMS density (g. cm ³)	HGMS volume fraction (%)	Theoretical densities (g. cm ³)	Experimental densities (g. cm ³)	T _g (°C)	T _m (°C)
E1 foam	High T _g Epoxy (E1)	0.15	From 0.3 to 0.6	0.538- 0.829	0.560 - 0.801	91 ± 2	-
E2 foam	Low T _g Epoxy (E2)	0.15	0.6	0.550	0.560 - 0.572	38 ± 1	
WAX foam	Paraffin (WAX)	0.15	From 0.3 to 0.6	0.450 - 0.713	0.475 - 0.713	-	58 ± 1

*T_g and T_m obtained from DSC measurements with a heating rate of 10 °C/min.

influencing the crush pressure of syntactic foams made with hollow glass microspheres (HGMS) under hydrostatic loading. The impact of the matrix mechanical properties and HGMS fraction in the material will be considered. While those parameters were already studied in the case of uniaxial compressive loading [26–28], there is no equivalent studies for the case of hydrostatic loading. For the present study, model materials will be used. After studying the influent parameters on the crush pressure, a simple empirical model describing the crush pressure of syntactic foams will be proposed and validated.

2. Material and methods

2.1. Materials

Model syntactic foams were produced by mixing hollow glass microspheres (mean density of 0.15 g/cm³) with different polymer matrixes. Three different types of matrix were used, a high T_g epoxy (named E1, density of 1.12 g/cm³), a low T_g epoxy (E2, density of 1.15 g/cm³) and a paraffin resin (WAX). HGMS and resin densities were measured through pycnometer measurements. Samples were processed by mixing the resin and microspheres with a special mixer at 50 °C when using the E1 epoxy resin, room temperature when using the E2 epoxy resin and 80 °C when using the paraffin resin, for a minimum of 30 min. After mixing, the liquid material was placed in a special holder with a volume close to 1 L. For the paraffin foam, samples were cooled at room temperature. For the epoxy foams, curing was performed at 60 °C for 20 h; then a 24 h post cure at 100 °C for the E1 foams and at 80 °C for the E2 foams was applied to fully cure the materials. Depending on the tests performed, samples were cut into plate samples of 50×50×5 mm³ using a CUTO 20 machine for the epoxy foams, and a PROMAC SX-815DA bandsaw for paraffin foam. Then, samples were polished using sandpaper (grain: P60 for epoxy foam, grain 120 for paraffin foam). To obtain larger samples, cubes of 100×100×100 mm³ were cut from larger syntactic foam blocks. Table 1 summarizes all the model materials considered here, with the HGMS volume fraction available for each material.

The syntactic foams studied showed almost no voids, only voids or porosities under 1 micrometre diameter have been detected (checked by SEM, see Fig. 6 with 1500X magnitude). In that case, materials can be considered homogeneous at a macroscopic scale. Measurements of HGMS density after foam incineration showed that less than 5% (by volume) of HGMS were broken during foam processing. The different HGMS volume fraction ranges were obtained by mixing different amounts of HGMS in the resin. The true HGMS volume fraction in foams was measured after processing of each sample. All samples tested here have a good interface between the matrix and the glass bubbles (as shown in Fig. 6).

2.2. Methods

2.2.1. Hollow glass microspheres volume fraction measurements

The volume fraction v of the syntactic foam samples tested here was calculated knowing the true sample density ρ_{SF} , the HGMS density ρ_{HGMS} and the resin density ρ_{resin} (all densities in g.cm⁻³) and using the law of mixtures [19]:

$$\rho_{SF} = v * \rho_{HGMS} + (1 - v) * \rho_{resin} \quad (1)$$

Which gives:

$$v = (\rho_{SF} - \rho_{resin}) / (\rho_{HGMS} - \rho_{resin}) \quad (2)$$

The true sample density is obtained by measuring the sample weight in air m_{air} (g) and in water m_{water} (g) at 21 °C, using a SARTORIUS balance (0.1 mg accuracy). Using those values, the sample volume (cm³) is calculated using Archimedes' formula and the water density at 21 °C ρ_{water} (g.cm⁻³):

$$m_{water} = (\rho_{water} * V - m_{air}) \quad (3)$$

Which gives:

$$V = (m_{air} - m_{water}) / \rho_{water} \quad (4)$$

And the sample density:

$$\rho_{SF} = m_{air} / V \quad (5)$$

2.2.2. Uniaxial compressive test

Compression tests were performed according to the ASTM D695M standard. The samples were right cylinders with a diameter of 12.5 mm and a height of 25 mm. Samples of E1 and E2 resin were manufactured using a hole saw, then their opposite surfaces are polished. WAX samples were moulded from a block heated at 80 °C, before casting in a rigid PVC tube of internal diameter 12.5 mm. The tube was cooled at room temperature before cutting into 26 mm lengths in order to follow sample dimension from the ASTM D695M standard. The PVC tube was then removed to obtain the WAX cylinder. The two faces were then polished until the length reached 25 mm.

