Characterisation of Expancel thermoplastic microspheres and their influence on the mechanical properties of all-polymer syntactic foams

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Abstract

Due to their highly favourable thermal, mechanical, and acoustic properties in extreme environments, syntactic foams have emerged as a popular material choice for a broad variety of applications. They are made by infiltrating a polymeric matrix, in either a glassy or polymeric state, with hollow microspheres made from a wide range of materials. In particular, hollow plastic microspheres, such as Expancel made by Nouryon have recently emerged as an important filler medium, with the resulting all-polymer composites taking on excellent damage tolerance properties, strong recoverability under large strains, and very favourable energy dissipation characteristics. There is however, a near-complete absence of statistical information on the diameter and shell-thickness distributions of these microspheres. In this work, using X-Ray computed tomography, focused ion beam, and scanning electron microscopy, we report on these quantities and observe the spatial distribution of microspheres within a syntactic foam. We then employ this data to predict the effective stress-strain response of the foams at small strains, using both analytical micromechanical methods and computational finite element methods, where the latter involves the construction of appropriate representative volume elements. We find excellent agreement between the predictions of the effective Young’s modulus and Poisson ratio from the computational and theoretical methods and good agreement between these predictions and experimental results for the macroscopic response.

Keywords: A. Polymer-matrix composites (PMCs), C. Finite element analysis (FEA), C. Elastic properties, D. Scanning Electron Microscopy (SEM), X-Ray Computed Tomography (CT)

1. Introduction

Syntactic foams are lightweight synthetic composites consisting of a metal, ceramic or polymer matrix and microsphere inclusions\cite{1-5}. The mechanical properties of syntactic foams can be tailored by adjusting the matrix material and/or type and volume fraction of the microspheres\cite{2-4}. For these reasons, syntactic foams are suitable for applications within numerous industries including the aerospace, automotive, marine and sports equipment sectors\cite{3,4,6-9}. In order to save time, effort, and money in the development of new syntactic foams, it is beneficial to be able to predict the mechanical response of syntactic foams, given information regarding their constituent parts and microstructure.

This study focusses on hollow plastic (Expancel) microsphere based syntactic foams, where the matrix is polyurethane. Such foams have been identified in previous research as having properties of interest for underwater applications\cite{10}. Despite this, plastic microsphere foams have received significantly less attention\cite{11-13} compared to glass microsphere foams\cite{15-21}.

It has been established that, in general, syntactic foams exhibit complex loading/unloading behaviour, which becomes more pronounced at higher microsphere filling fractions\cite{3,21,22}. Under uniaxial compression, the stress-strain response of a typical glass-based syntactic foam, with a large (40-50\%) microsphere volume fraction, consists of three regimes. At low strains the deformation is entirely linearly elastic, with the microspheres providing a strong stiffening mechanism. At medium strains, the macroscopic response exhibits a plateau region, due to the crushing failure of individual microspheres, i.e., the filling of the microsphere cavities with debris. For this reason, glass microsphere foams are non-recoverable over a large strain regime and are therefore inappropriate in applications involving large repetitive strains. Hollow plastic microspheres appear to be more suitable under such loading, as the shells tend to flatten and buckle under load, without damage\cite{5,23}. An all-polymer syntactic foam is therefore identi-
fied as possessing significantly higher “recoverability” than glass-based systems.

An important focus in modelling the mechanical behaviour of syntactic foams has been the linear elastic regime; for which both analytical and computational models have been proposed [24,25]. Computational models are predominantly finite element models of representative volume elements (RVEs) drawn from idealised or imaged microstructures. A significant bottleneck which hampers the success of such models however is the quality of the microstructural data used as inputs. Here, in order to address this issue for the material in question, Expancel thermoplastic microspheres are characterised using X-Ray computed tomography (CT), focussed ion beam (FIB) and scanning electron microscopy (SEM). These results represent the first statistical description of the wall thickness and diameter of Expancel microspheres and their arrangement within syntactic foams. We then employ this data in both RVE and analytical methods, which coupled with experimental data allows us to predict the effective Young’s modulus and Poisson ratio of the syntactic foam, simultaneously permitting an estimate for the Poisson ratio of the microsphere shell itself.

