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On the elastic behavior of syntactic foams

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Abstract

This work concerns composite materials called "syntactic foams", i.e., materials made by a polymeric matrix filled with hollow solid inclusions. Explicit formulae for the homogenized values of the elastic moduli of these materials are derived, by means of the physical model and the corresponding elastic solution used by Hervé and Pellegrini [Hervé, E., Pellegrini, O., 1995. Archives Mechanics. 47 (2), 223–246.]. The morphologically representative patterns theory of Bornert et al. [Bornert, M., Stolz, C., Zaoui, A., 1996. Journal of the Mechanics and Physics of Solids 44, 307–331.] is used to take into account both the influence of the filler gradation and the presence of "unwanted" voids in the matrix, factors that are shown to be important in characterizing the mechanical behavior of syntactic foams. Comparisons with both experimental and numerical results show that the techniques used are capable of predicting, with good accuracy, the elastic moduli of real syntactic foams, i.e., those arising from an actual production process.

Keywords: Homogenization; Syntactic foams; Composite materials

1. Introduction

Syntactic foams are particulate composites obtained by filling a polymeric matrix with hollow solid inclusions, most often approximately or exactly spherically shaped. Syntactic foams are preferred to standard foams (containing voids only) when high specific mechanical properties are required, rather than just low density.

Typical applications of such composites range from aerospace plug manufacturing to ablative heat shields for re-entry vehicles, underwater buoyancy aids and, more recently, structural components such as hulls and bulkheads of ships and submarines. In these last cases, syntactic foams have been recently employed also as the core material of sandwiches (Bardella and Genna, 2000). These applications often exploit several features typical of syntactic foams, beside the high specific mechanical properties, such as the low dielectric constant, the good ablation behavior, the good match to acoustic impedance of water (for sonar applications), and the good thermal and water insulation properties.

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The computation of the elastic properties of syntactic foams can be tackled by means of homogenization techniques. However, the use of standard methods is somewhat made difficult by the presence of a void phase, which may cause some classical techniques to furnish zero bounds and that causes a poor behavior of methods which cannot properly take into account the connectedness of the matrix, a crucial ingredient if a void phase is present.

We have been able to find four methods proposed in the literature to deal with the computation of the effective elastic moduli of syntactic foams. The simplest one is that of Nielsen and Landel (1994), who suggest to first homogenize the inclusion alone, using, for the shear modulus, a very simple formula derived by Nielsen, and then to choose from any of the standard methods available to homogenize particulate composites. More refined approaches are proposed by Lee and Westmann (1970) and Huang and Gibson (1993). The first one makes use of Hashin's CSA technique (Hashin, 1962), modified to account for hollow inclusions, thereby obtaining a single result for the homogenized bulk modulus, and bounds for the shear modulus. The second one uses a similar approach, which requires the knowledge of elastic solutions for the problem of a cube of finite size, containing a hollow sphere centered on its centroid. Both techniques, however, produce rather inaccurate results, specially for high volume fractions of filler.

The fourth method is given by Hervé and Pellegrini (1995). Starting from a work by Christensen and Lo (1979), who considered a material containing filled homogeneous spherical inclusions, and who computed only a "self-consistent-scheme" estimate of the homogenized elastic moduli (Hill, 1965; Budiansky, 1965), Hervé and Pellegrini (1995) studied the problem of a composite material made by n-layered isotropic spherical inclusions, and, by exploiting the theory of the Morphologically Representative Patterns (MRP) (Bornert et al., 1996), they were able to compute a complete set of estimates of the homogenized elastic moduli. In this case, the used MRP is similar to the "composite sphere" of Hashin (1962), here defined by an $(n-1)$-layered sphere, included within a spherical shell of matrix, whose thickness is such that the volume fraction of the composite sphere (an n-layered inclusion) is the same as that of the syntactic foam.