Tests were performed on an Instron MTS machine (model 5566) at temperatures from 21 °C to 100 °C. The test loading rate was 1 mm.min⁻¹, and the load was measured with a 10 kN load cell.

Samples were heated for 5 h at the test temperature before testing in order to ensure thermal homogeneity. Sample initial length l_0 (mm) and initial radius r_0 (mm) were measured with a calliper (0.01 mm precision). The test machine records the crosshead displacement Δd (mm) and the load F (kN) during the test. Sample strain ϵ (no unit) and stress σ (MPa) are calculated:

$$\epsilon = \Delta d / l_0 \quad (6)$$

$$\sigma = 1000 * F / (\pi * r_0^2) \quad (7)$$

Finally, the elastic modulus of the resin under uniaxial loading E_{resin} (MPa) is calculated by measuring the slope of the linear part of the curve $\sigma = f(\epsilon)$ according to the standard.

2.2.3. Hydrostatic pressure testing

2.2.3.1. Syntactic foam testing. Syntactic foam samples were tested under hydrostatic loading using two different methods presented by Le Gall et al. [6]: hyperbaric compression tests based on buoyancy measurement and hyperbaric compression test based on piston displacement.

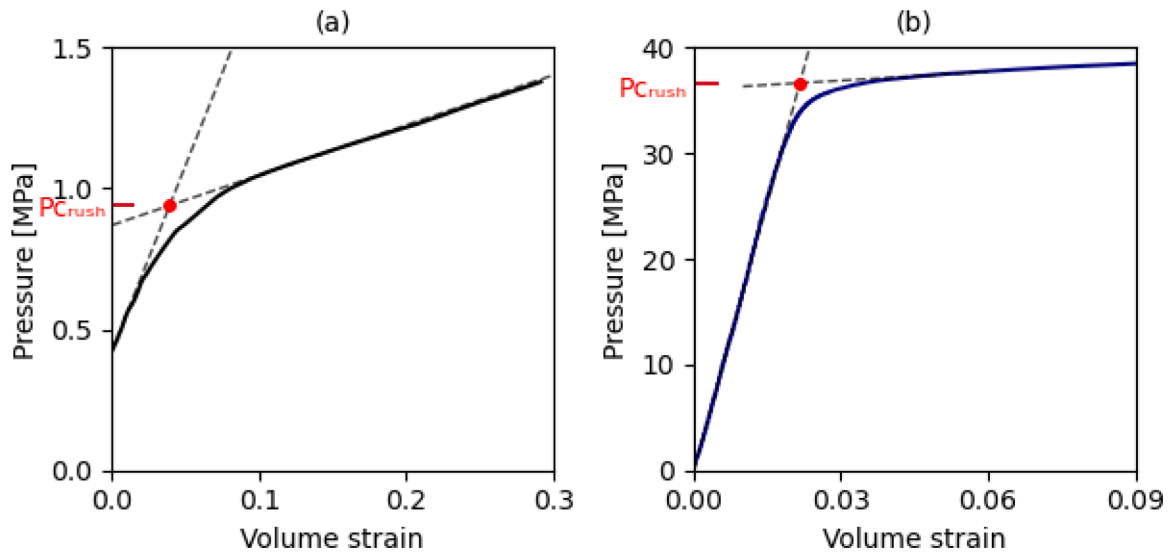


Fig. 1. Pressure/volume strain curve during HCP test at 21 °C on the HGMS only (a) and on the foam made with the HGMS and the E1 resin (HGMS volume fraction of 0.57) (b).

The first method allows samples to be pressurized up to 60 MPa, with temperature control from 20 °C to 120 °C. Sample volume measurements are calculated from buoyancy measurements using a SIXAXE FF2 load cell (accuracy 0.01 N). For accuracy of buoyancy variation measurements, large cubic samples described previously need to be used. Volume variation evaluation is made from buoyancy measurements using Archimedes' principle, as described in [6]. The pressurization is applied by injecting water into the vessel at 1.5 MPa/min, starting at the pressure of the water network (0.4 MPa).