It is well-established that, like other composites, syntactic foams of a given microsphere volume fraction can exhibit differing mechanical properties according to the size, shape and distribution of the embedded microspheres [24,26,27,29]. Therefore a key parameter required as an input to such models is the distribution of the diameter, $a$, of the microspheres. For the Expancel microspheres studied here, a range of microsphere diameters is specified by the manufacturer [30] but precise information and distributions appear to be unknown. Similarly, it is also unknown whether a homogenous distribution of microspheres is achieved within the final foams, or if there is residual clustering from the manufacturing process. Clustering of microspheres may lead to anisotropy in the mechanical properties of the final foam and also the potential for lower damage tolerance [20].

Previously, microsphere diameter distributions have been obtained through stereography of 2D optical micrographs [4,21]. More recently, X-Ray CT has been used to image thermoplastic microspheres, with 2D analysis of the digital CT slices revealing the diameter distribution [31]. Here, we deduce the spatial arrangement and diameter distribution of in-foam microspheres through micro-scale X-Ray CT and automated 3D analyses.

In addition to microsphere diameter, the microsphere shell thickness affects the mechanical properties of syntactic foams, even when the volume fraction is held constant [22,25,32]. The shell thickness, $h$, is therefore another key parameter for any modelling scheme. The shells of the Expancel microspheres studied here are expected to be of the order of hundreds of nanometres in thickness and therefore unresolvable using conventional micro-scale X-Ray CT. As with the diameters, statistical information regarding shell thickness distributions is not available [30]. Previous modelling works have inferred the thicknesses of hollow microspheres by considering the size and densities of the microspheres [2,32,33]. This approach assumes that microspheres of a given diameter have identical shell thicknesses. This assumption has not been tested for the Expancel microspheres studied here, but was shown to be incorrect for the thick (micrometre-scale) carbon microspheres in [31]. It is likewise unknown whether the thickness of each individual microsphere is constant [2,33]. To assess these assumptions and inform models, the shell thickness of Expancel microspheres are measured here using nano-scale X-Ray radiography. To validate these measurements, and reveal any variation in the shell wall thicknesses, additional microspheres are investigated using FIB-SEM techniques, analogously to previous studies of solid plastic [34] and hollow glass [35] microspheres.

Finally, we employ the experimentally deduced parameters and microstructures in order to infer the Poisson ratio of the shell. Although the Young’s modulus of the shell is considered as known, with previous values appearing in the literature, the Poisson ratio is not. This therefore completes the characterisation of the geometrical and mechanical properties of Expancel microspheres, providing important baselines for the future study of composite materials made with polymeric microspheres.

2. Microsphere Diameters and in-foam Distribution

The syntactic foams examined here are made using two different hollow thermoplastic microspheres. These are the ‘920 DE 80 d30’ and ‘551 DE 40 d42’ Expancel grades [30], hereafter termed ‘920’ and ‘551’ respectively. These microspheres were distributed within a polyurethane matrix at three different volume fractions (2%, 10% and 40%) for a total of six different samples (see [5] for details regarding the manufacture of the samples). In this section, we characterise the diameter distribution and spatial arrangement of the embedded microspheres using X-Ray CT.

2.1. Method

For each grade and volume fraction combination, matchstick samples (approximately 1 - 2 mm thickness and of arbitrary height) were scanned using an Xradia Versa 520 X-Ray CT instrument. Scanning was done using a beam energy of 80 kV and current of 4.0 W. For each scan, 1601 projections were collected using a 10x optical lens and 4x4 detector binning, resulting in a voxel size of ~1.5 μm. To ensure good signal/noise levels in the final reconstruction, the exposure time of each projection (~10 s) was set to provide at least 5000 counts; requiring ~5 hours per sample. Reconstruction was achieved via filtered back-projection, using XMRecon software.

Analysis of the CT results was done using Avizo 9.70 software. For each dataset, the microspheres were segmented to facilitate automated analysis. Segmentation is the act of assigning voxels to different labels intended to
Figure 1: Example slices taken from the X-Ray CT reconstruction of the six foam samples. The white boxes highlight regions where microspheres are clustered.

Figure 2: Example of the segmented CT data, from the 10% 920 grade sample: a) 2D slice showing the labelling of microspheres as discrete objects, with each colour representing a distinct microsphere (although only eight unique colours were used here); b) 3D rendering of the microspheres present in each slice of the CT dataset, from an arbitrary perspective.
Figure 3: Diameter statistics for the 920 (a) and 551 (b) grade Expancel microspheres, obtained through segmentation and label analyses of the X-Ray CT results. Microspheres below 5 µm equivalent diameter have been removed, as these are finer than the scan resolution. The mean diameters of the 920 and 551 grade microspheres are 35.9 µm and 21.2 µm, respectively. The diameter, \(a\), is lognormally distributed as \(\ln(a) \approx N(\mu, \sigma)\), where \(N\) denotes a normal (Gaussian) distribution, with the fitting parameters: \(\mu(920)=3.34979, \sigma(920)=0.696313; \mu(551)=2.93424, \sigma(551)=0.485412\), where \(\mu\) is the the mean of the logarithmic diameter values and \(\sigma\) is the standard deviation of logarithmic diameter values.