Hervé and Pellegrini were able to find the complete elastic solution of the problem of such an MRP embedded within an infinite medium made by an arbitrary elastic isotropic material. Starting from this solution, they computed estimates of the elastic moduli of both standard foams (in which the MRP is a two-layered inclusion – the void and the matrix) and syntactic foams, in which the MRP is a three-layered inclusion.

When trying to apply the results of Hervé and Pellegrini (1995) to real syntactic foams, however, one may encounter some difficulties. The first source of uncertainty is given by the presence of unwanted voids in the composite, a consequence of the production modalities. This fact is quite important, and it is admittedly one of the sources of scatter in the experimental results reported by Huang and Gibson (1993), as well as a possible source of discrepancy between theoretical estimates and experimental results. The second one derives from the fact that quite often the filler particles exhibit a significant scatter in their effective density, not taken into account by the solution of Hervé and Pellegrini. Even when the filler particles are nominally identical to each other, such as, for instance, in the material studied by Huang and Gibson (1993), such scatter, due to the production modalities of the particles, is not negligible. A final (and minor) difficulty is given by the rather involved aspect of the formulae in the paper of Hervé and Pellegrini, which are particularized only to the case of standard foams.

In this work, we give some explicit formulae for the estimates of the elastic moduli of syntactic foams, and illustrate the results obtained by extending the theory of Hervé and Pellegrini (1995), for the three-layered inclusion case, to account for the presence both of unwanted voids and a graded filler. The extension is again based on the MRP theory and consists of a superposition of multiple MRPs into the same Representative Volume Element (RVE); the elastic solution required to compute all the relevant averages is that found by Hervé and Pellegrini (1995), in which both matrix and inclusions are taken to be isotropic linear elastic, and the interfaces between the phases are considered perfectly bonded. Such an extension has already been developed in some cases (e.g., Bornert et al., 1994) but, to the best of our knowledge, not for syntactic foams.

In Section 2 the homogenization formulae will be illustrated, and some details enabling to use them will be reported in Appendix A. Next, the analytical results will be compared both with the few experimental results we have been able to find in the literature, and with the results of tests on several syntactic foams studied both at the University of Brescia, by the authors, and at the Politecnico of Milano (Maier, 1998). The analytical predictions will also be compared with the results of numerical simulations, performed on unit cell models.

2. Homogenization of syntactic foams with graded filler and "unwanted" voids

Here we give the trace of the procedure followed to obtain the analytical estimates of the elastic moduli of syntactic foams made by graded filler with possible unwanted voids. The basic theory is the same described in detail in Hervé and Pellegrini (1995) which the reader is referred to for more details.

A four-phase model is considered (Fig. 1), made by a single composite sphere (Hashin, 1962) surrounded by an infinite homogeneous medium of arbitrary elastic constants. The composite sphere is defined by an inner hollow spherical shell, made by the filler material, surrounded by a shell of matrix material. The thickness of the external shell is such that the cubic power of the ratio between the outer radius of the inclusion, b, and the outer radius of the composite sphere, c, is equal to the volume fraction f of the filler of the composite.

If the syntactic foam is treated as a macroscopically homogeneous and isotropic medium, we need to estimate two elastic constants, the effective bulk modulus K_0 and the effective shear modulus G_0.

To compute estimates of the effective shear modulus we must start by solving the elastic problem defined on the four-phase model of Fig. 1, applying a simple shear boundary condition at infinity. Using Love's