The second method does not allow sample volume variations to be measured during the test, and is limited in temperature to 21 °C, but the vessel used allows small plate samples to be pressurized under hydrostatic loads up to 100 MPa. The piston displacement speed is 0.51 mm/min, chosen to be equivalent to a load speed of 1.5 MPa/min.

2.2.3.2. Hollow glass microsphere tests. HGMS were mixed in glycerol (volume fraction of HGMS in the mixture: 0.55), and 1 L of the mixture was placed in a sealed plastic bag. Vacuum was drawn before sealing to remove the air entrapped in the bag. Then the sample was tested using

the hyperbaric compression test based on buoyancy measurement, at 21 °C. A correction was required to the sample volume calculation, since glycerol volume variations are not negligible. This correction is detailed in the APPENDIX section.

2.2.4. SEM visualization

SEM pictures were performed using a ThermoFisher Quanta 200 in order to visualize microstructure of the syntactic foams. Prior to visualization samples were broken using cryogenic fraction, placed on metallic spin and covered with an Au-Pb coating.

3. Results and discussion

3.1. Role of the polymer matrix on microsphere collapse

In order to highlight the role of the polymer matrix in a syntactic foam, this study focused on the behaviour of glass microspheres embedded in polymer matrix or not embedded, meaning not surrounded by polymer matrix.

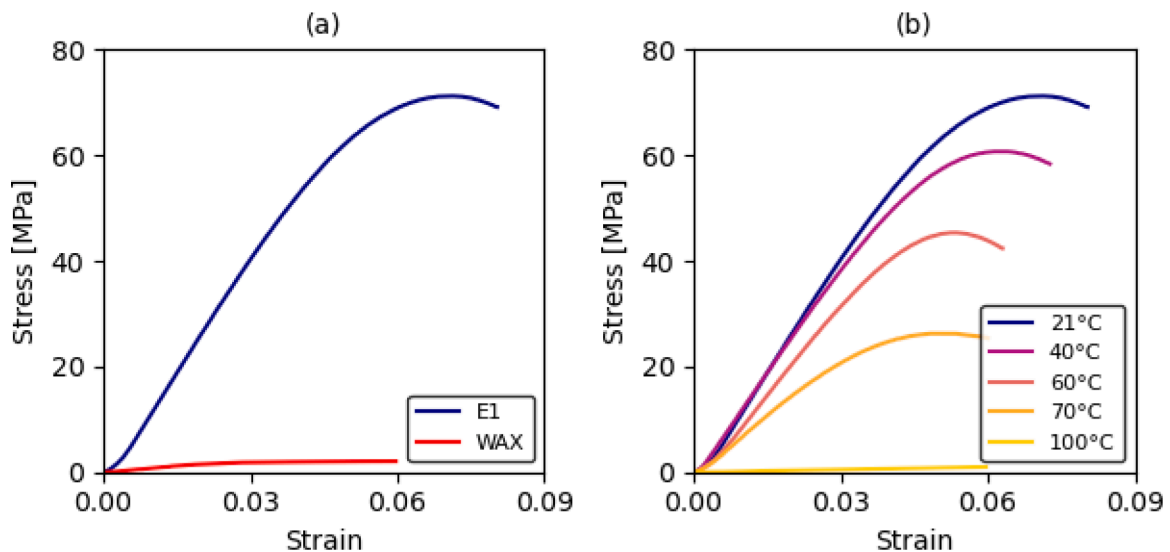


Fig. 2. (a) Stress/strain curves during uniaxial compressive tests on pure resins E1 and WAX at 21 °C (b) Stress/strain curves during uniaxial compressive test on the pure resin E1 at different temperatures.

Table 2

Resin properties determined during uniaxial compressive tests.

Resin	Testing Temperature (°C)	Uniaxial Compressive modulus (MPa)
WAX	21	90 ± 4
E1	21	1509 ± 24
	40	1371 ± 19
	60	1223 ± 27
	70	791 ± 7
	100	22 ± 1

First the behaviour of glass microspheres without matrix was studied under hydrostatic loading. The hyperbaric compression test based on buoyancy measurement method, described previously, was used to measure HGMS volume change during the test. Between 0.4 MPa (which is the minimal water pressure in the hyperbaric tank) and 0.7 MPa, a linear behaviour is observed that is related to the elastic deformation of the microspheres [25]. Then the volume loss increases much faster when higher hydrostatic pressure is applied; this is due to the collapse of microspheres induced by the mechanical loading [25]. Based on this in situ measurement of volume variation under hydrostatic pressure, it is possible to define a collapse pressure using the tangent method, as shown in Fig. 1a. For the microspheres considered in this study, this collapse pressure is equal to 0.9 MPa.