represent the phases within a material (e.g. the matrix and microspheres). Assignment is typically done on the basis of the greyscale value (i.e. density) of each voxel. Here, segmentation was achieved using the ‘Interactive Thresholding’ module in Avizo, to select dark (low density) features. Prior to segmentation, a non-local means filter was applied to reduce noise. The microsphere label was then cleaned using the ‘Fill Holes’ and ‘Remove Spots’ modules, to remove features smaller than the scan resolution (nominally 3 - 4 × voxel size). The ‘Separate Objects’ module was used to split microspheres in contact into discrete objects; ensuring valid diameter statistics. Label analysis was then performed; giving positional and geometric data for each microsphere.

2.2. Results and Discussion

Figure 1 shows example 2D slices extracted from the 3D reconstruction of each sample. In these images, the microspheres can be identified as the dark (low density) circular features. It is evident in the lower volume fraction samples that there is a tendency for microspheres to arrange into clusters, as highlighted in Figure 1. The presence of irregular lighter patches in the polyurethane matrix is noted and we conjecture that these are small inhomogeneities arising from the polyurethane mixing process that will not affect the mechanical behaviour of the samples significantly. For each scan, the microspheres were segmented, as described in Section 2.1 and depicted in Figure 2. Label analysis was conducted to give diameter statistics for each microsphere grade, which are shown in Figure 3, with lognormal distribution fits as described in the caption of the figure. We calculated the mean diameters to be 21.20 ± 0.04 µm and 35.89 ± 0.10 µm for the 551 and 920 grades, respectively. Interestingly, the manufacturers quote a range of 30 - 50 µm for the 551 grade and 55 - 85 µm for the 920 grade [30]. It is unclear however, how the ranges quoted in the manufacturer specifications were obtained. In each sample we have scanned, over 60,000 microspheres were identified and analysed. Regardless, it is possible that microspheres segregate according to their size as they are dispersed into the foam matrix; potentially leading to a population of smaller microspheres in our samples. This could be explored in the future by scanning samples of foam taken from different regions of the same mould.

3. Microsphere shell thickness

In this section, nano-scale X-Ray radiography was used to measure the shell thicknesses of multiple 920 grade microspheres, of various diameters. To validate these results, FIB sectioning of selected microspheres was performed, with the shell thickness recorded through SEM imaging.

3.1. Method

Individual microspheres were picked up electrostatically and then mounted onto needles with glue. These microspheres were then imaged using an Xradia Ultra nanoCT instrument, operating in high-resolution mode (16 nm pixel). Imaging was conducted using a beam energy of 8 kV and power of 0.9 kW. For each microsphere, five radiographs (exposure time ≥ 200 s ; 1×1 binning) were collected and averaged. Line profiles were plotted across the shells revealed in the averaged radiographs to infer the shell thicknesses, as depicted in Figure 4.

To validate the radiography results, FIB sectioning of individual needle-mounted spheres was also performed.
Figure 4: Depiction of the shell thickness measurement method: a) X-Ray Radiograph showing part of the shell of a hollow plastic microsphere; i) optical image showing the needle-mounted sphere and the the location where the radiograph was taken; b) 10 pixel wide line profile of the arrow plotted on a), the shell wall is taken as the difference of the two highlighted points.

Figure 5: Summary of the shell thickness measurements from the radiography investigations. The solid line denotes the mean shell thickness from our measurements, whereas the dotted line is an estimate of the mean from the manufacturer [30, 36]. The shaded regions represent the confidence intervals, derived from the variance of our measurements.