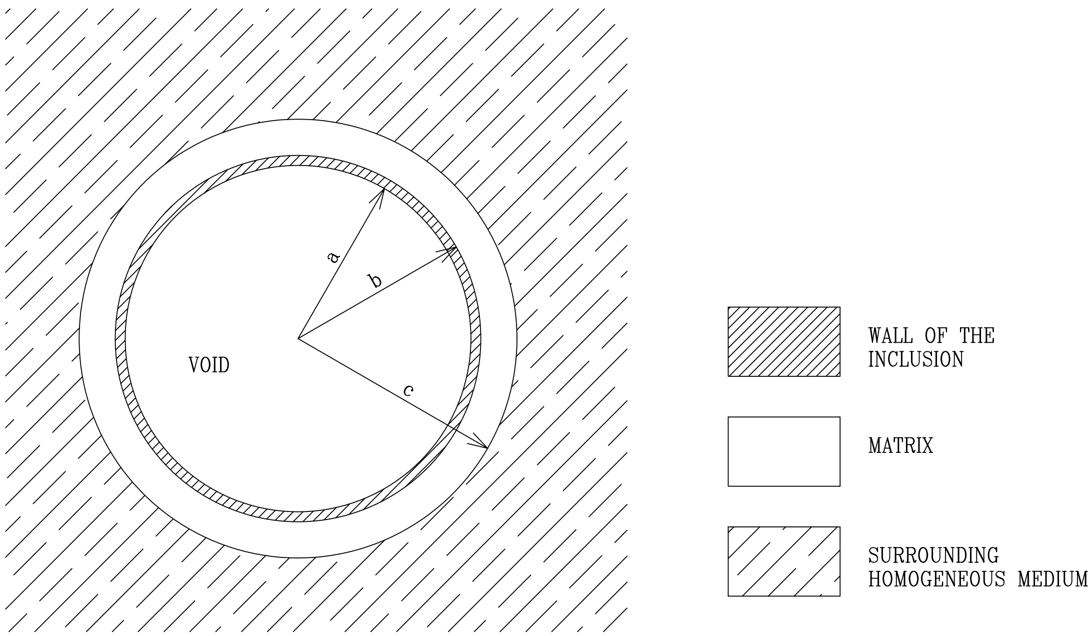

Fig. 1. The four-phase model.

results (Love, 1944) for the case of simple shear, the problem can be solved in terms of spherical solid harmonics of integral degree 2 and −3 (Hashin, 1962). Since the results of the homogenization process are the same if one applies stress or displacement boundary conditions, here we refer to displacement boundary conditions only, applied at infinity on the four-phase model:

$$u_i^0 = E_{ij}^0 x_j, \tag{1}$$

where x_j, $j = 1, \ldots, 3$, are the cartesian coordinates of a reference frame with the origin in the center of the composite sphere in the four-phase model, u_i^0 are the displacements prescribed at infinity and E_{ij}^0 represents the homogeneous strain field applied to the boundary of the four-phase model.

Following Hashin's procedure, we apply a simple shear strain condition, i.e.,

$$E_{12}^0 = E_{21}^0 = \gamma \neq 0, \qquad \text{all other components } E_{ij}^0 = 0, \tag{2}$$

which corresponds to the following choice of simple shear displacements:

$$u_1 = \gamma x_2, \qquad u_2 = \gamma x_1, \qquad u_3 = 0, \tag{3}$$

where γ is a given arbitrary constant known term.

The solution of this problem, which can be found following the general path indicated by Hervé and Pellegrini (1995), yields the strain field in the four phases of the model, $\varepsilon_{ij}^{(\zeta)}$, where the index ζ becomes v in the inner void of the inclusion, i in the wall of the inclusion, m in the matrix shell, and s in the surrounding medium.

We must now use this result within the context of an RVE. For a syntactic foam filled by spheres exhibiting different wall thicknesses and including voids, we consider, as our RVE, a Composite Sphere Assemblage made by N types of composite spheres, each characterized by a known ratio a_λ/b_λ, $\lambda = 1, \ldots, N$. The presence of voids is taken into account by simply considering a type of inclusion with wall thickness $b_\lambda - a_\lambda = 0$, i.e., $a_\lambda/b_\lambda = 1$. The RVE is therefore made up of N types of composite spheres that have variable size and that fill the whole space; we assume that *every* composite sphere is such that the cubic power of the ratio between the outer radius of the inclusion and the outer radius of the composite sphere is equal to the volume fraction, f, of the filler in the syntactic foam. There are other ways to prescribe that the volume fraction of the filler in such a model is equal to the volume fraction f of the studied composite. Here, we have not pursued the analysis of this aspect in detail; this is another so far unexplored interesting application of the extension to a multiple pattern RVE of the basic MRP theory.