Then, the behaviour of the composite material, made with the same microspheres (i.e. 0.15 g/cm³) embedded within the epoxy matrix E1, was investigated. In the same manner as for HGMS, crush pressure (i.e. hydrostatic strength) of syntactic foam was characterized using hyperbaric compression tests based on buoyancy measurement. A typical result is presented in Fig. 1b where the sample volume variation with hydrostatic pressure is plotted. Here again, a linear behaviour is observed before a densification plateau occurs when the glass microspheres collapse. It is thus possible to define a crush pressure for the syntactic foams tested here using the tangent method as shown in red in Fig. 1b. The most interesting point is that HGMS resistance is greatly improved by using epoxy as a matrix. Without the matrix, the collapse pressure of the HGSM is less than 1 MPa, whereas when they are embedded in an epoxy resin the crush pressure of the syntactic foam is 38 ± 1 MPa.

The following part of this paper will focus on the study of this large improvement in collapse pressure to identify key parameters and propose a simple mathematical description of the results.

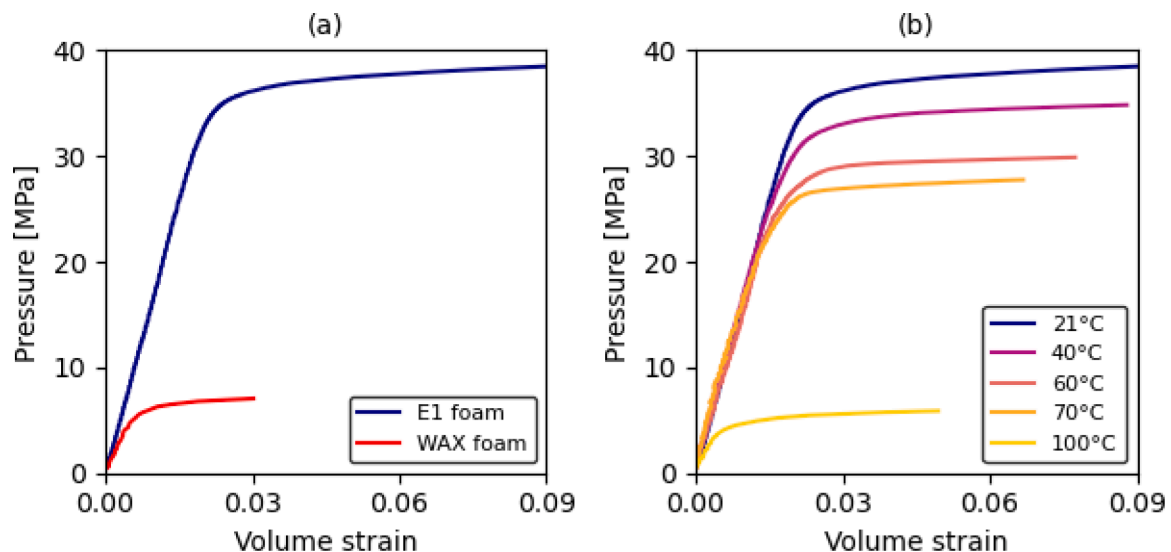


Fig. 3. (a) Hydrostatic load tests on E1 and WAX foams at 21 °C (a) and on E1 foam at different temperatures (b). HGMS volume fraction of 0.57 in the foams.

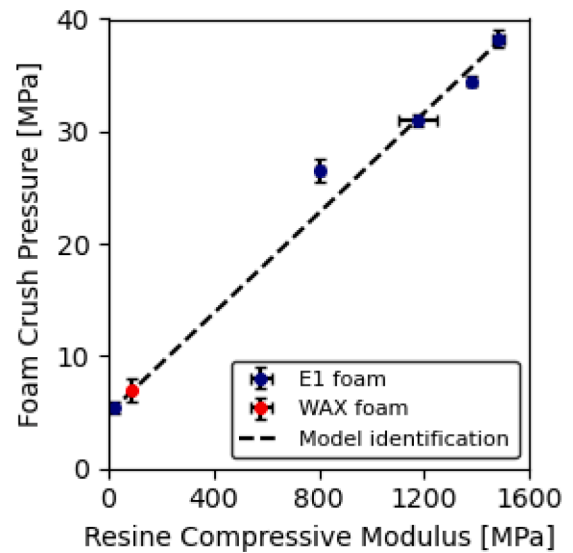


Fig. 4. Crush pressure of E1 and WAX foams versus the resin modulus under uniaxial compressive loading. HGMS volume fraction of 0.57 in the foams.