Figure 6: Results of the FIB sectioning investigation: a) secondary electron (SE) image of a Ag-Pd coated microsphere prior to sectioning; b) SE image of the sectioned microsphere, at 52° stage tilt (normal to ion beam); c) higher magnification image of the highlighted area, showing the shell thickness measurements.
This was done using a FEI NovaLab 660 FIB-SEM instrument comprising a Ga\(^+\) ion beam column coupled with a scanning electron microscope. Prior to sectioning, the needle-mounted microspheres were attached to a SEM stub and coated with 15 nm of Ag-Pd, using a Quorum Q150T sputter coater, to ensure good conductivity. Sectioning of each sphere was done using an ion beam energy of 30 keV and a current of 21 nA, using the ‘Si-CCS’ (silicon cleaning cross-section) routine. In each case, the final cut line was positioned along the centre of the microsphere. Regardless of the actual microsphere diameter, the FIB was set to mill to an accumulated depth of 10 µm (calibrated against Si.) This was sufficient to fully section microspheres up to give a single shell thickness value. The shell thickness was taken as the difference in position between the lowest greyscale point and the peak associated with outer shell wall. This method was tested in MatLab and depicts the procedure used to infer the shell thick-ness from up to five unique line profiles were averaged to recover a known shell thickness. For each microsphere, the hollow microsphere and was found to be a reliable way to measure the microsphere material, compared to Si. The cross-section of each microsphere was then inclined normal to the electron beam and imaged using the secondary electron (SE) imaging mode, at a beam energy of 5 keV and current of 0.43 nA.

### 3.2. Results and Discussion

Figure 4 shows an example of the collected radiographs and depicts the procedure used to infer the shell thicknesses. For each radiograph, lines profile were plotted from the microsphere interior, across the shell, to the exterior. The shell thickness was taken as the difference in position between the lowest greyscale point and the peak associated with outer shell wall. This method was tested in MatLab simulations of X-Ray attenuation through an idealised hollow microsphere and was found to be a reliable way to recover a known shell thickness. For each microsphere, the results from up to five unique line profiles were averaged to give a single shell thickness value.

Radiography was performed for 25 microspheres, covering a diameter range of 18 – 110 µm (approximately 66% of the 920 grade distribution shown in Figure 3). The results of this investigation are summarised in Figure 5. The mean shell thickness and three confidence intervals, derived from the standard deviation of the line profile measurements, are also plotted. The diameter of each microsphere was measured using the optical microscope attached to the Xradia Ultra system (see inset of Figure 4). Interestingly, we find little correlation between microsphere diameter and shell wall thickness, mirroring results for the thick (micrometre-scale) walled carbon microspheres in [3].

To confirm the shell thickness measurements from the radiography investigations, FIB sectioning of five needle-mounted microspheres was conducted. Figure 6 shows an example of the SEM images which were collected. Table 1 summarises the shell measurements for each microsphere which was investigated. For each microsphere, the measured shell thickness is compared to the corresponding radiography result, which reveals a good level of agreement between the two techniques. The SE images collected reveal significant variation in the shell thickness. This can be as large as 256%, at points separated by only a few microns, as shown in Figure 6(c,d). The reason for such large local variations is unknown but may be related to variations inherent in the original, unexpanded microspheres and/or the expansion process itself.

### 4. Homogenisation schemes and estimates for the elastic constants of the thermoplastic shell

Having determined statistics for the diameters and shell wall thicknesses of Expancel microspheres, we now describe two schemes that can be employed to estimate the effective properties of the syntactic foam with 920 grade Expancel microspheres distributed throughout. One is a finite element-based procedure whereas the other is entirely theoretical, based on classical methods from micromechanics. In both cases we employ the statistical distributions obtained above on the microsphere diameters and the measurements of the shell thicknesses. It appears that previously only average data on microsphere diameters has been used. These homogenisation methods allow us to estimate the small-strain linear elastic parameters of the shell material, using previously obtained experimental results for syntactic foams from [5].

Both schemes rely on solving the elastostatic equations

$$\mu u_{i,j,j} + (\mu + \lambda) u_{j,j} = 0,$$

where $\mu$ and $\lambda$ are Lamé coefficients which vary within the RVE depending whether the field point is inside the matrix, shell or the interior of the microsphere, and $u_j$ denotes the displacement from equilibrium, $i, j = \{x, y, z\}$.

#### 4.1. Finite Element Computational Procedure

We briefly outline an energy-based homogenisation method [37-41] valid for dilute foams, which involves solving (1) in some finite domain $\Omega$, which is a representative volume element (RVE): here we use a cube of volume $L_0^3$. First, microspheres are distributed inside a RVE (example shown in Figure 7(a)) defined by statistics on their diameters and shell thickness as derived experimentally above. The boundary conditions employed are perfect continuity of displacement and traction across microsphere/matrix boundaries and vanishing normal stress $\sigma_{ij}n_j = 0$ on the boundaries.