For each composite sphere λ, we consider the four-phase model of Fig. 1, with the boundary conditions at infinity described above, and compute the relevant elastic solution $\varepsilon_{ij}^{(\zeta),\lambda}$.

Following the path of reasoning of Zaoui (1997), we now prescribe that the applied strain field E_{12} at the boundary of the RVE coincides with the volume average of the corresponding local fields in such an ensemble of composite spheres, i.e.,

$$E_{12} = \frac{1}{V} \int_V \varepsilon_{12}(x_i)\, \mathrm{d}V = \langle \varepsilon_{12} \rangle \tag{4}$$

(the symbol $\langle \cdot \rangle$ indicates the volume average over the RVE, whose volume is V), i.e., by taking account of the presence of N different composite spheres,

$$\langle \varepsilon_{12} \rangle = \sum_{\lambda=1}^{N} f_\lambda \bar{\varepsilon}_{12}^{(\mathrm{CS}),\lambda}, \tag{5}$$

where the symbol f_λ indicates the fraction of the filler type λ to the whole filler, and $\bar{\varepsilon}_{12}^{(\mathrm{CS}),\lambda}$ indicates the volume average computed on the single composite sphere λ.

By writing the average stress–strain relationship for the RVE,

$$2G_0^{\mathrm{est}}\langle\varepsilon_{12}\rangle = \langle\tau_{12}\rangle, \tag{6}$$

one can obtain the desired estimate for the homogenized shear modulus. In fact, the volume average of the stress τ_{12} can be written, on the basis of the local strain fields, as

$$\begin{aligned}\langle\tau_{12}\rangle &= \frac{2}{V}\int_V G(x_i)\varepsilon_{12}(x_i)\,\mathrm{d}V = \frac{2}{V}\left[\sum_{\lambda=1}^{N}\left(\int_{V_\lambda^{(\mathrm{i})}} G_\lambda^{(\mathrm{i})}\varepsilon_{12}(x_i)\,\mathrm{d}V + \int_{V_\lambda^{(\mathrm{m})}} G_\lambda^{(\mathrm{m})}\varepsilon_{12}(x_i)\,\mathrm{d}V\right)\right] \\ &= 2\sum_{\lambda=1}^{N}\left[G_\lambda^{(\mathrm{i})} f_\lambda^{(\mathrm{i})}\bar{\varepsilon}_{12}^{(\mathrm{i}),\lambda} + G_\lambda^{(\mathrm{m})} f_\lambda^{(\mathrm{m})}\bar{\varepsilon}_{12}^{(\mathrm{m}),\lambda}\right],\end{aligned} \tag{7}$$

where $G_\lambda^{(\mathrm{i})}$ indicates the shear modulus of the inclusion material in composite sphere λ, $f_\lambda^{(\mathrm{m})}$ and $f_\lambda^{(\mathrm{i})}$ indicate the volume fraction of matrix and inclusion materials of composite sphere λ respectively, and $\bar{\varepsilon}_{12}^{(\zeta),\lambda}$ indicates the volume average of the shear strain over layer ζ of composite sphere λ, i.e.,

$$\bar{\varepsilon}_{12}^{(\zeta),\lambda} = \frac{1}{V_\lambda^{(\zeta)}}\int_{V_\lambda^{(\zeta)}} \varepsilon_{12}(x_i)\,\mathrm{d}V. \tag{8}$$

Here, we have used the symbol $G_\lambda^{(\mathrm{m})}$ to indicate a different shear modulus of the matrix associated to each different composite sphere λ. Although such distinction is unnecessary in a linear analysis, where the shear modulus of the matrix is constant over the whole RVE, it becomes essential in a nonlinear analysis, subject of work in progress.