3.2. Role of mechanical properties of the matrix on syntactic foam hydrostatic strength

In order to characterize the impact of the matrix mechanical properties on the failure of syntactic foam, two approaches were used here. Firstly, a new model material with a paraffin matrix was introduced. Secondly, the test temperature was changed in order to modify mechanical properties of the epoxy E1 over a wide range.

3.2.1. Determination of the mechanical properties of the matrix

Matrix properties were determined using uniaxial compressive tests, results are presented in Fig. 2. Fig. 2a plots results obtained at 21 °C with the two matrix materials considered here, i.e. E1 and WAX. A large difference in terms of behaviour is observed. For the epoxy matrix a linear behaviour is observed up to 60 MPa followed by a yield, with a maximal compressive stress of 71 ± 1 MPa. For the WAX, a linear behaviour is also observed but only up to 2 ± 0.1 MPa, without a clear maximal compressive stress. These results are in accordance with existing knowledge in published literature [29–31]. In order to have a wide range of matrix properties, the epoxy matrix was tested at several

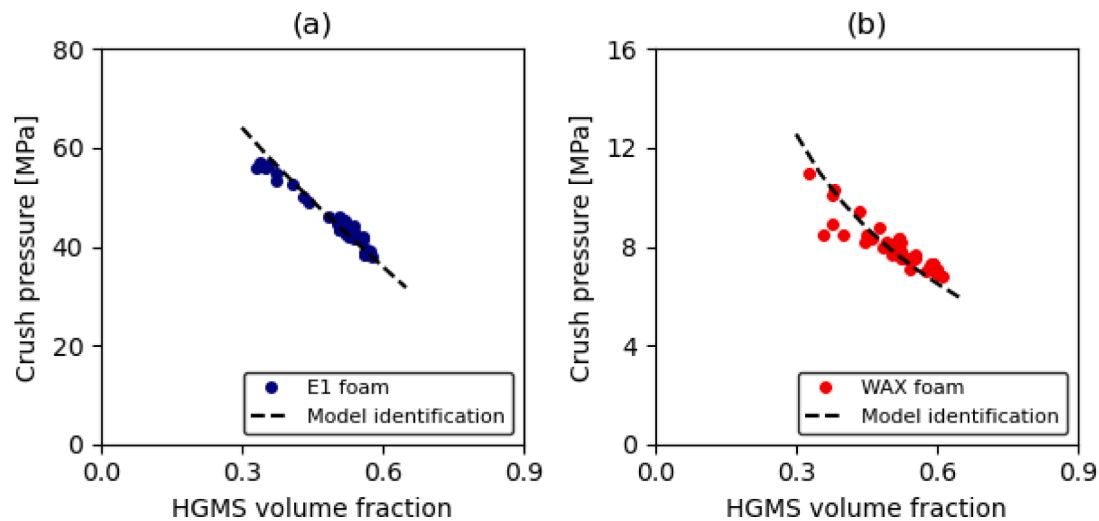


Fig. 5. Comparison between experimental results and model, crush pressure of syntactic foams made with resins E1 (a) and WAX (b) depending on HGMS volume content, at 21 °C.

temperatures, from 21 °C to 100 °C; results are presented in Fig. 2b. As long as the test temperature increases, a decrease in both modulus and yield stress is observed. Results obtained here are summarized in Table 2.

3.2.2. Determination of crush pressure of syntactic foam depending on matrix properties

Syntactic foams were characterized by in situ volume variation measurements during hydrostatic loading under the same conditions as presented previously for the matrix. Results are shown in Fig. 3. For all results presented here, the same behaviour is observed: first the foams present an elastic behaviour and then, when microspheres collapse, a densification plateau. However, large differences are observed for the pressure at which the densification plateau occurs. In other words, mechanical properties of the matrix largely impact the crush pressure of the syntactic foam. A comparison of crush pressure determined in Fig. 3 with uniaxial modulus of the matrix determined in Fig. 2 is proposed in Fig. 4. It clearly appears that the stiffer the matrix, the higher the collapse pressure of the syntactic foam. The dotted black line represents a model of this behaviour that will be described in Section 3.4.

To conclude on those results, the present work has clearly highlighted a relationship between the crush pressure of a syntactic foam and the mechanical properties of the matrix used. The stiffer the matrix, the higher the collapse pressure of the syntactic foam. In the next section, the impact of the volume fraction of microspheres on the syntactic foam crush pressure will be studied.