| # | Diameter $a$ (µm) | FIB-SEM $h$ (µm) | $\sigma_h$ (nm) | Radiography $h$ (µm) | $\sigma_h$ (nm) |
|---|---|---|---|---|---|
| 1 | 33.5 | 249 | 71 | 212 | 41 |
| 2 | 40.0 | 261 | 84 | 312 | 26 |
| 3 | 45.8 | 369 | 79 | 268 | 39 |
| 4 | 69.9 | 245 | 59 | 292 | 61 |
| 5 | 79.1 | 230 | 78 | 230 | 25 |

Table 1: Comparison of the FIB-SEM and nano-scale radiography measurements of the microsphere shell thickness, $h$, and standard deviation, $\sigma_h$. 
interior walls of the hollow shells, where $\sigma_{ij}$ is the $ij$th component of the Cauchy stress and $n_j$ is the $j$th component of the (inward pointing) normal to the interior wall of the microsphere. As two elastic constants are sought, we approximate two fundamental modes of deformation on the RVE, each of which isolates one of the elastic moduli.

Figure 7: Example volume element with a 10% filling fraction of Expancel microspheres, generated from the diameter distributions in Figure 4 for use in the FE modelling.

The first such mode of deformation is a hydrostatic compression, obtained by imposing the conditions

$$u_x(\pm L_0/2, y, z) = u_y(x, \pm L_0/2, z) = u_z(x, y, \pm L_0/2) = \mp \delta L_0/2$$

for some small $\delta > 0$. Subsequently we solve the elastostatic system (2) everywhere inside the RVE and then calculate the total strain energy density

$$W_{\text{tot}} = \frac{1}{2} \int_{\Omega} \sigma_{ij} \varepsilon_{ij} \, dV_i$$

(2a)

where $\sigma_{ij}$ and $\varepsilon_{ij}$ denote the $ij$th component of the Cauchy stress and linear strain tensors respectively. Next, in order to deduce the effective elastic properties, we assume a form for the constitutive law that is isotropic and homogeneous, i.e., $\sigma_{ij} = K^\text{FE} \varepsilon^\text{eff}_{ij} + 2\mu^\text{FE} \varepsilon^\text{eff}_{ij} - \frac{1}{3} \varepsilon^\text{eff}_{kk} \delta_{ij}$, where $\delta_{ij}$ is the Kronecker delta and we write the effective strain energy density

$$W^\text{FE} = \frac{1}{2} \left(K^\text{FE} \varepsilon^\text{eff}_{kk} \delta_{ij} + 2\mu^\text{FE} \left(\varepsilon^\text{eff}_{ij} - \frac{1}{3} \varepsilon^\text{eff}_{kk} \delta_{ij}\right)\varepsilon^\text{eff}_{ij}\right).$$

(2b)

For the displacement conditions specified above, $\varepsilon^\text{eff}_{xx} = \varepsilon^\text{eff}_{yy} = \varepsilon^\text{eff}_{zz} = -\delta'$ and $\varepsilon^\text{eff}_{xy} = \varepsilon^\text{eff}_{xz} = \varepsilon^\text{eff}_{yz} = 0$. Upon calculating the actual strain energy density in the RVE associated with this deformation $W_{\text{tot}} = W^\text{FE}$ and equating this with the effective form in (2), we get the effective bulk modulus

$$K^\text{FE} = 2W^\text{FE}/(3\delta')^2.$$

(3a)

The second mode of deformation considered is a simple shear, obtained through the conditions $u_j(\pm L_0/2, y, z) = \mp z\delta \delta_{ix}/2$, $u_y(x, -L_0/2, z) = u_y(x, L_0/2, z) = 0$, where $\delta > 0$ is small and we also impose periodic conditions for improved numerical convergence $u_j(-L_0/2, y, z) = u_j(L_0/2, y, z)$. Once again equating the actual ($W^\text{tot}_n$) and effective energies, we find that $\mu^\text{eff} = 2W^\text{FE}/\delta^2$.

(3b)

In order to obtain averaged values for the effective properties, we carry out this procedure using COMSOL multiphysics software, within Matlab. We use RVEs with a fixed volume fraction of microspheres which are defined via the statistical diameter distributions derived above. We ensemble average elastic constant values over a sample of 10 RVEs of $L_0 = 100 \mu$m length for each filling fraction, where each cell contains non-overlapping spheres whose diameters are randomly chosen from the lognormal distribution determined earlier and whose positions are drawn from a uniform distribution. For the matrix material we use $E = 7.08$ MPa, $\nu = 0.49$, and $\rho = 1112$ kg/m$^3$ and for the shell material we use $E = 3$ GPa [12], $\nu = 0.2$, $\rho = 71$ kg/m$^3$ and a fixed shell thickness of 290 nm (from Figure 5).