Replacing results (7) and (5) into Eq. (6) one can thus obtain the desired estimate of the homogenized shear modulus G_0^{est}:

$$G_0^{\mathrm{est}} = \frac{\sum_{\lambda=1}^{N}\left[G_\lambda^{(\mathrm{i})} f_\lambda^{(\mathrm{i})}\bar{\varepsilon}_{12}^{(\mathrm{i}),\lambda} + G_\lambda^{(\mathrm{m})} f_\lambda^{(\mathrm{m})}\bar{\varepsilon}_{12}^{(\mathrm{m}),\lambda}\right]}{\sum_{\lambda=1}^{N} f_\lambda \bar{\varepsilon}_{12}^{(\mathrm{CS}),\lambda}}. \tag{9}$$

Finally, recalling that, owing to the definitions,

$$f_\lambda^{(\mathrm{i})} = \frac{V_\lambda^{(\mathrm{i})}}{V} = f_\lambda f\left[1 - \left(\frac{a_\lambda}{b_\lambda}\right)^3\right], \tag{10}$$

$$f_\lambda^{(\mathrm{m})} = \frac{V_\lambda^{(\mathrm{m})}}{V} = f_\lambda(1-f), \tag{11}$$

Eq. (9) can be rewritten as follows:

$$G_0^{\mathrm{est}} = \frac{\sum_{\lambda=1}^{N} f_\lambda\left\{G_\lambda^{(\mathrm{i})} f\left[1 - \left(\frac{a_\lambda}{b_\lambda}\right)^3\right]\bar{\varepsilon}_{12}^{(\mathrm{i}),\lambda} + G_\lambda^{(\mathrm{m})}(1-f)\bar{\varepsilon}_{12}^{(\mathrm{m}),\lambda}\right\}}{\sum_{\lambda=1}^{N} f_\lambda \bar{\varepsilon}_{12}^{(\mathrm{CS}),\lambda}}. \tag{12}$$

The volume averages over the RVE and over the single layers all contain the shear modulus $G^{(\mathrm{s})}$ of the arbitrary surrounding medium in the four-phase model of Fig. 1; therefore, one can obtain several estimates of the homogenized shear modulus by choosing different values for $G^{(\mathrm{s})}$. The best choice is the Self-Consistent one, in which $G^{(\mathrm{s})} = G_0^{\mathrm{est}}$; this makes Eq. (12) implicit in the unknown G_0^{est}.

In Appendix A we summarize all the equations needed to compute G_0^{est}, and we also furnish a quadratic equation whose solution gives the Self-Consistent estimate of the homogenized shear modulus in the basic case of a single composite sphere (i.e., the case studied also by Hervé and Pellegrini for $n = 3$).

The computation of the homogenized bulk modulus $K_0^{\rm est}$ follows exactly the same path, starting, however, from volumetric boundary conditions at infinity on the four-phase model of Fig. 1, i.e.,

$$E_{11}^0 = E_{22}^0 = E_{33}^0 = \theta \neq 0, \qquad \text{all other components } E_{ij}^0 = 0, \tag{13}$$

where θ is an arbitrary constant known term. By proceeding in the same way as for the shear modulus, one thus arrives at the following expression of $K_0^{\rm est}$:

$$K_0^{\rm est} = \frac{\sum_{\lambda=1}^{N} f_\lambda \left\{ K_\lambda^{\rm (i)} f \left[1 - \left(\frac{a_\lambda}{b_\lambda} \right)^3 \right] \bar{\varepsilon}_{kk}^{{\rm (i)},\lambda} + K_\lambda^{\rm (m)} (1-f) \bar{\varepsilon}_{kk}^{{\rm (m)},\lambda} \right\}}{\sum_{\lambda=1}^{N} f_\lambda \bar{\varepsilon}_{kk}^{{\rm (CS)},\lambda}}, \tag{14}$$

where ε_{kk} is the volumetric strain. Again, in Appendix A, we give all the equations necessary to apply Eq. (14) together with the result for the case of a single composite sphere, independent of the choice of the surrounding medium and already reported explicitly by Lee and Westmann (1970).