3.3. Role of HGMS content on syntactic foam collapse

The crush pressure of several model foams with both WAX and E1 matrixes with different amount of HGMS were measured via hyperbaric compression test based on piston displacement. Results are plotted in Fig. 5a and 5b. For both matrix materials, a decrease in HGMS volume fraction leads to an increase in crush pressure of the syntactic foam. For example, for the epoxy matrix, when the volume fraction is decreased from 0.6 to 0.3, the crush pressure increases from 37 MPa to 57 MPa. As far as we are aware, this is the first time that the impact of HGMS amount on crush pressure of syntactic foam under hydrostatic loading has been presented in the literature. It is worth noting that we usually try to increase the HGMS content in a syntactic foam in order to decrease the material density and to provide maximum uplift.

3.4. Fractography visualisation

SEM pictures have been performed before and after crush tests in order to evaluate samples quality and especially the interfaces between glass bubbles and matrix. Results are presented in Fig. 6 for epoxy and WAX matrix containing 55% of glass bubbles. General comments can be made here:

- Before testing (i.e. measure the hydrostatic crush pressure), a good interface between glass bubbles and matrix is observed especially with pictures obtained at a magnitude of 1500. This behaviour is noticed for both epoxy and WAX matrixes.
- After crush test, the amount of collapsed microspheres increases as expected. In fact, it has been shown in literature [6] that the crush of syntactic foam is due to collapse of a large amount of microsphere that leads to a volume reduction of the sample. Nevertheless, even after crush test the interface between matrix and glass bubbles still looks cohesive.

Based on SEM observation, it clearly appears that syntactic foams used in this study presents a good interface between glass bubbles and matrix.

The next step is devoted to setting up and validating a simple mathematical model that can describe the influence of both the matrix stiffness and HGMS volume fraction on the crush pressure of a syntactic foams made with HGMS of mean density of 0.15 g/cm³.

3.5. Modelling hydrostatic strength of HGMS15 syntactic foam

3.5.1. Model description and identification

This section is devoted to the proposition of a model to describe changes in crush pressure considering both matrix stiffness and HGMS volume fraction. As the exact physical mechanisms involved here are not fully understood yet, a phenomenological model is preferred. Furthermore, we have tried to keep this model as simple as possible. The following equation is proposed:

$$P_{crush} = \alpha E(1 - \nu) + \delta/\nu \quad (8)$$

With P_{crush} the crush pressure of the foam, E the compressive modulus of the resin, ν the microsphere volume fraction, and α and δ two empirical constants that have to be determined from experimental data. The first term describes the correlation between the compressive modulus, volume fraction of HGMS, and foam crush pressure, and the