4.2. Micromechanical Theoretical Procedure

We employ a modified version of the micromechanical method proposed for the dilute volume fraction regime in [43], with the modification here being to average over distributions of diameters derived experimentally above. The canonical isolated shell problem (a single shell in an unbounded matrix) is studied in both hydrostatic compression and shear, see e.g. [44, 45]. The actual energy in a sphere of radius $R$ centred on the centre of a microsphere is then equated to the effective energy inside a sphere of the same size within a homogeneous medium having effective moduli $\tilde{K}^\text{Mic}$ and $\tilde{\mu}^\text{Mic}$. The radius $R$ is then chosen such that the actual volume fraction in the medium is $\Phi = (a/2)^3/R^3$. As derived in [43] it can be shown that

$$\tilde{K}^\text{Mic} = K_0 + \Phi \left(\frac{a_0 + a_3 \delta^3}{b_0 + b_3 \delta^3}\right),$$

(4)

$$\tilde{\mu}^\text{Mic} = \mu_0 + \Phi \left(\frac{c_0 + c_3 \delta^3 + c_7 \delta^7 + c_10 \delta^{10}}{d_0 + d_3 \delta^3 + d_7 \delta^7 + d_{10} \delta^{10}}\right),$$

(5)

with $\eta = 1 + 2h/a$, where as already introduced $h$ is the shell thickness and $a$ is the shell diameter. We provide the expressions for $a_n, b_n, c_n$ and $d_n$ in Appendix A noting in particular the typographical error in $b_0$ in [43], which we correct here. Note that these expressions have the correct limiting behaviour to recover the dilute volume fraction expressions when $h \rightarrow a/2$ ($\eta = 0$, solid inclusions) and $h \rightarrow 0$ ($\eta = 1$, voids), see e.g. [46, 47].

We now introduce the probability distribution function $p_\eta(a)$ with $\mu(920) = 3.34979$ and $\sigma(920) = 0.696313$, the lognormal distribution fitted to the 920 grade microspheres.
described above. In order to incorporate the variation in the microsphere diameter into the model we define

\[ K_{\text{Mic}} = K_0 + \Phi \int_0^\infty p_a(a) \left( \frac{a_0 + a_3 a^3}{b_0 + b_3 a^3} \right) \, da, \]  
\[ \mu_{\text{Mic}} = \mu_0 + \Phi \int_0^\infty p_a(a) \left( \frac{c_0 + c_3 a^3 + c_5 a^5 + c_7 a^7 + c_{10} a^{10}}{d_0 + d_3 a^3 + d_5 a^5 + d_7 a^7 + d_{10} a^{10}} \right) \, da. \]  

Recalling that \( \eta = 1 - 2h/a \), as with the FE procedure we fix \( h = 290 \text{ nm} \) and employ \( E_0 = 7.08 \text{ MPa}, \) \( \nu_0 = 0.49 \) and for the shell material we use \( E_s = 3 \text{ GPa} \) \cite{42}, \( \nu_s = 0.2 \).

### 4.3. Results and discussion

Results for both the Finite Element and Micromechanical methods at 2% and 10% volume fraction are compared against experimentally obtained values from \cite{5} in Table 2 for syntactic foams made from grade 920 Expancel microspheres. The schemes above predict the effective linear elastic bulk and shear moduli. Using the relations of linear elasticity the effective Young’s modulus and Poisson’s ratio are within 10% and 15% of experimental measurements of the effective properties at 0% volume fraction. In particular in \cite{42} the linear elastic moduli at 40% filling fraction were deduced as \( E_{\text{exp}} = 10.9 \text{ MPa} \) and \( \nu_{\text{exp}} = 0.34 \). We found that the micromechanical model predicts \( E_{\text{eff}} = 11.7 \text{ MPa}, \) \( \nu_{\text{eff}} = 0.439 \). This indicates that the predictions of the Young’s modulus are fairly reasonable even at higher volume fractions in this case, although clearly there is a departure of the Poisson’s ratio prediction away from experimental values for this dilute model, as should perhaps be expected at such high volume fractions.