Note that in both Eqs. (12) and (14) both the shear and the bulk moduli of the infinite surrounding medium appear in the averages of the local fields, which depend in any case on both moduli. Therefore, in the Self-Consistent case, the computation of the homogenized moduli is coupled, except for the trivial case of a single inclusion type ($N = 1$), when the computation of the bulk modulus is independent of the stiffness of the surrounding medium, and, therefore, the computation of the shear modulus becomes uncoupled.

3. Comparison with reference experimental results

In this section we test expressions (12) and (14), in their Self-Consistent version, against experimental results given in the paper of Huang and Gibson (1993).

These results are particularly interesting with respect to the problem of unwanted voids in the matrix, present in the syntactic foam studied by Huang and Gibson. They do actually furnish values of the volume fractions of such voids, thus enabling us to homogenize them together with the filler using the technique described in Section 2. On the contrary, we have no information at all about the granulometry of their filler, which will therefore be characterized by the average values of wall thickness only.

All the necessary data are taken from the microstructural characterization of dog-bone specimens given by Huang and Gibson, shown in Table 1, where f is the volume fraction of the filler, v is the volume fraction of the unwanted voids and m is the volume fraction of the matrix. Table 1 reports also the experimental values of the Young modulus obtained by uniaxial tension tests, together with the analytical estimates computed using Eqs. (12) and (14).

In Fig. 2 we have plotted the results of the homogenization method: the agreement with the experimental data is extremely good from the qualitative viewpoint, and except for case D5, quite acceptable also from the quantitative viewpoint. The maximum error between the predicted and experimental Young modulus values is of about 16% (case D5 excluded).

These results indicate that the presence of unwanted voids in the matrix has a significant effect on the overall elastic properties of the composite. The application of the same homogenization technique to the same composite is performed also by Hervé and Pellegrini *without taking into account the presence of unwanted voids*. Huang and Gibson too compute the homogenized elastic moduli of their material by means of their own homogenization method but again without properly taking the void phase into account; indeed, to account for the unwanted voids, Huang and Gibson propose to compute the stiffness of a fictitious matrix, weaker than the real one. Unfortunately, the use of this inconsistent sequential homogenization cannot give assurance of obtaining good estimates of the effective moduli; indeed, the results of Huang and

Table 1
Microstructural characterization of dog-bone specimens and experimental and analytical Young modulus (Huang and Gibson, 1993)

Specimen	f [%]	m [%]	v [%]	E [MPa]	E [MPa] (12)–(14)
D_1	0.00	100.00	0.00	4890	4890
D_2	2.41	97.21	0.38	4770	4734
D_3	5.17	92.79	2.04	4340	4451
D_4	8.31	89.48	2.21	4370	4293
D_5	9.41	88.53	2.06	3300	4256
D_6	17.54	77.66	4.80	3330	3681
D_7	17.19	74.07	8.74	3120	3390
D_8	18.45	71.19	10.36	2860	3220
D_9	24.51	65.62	9.87	2680	3027
D_{10}	27.17	59.61	13.22	2320	2697
D_{11}	30.20	56.20	13.60	2290	2566
D_{12}	35.33	46.97	17.70	2170	2136