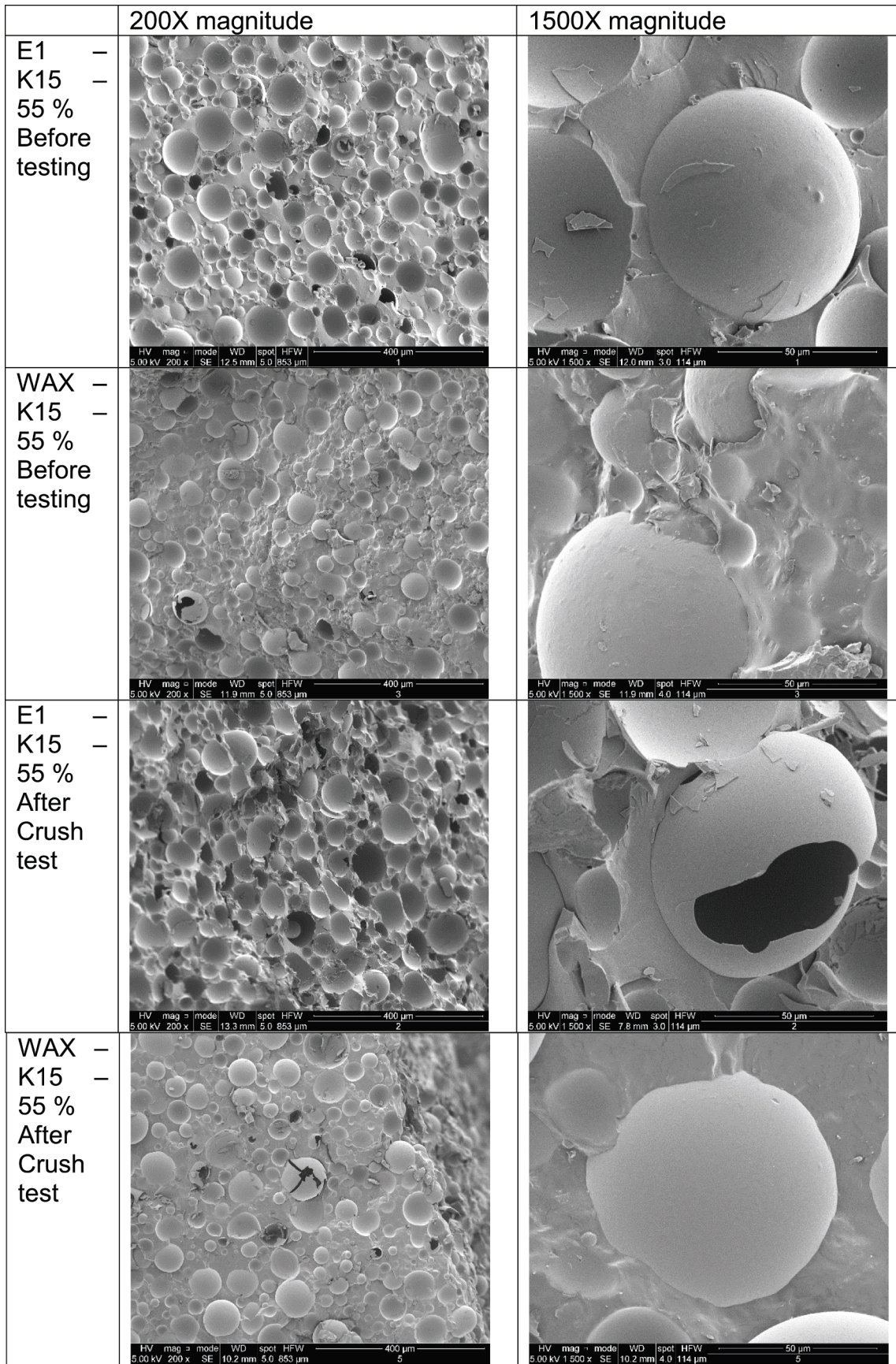


Fig. 6. SEM images before and after crush test for both Epoxy and WAX resins used in this study. .

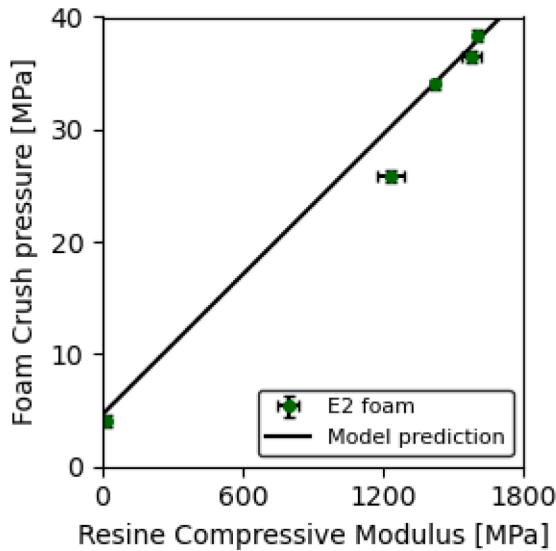


Fig. 7. Application of the numerical model to syntactic foam with E2 resin (HGMS volume content = 0.60).

second term describes the fact that there is no crush pressure for a pure resin (volume fraction of 0).

The parameters α and δ can be determined by solving the following matrix equation:

$$\begin{pmatrix} E_0(1-\nu_0) & 1/\nu_0 \\ \vdots & \vdots \\ E_n(1-\nu_n) & 1/\nu_n \end{pmatrix} * \begin{pmatrix} \alpha \\ \delta \end{pmatrix} - \begin{pmatrix} P_c^0 \\ \vdots \\ P_c^n \end{pmatrix} = 0 \quad (9)$$

With E_i , the resin compressive modulus, ν_i the HGMS volume fraction, and P_c^i the crush pressure of the tested sample indexed by i , with i between 0 and the number of tested samples n (in our case, $n = 96$). The equation was solved using the function `linalg.lstsq` implemented in `python`, that computes a least-squares solution of the matrix equation [32]. Results give $\alpha = 0.0519$ and $\delta = 2.79$ (coefficient of determination $R^2 = 0.99$).

As shown by the dotted line in Figs. 4, 5a and 5b, the proposed model is able to describe both the impact of matrix stiffness and microsphere volume fraction within the range considered here, i.e. compressive modulus between 5 Pa and 1600 MPa and volume fraction of HGMS between 0.3 and 0.6. In order to check the relevance of the proposed model as a predictive tool for the syntactic foams collapse pressure, a new syntactic foam has been considered in the next section.