It is clear that both FE and micromechanical methods agree fairly well in the dilute volume fraction regime considered above differing by 10% at most. There is reasonable agreement of these theoretical predictions with the experimental measurements with a slight discrepancy, differing by 15% at most. There are a number of possible explanations for this discrepancy. The first of these is that the boundary conditions between the spheres and the matrix may not be ideal, i.e., the outer shell walls and the matrix may not be in ideal contact as is assumed in any theoretical analysis. The second is that the (potentially) entrained gas has an impact \cite{49}. A third reason is that there could be a persistent gradient in the microsphere positional distributions may not reflect that observed in the disc samples. In future work this hypothesis could be tested by assuming the microsphere shell material to be pure polystyrene (with a Young’s modulus 3 - 3.5 GPa and Poisson’s ratio 0.34), for example, and introducing gradients. It could also be investigated experimentally by imaging small syntactic foam samples taken from different regions of the mould, as suggested in Section 2.2.

### 5. Conclusions

In this work, syntactic foams containing Expancel thermoplastic microspheres have been investigated using X-Ray computed tomography (CT), nano-scale radiography and secondary electron (SE) imaging, in combination with focussed ion beam (FIB) sectioning. The aim was to characterise both the diameter distribution and shell thicknesses of these microspheres. Prior to this work, no statistical information on these parameters was available.

X-Ray CT revealed that the 551 and 920 grades of Expancel microspheres exhibit lognormal diameter distributions. Mean diameters of 21.20 \pm 0.04 \text{ µm} and 35.89 \pm 0.10 \text{ µm} were computed for the 551 and 920 grades, respectively. It is noted that these values are both below

| \% | \( E_{\text{exp}} \) | \( \nu_{\text{exp}} \) | \( E_{\text{eff}}^{\text{FE}} \) | \( \nu_{\text{eff}}^{\text{FE}} \) | \( E_{\text{eff}}^{\text{Mic}} \) | \( \nu_{\text{eff}}^{\text{Mic}} \) |
|---|---|---|---|---|---|---|
| 0 | 7.08 | 0.49 | 7.3 | 0.489 | 7.33 | 0.489 |
| 2 | 7.10 | 0.48 | 7.3 | 0.489 | 7.33 | 0.489 |
| 10 | 7.53 | 0.46 | 8.6 | 0.487 | 8.31 | 0.486 |

Table 2: Comparison of small-strain elastic constants \( E \), the Young’s modulus (MPa) and \( \nu \) the Poisson ratio, for syntactic foams made with 920-grade Expancel microspheres where subscripts “exp” and “eff” denotes experimental and effective values respectively. Superscripts “FE” and “Mic” on the effective properties refer to the Finite Element and Micromechanical approaches respectively.
the manufacturers specifications. The segregation of microspheres according to their size during assembly of the foams is proposed as one possible reason for the discrepancy, which should be investigated further. The tomography has revealed that within the foams, microspheres have a tendency to cluster together. This was particularly pronounced in the dilute (2% and 10%) foams and could potentially lead to local anisotropy in the material properties.

Nano-scale radiography was conducted on individual microspheres and revealed a high degree of variation in the shell thicknesses. No correlation was found between the shell thickness and microsphere diameter, however. FIB sectioning of microspheres allowed for direct observations (using SE imaging) of the microsphere shell walls. The images verified our radiography measurements and demonstrated the substantial variation in shell thickness of individual microspheres.

The diameter and shell thickness statistics were utilised, alongside previous experimental results, to conduct finite element modelling and theoretical micromechanical modelling of syntactic foams comprising polyurethane matrices and Expancel microspheres. The computational approach is an energy-based homogenisation method, which involves imposing hydrostatic and then shear deformations, separately, to recover the effective Young’s modulus and Poisson ratio of the material. The theoretical approach solves canonical isolated shell problems and equates the strain energy of this problem in the locality of the shell with an equivalent effective homogeneous medium. For dilute foams, the recovered effective properties from these methods are within 15% of experimentally measured values. With refinement of our estimate for the Poisson ratio of the microsphere shell, $\nu_{\text{shell}}$, it is possible that this agreement could be further improved, although it could be that this discrepancy arises for other reasons, which were outlined above. The success of the methods highlights the potential for experimentally-informed models to accurately predict the behaviour of other existing foam systems or even to assist in the digital design of new foams with bespoke material properties.