3.5.2. Relevance of the proposed model

A new syntactic foam based on the same HGMS but a different epoxy matrix (E2) will be considered in this section. This part of the work has been performed in order to evaluate the relevance of the phenomenological model proposed above. The epoxy used here has different mechanical properties to the one used for identification (i.e. E1). Results from experimental data are compared to the results obtained with the model described in Section 3.5.1 in Fig. 7. The resin compressive modulus, and foam crush pressure, were determined using the same

method as previously, at testing temperatures of 21, 25, 30, 35 and 50 °C; results are presented in Fig. 7. As already observed, an increase in testing temperature leads to a decrease in matrix stiffness as well as a decrease in collapse pressure of the foam. These experimental results (points in Fig. 7) are compared with the empirical prediction proposed here (line in Fig. 7) and show a reasonable correlation. This suggests that the proposed model can be used to describe the crush pressure of any syntactic foam made of HGMS of 0.15 g.cm⁻³ density, knowing both resin properties and microspheres volume fraction within the range considered here (i.e. i.e. compressive modulus between 5 Pa and 1600 MPa and volume fraction of HGMS between 0.3 and 0.6). It is worth noting that it is possible to describe the crush pressure of syntactic foam here because the interface between the matrix and the polymer is good. In fact, as already shown in literature [14], if the interface is not good enough it leads to lower mechanical properties. Moreover, in our case loading rate has been kept constant for all experiments. In the future the impact of loading rate on crush pressure of syntactic foams will be considered.

4. Conclusions

The strength of syntactic foams made with HGMS under hydrostatic loading has been considered in this study. For that 3 model syntactic foams have been characterized. All of them having the same HGMS but made with three different types of matrixes and several HGMS volume fractions in the foam. More than 100 model material samples have been considered in this study.

From experimental results, it clearly appears that syntactic foams strength under hydrostatic loading depends strongly on the mechanical properties of the matrix. As long as the interface between glass bubble and matrix is good, it appears that the stiffer the matrix, the higher its crush pressure. The present work also highlighted that the hydrostatic resistance of a syntactic foam largely depends on the hollow glass microsphere volume fraction. The less microspheres are used, the higher is the crush pressure. But the use of a low glass microspheres content leads to an increase in syntactic foams density and therefore to a decrease of the buoyancy, this is crucial from a practical point of view.

A simple empirical model has been proposed for the first time to describe changes in crush pressure induced by both matrix properties and HGMS volume fraction. Two parameters have to be identified in order to predict the crush pressure of syntactic foam; these two parameters have been identified for the glass microspheres considered in this study (i.e. with a density of 0.15 g/cm³). Then this model has been validated using data obtained with a third syntactic foam (with a different epoxy matrix).

When higher hydrostatic resistance is needed for deeper applications, the nature of glass microspheres is changed; HGMS with a smaller diameter and a thicker wall, therefore with a higher density, are used. It would be interesting to consider if the model proposed here for one type of HGMS can be adapted to the other types of microspheres.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix

When testing HGMS under hydrostatic loading, the buoyancy measurements lead to volume variations measurements of the glycerol/HGMS mixture. Since the glycerol compressibility is not negligible with respect to the HGMS volume variations, it must be deduced from the measurements.

Since the volume fraction of HGMS in the mixture is 0.55, the mixture volume can be expressed as:

$$V_{HGMS}(P) = V_{mixture}(P) - V_{glycerol}(P) \quad (A.1)$$

With V_{HGMS} the volume (L) of microsphere, $V_{mixture}$ the measured volume (L) of the mixture and $V_{glycerol}$ (L) the volume of glycerol in the mixture, and P the applied hydrostatic pressure (MPa). Considering the glycerol as a compressible fluid, its volume can be expressed as:

$$V_{glycerol} = V_{glycerol}^0 - V_{glycerol}^0 * P / \beta \quad (A.2)$$

With $\beta = 2.1 \times 10^{-16} \text{ MPa}^{-1}$ the glycerol compressibility, P the applied hydrostatic pressure (MPa), and $V_{glycerol}^0$ the initial volume of glycerol in the mixture. Having a volume fraction of HGMS of 0.55 in the mixture, and 1 L of the mixture being tested, the initial volume of glycerol becomes $V_{glycerol}^0 = 0.45 \text{ L}$

Finally:

$$V_{HGMS}(P) = V_{mixture}(P) - 0.45 * (1 - P / \beta) \quad (A.3)$$

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