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Appendix A. Expressions in the micromechanical method

For a single type of shell of constant thickness and diameter, of volume fraction $\Phi$ in the matrix the following expressions are derived for the effective bulk and shear moduli.

\[
\tilde{K}_{\text{eff}}^{\text{Mic}} = K_0 + \Phi \frac{a_0 + a_3 \eta^3}{b_0 + b_3 \eta^3}, \tag{A.1}
\]

\[
\tilde{\mu}_{\text{eff}}^{\text{Mic}} = \mu_0 + \Phi \left( \frac{c_0 + c_5 \eta^5 + c_7 \eta^7 + c_{10} \eta^{10}}{d_0 + d_3 \eta^3 + d_5 \eta^5 + d_{10} \eta^{10}} \right), \tag{A.2}
\]

where $\eta = 1 - 2h/d$, $h$ is the shell thickness and $d$ is the shell diameter. Furthermore

\[
a_0 = 4\mu_s(K_s - K_0)(3K_0 + 4\mu_0), \tag{A.3}
\]

\[
a_3 = -K_s(3K_0 + 4\mu_s)(3K_0 + 4\mu_0), \tag{A.4}
\]

\[
b_0 = 4\mu_s(3K_0 + 4\mu_0), \tag{A.5}
\]

\[
b_3 = -12K_s(\mu_s - \mu_0), \tag{A.6}
\]

noting that our $b_0$ corrects the typographical error in [33] and finally,

\[
c_0 = 15\mu_0(\lambda_0 + 2\mu_0)(\mu_s - \mu_0)(9\lambda_0 + 14\mu_0)[14\mu_s(4\mu_0 + \mu_s) + \lambda_s(16\mu_0 + 19\mu_s)], \tag{A.7}
\]

\[
c_3 = -375\mu_0(\lambda_0 + 2\mu_0)[3(9\mu_s^2 - 10\mu_0\mu_s + 8\mu_0^2)\lambda_s^2 + 4\mu_s(14\mu_0^2 - 9\mu_0\mu_s + 16\mu_s^2)\lambda_s + 28(\mu_s^2 + 2\mu_0\mu_s^1)], \tag{A.8}
\]

\[
c_5 = 15120\mu_0(\lambda_0 + 2\mu_0)(\mu_s - \mu_0)^2(\lambda_s + \mu_s)^2, \tag{A.9}
\]

\[
c_7 = -375\mu_0(\lambda_0 + 2\mu_0)(\mu_s - \mu_0)^2(27\lambda_s^2 + 56\mu_s\lambda_s + 28\mu_s^2) \tag{A.10}
\]

\[
c_{10} = 15\mu_0(\lambda_s + 2\mu_0)(\mu_s - \mu_0)(19\lambda_0 + 14\mu_0)[\lambda_s(9\lambda_0 + 6\mu_0) + 2\mu_s(7\mu_0 + 8\mu_0)], \tag{A.11}
\]

\[
d_0 = (9\lambda_0 + 14\mu_s)[\lambda_0(6\mu_s + 9\mu_0) + 2\mu_0(8\mu_s + 7\mu_0)][\lambda_s(19\mu_s + 16\mu_0) + 14\mu_s(\mu_s + 4\mu_0)], \tag{A.12}
\]

\[
d_3 = -50 \left[ 3(9\lambda_0(3\mu_s + \mu_0\mu_s - 4\mu_0^2) - 2\mu_0(-36\mu_s^2 + 15\mu_0\mu_s + 28\mu_0^2))\lambda_s^2 \right.
\]

\[
+ 2\mu_s(3\lambda_0(28\mu_s^2 + 13\mu_0\mu_s - 8\mu_0^2) + 14\mu_0(16\mu_s^2 + 3\mu_0\mu_s - 16\mu_0^2))\lambda_s
\]

\[
+ 28\mu_0^2(2\mu_0(4\mu_s^2 + 3\mu_0\mu_s - 7\mu_0^2) + 3\lambda_0(\mu_s^2 + \mu_0\mu_s - 3\mu_0^2)) \right], \tag{A.13}
\]

\[
d_5 = 1008(\mu_s - \mu_0)(\lambda_s + \mu_0)^2(2\mu_0(8\mu_s + 7\mu_0) + \lambda_0(6\mu_s + 9\mu_0)), \tag{A.14}
\]

\[
d_7 = -25(\mu_s - \mu_0)(2\lambda_s^2 + 56\lambda_0\mu_s + 28\mu_s^2)(2\mu_0(8\mu_s + 7\mu_0) + \lambda_0(6\mu_s + 9\mu_0)), \tag{A.15}
\]

\[
d_{10} = 2(\mu_s - \mu_0)(19\lambda_0 + 14\mu_0)[3\lambda_0(9\lambda_0(\mu_s - \mu_0) + 2\mu_0(12\mu_s - 7\mu_0))
\]

\[
+ 2\mu_s(3\lambda_0(7\mu_s - 12\mu_0) + 56\mu_0(\mu_s - \mu_0))]. \tag{A.16}
\]