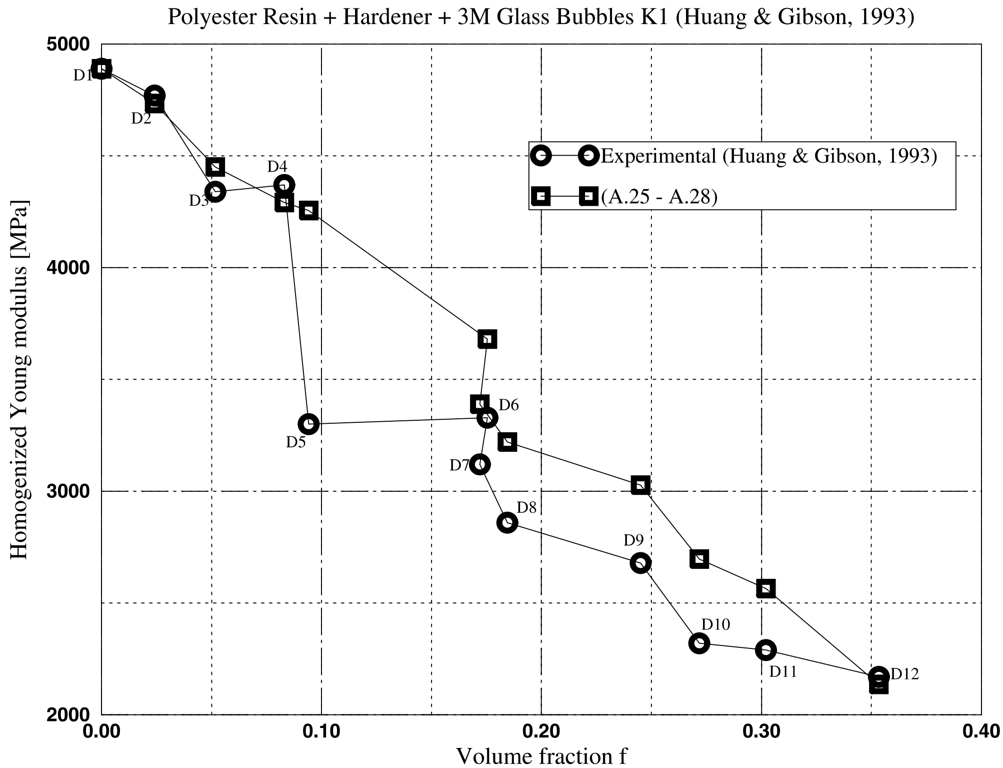

Fig. 2. Analytical and experimental results for the syntactic foam Polyester Resin + Hardener + 3M Glass Bubbles K1 of Huang and Gibson (1993).

Gibson as well as those of Hervé and Pellegrini become rather poor for volume fractions of filler higher than $f = 0.08$, when, as apparent from the data of Table 1, the unwanted void content becomes significant. Hervé and Pellegrini attribute the discrepancy between their estimates and the experimental results to the testing modalities (uniaxial tension tests), which, in their opinion, induce debonding between matrix and filler and therefore weaken the composite. Although this effect might certainly arise (and is avoided by the experimental technique used by Hervé and Pellegrini), we feel that, at reasonably low values of loading, it should be much less significant than the effect of the presence of voids in the matrix. Our computations do indeed confirm this hypothesis.

4. Experimental results on syntactic foams and comparison with analytical estimates

We report here the results of experiments carried out at the Laboratory for Tests on Materials "Pietro Pisa" of the Department of Civil Engineering, University of Brescia, on several syntactic foams. The results refer to five types of syntactic foams, made by two different epoxy resins. Together with these data, obtained by the authors, other results are reported on similar syntactic foams, tested at the Laboratory for Tests on Structures of the Department of Structural Engineering, Politecnico of Milano (Maier, 1998).

Throughout this section, we will deal with fillers characterized by only the average values of wall thickness and diameter, whereas we will consider, in several cases, composites including voids. The analysis of a composite whose filler gradation is known will be done in the next section.

We summarize next the main characteristics of the basic "ingredients" of the five syntactic foams, and report the results of the laboratory tests, together with the corresponding analytical predictions.

4.1. Syntactic foam type 1

- Epoxy resin DGEBA, produced by Dow Chemicals under the name DER 332, with hardener DDM Fluka 32950. The basic properties of this resin, in the fully hardened state, are: Young modulus $E_r = 2800$ MPa, Poisson coefficient $\nu_r = 0.41$, density $\rho_r = 1.18$ g/cm^3. These data have been obtained by one of the authors, and are the average values of several experimental tests (Bardella, 1997);
- filler made by hollow glass microspheres, produced under the name "Scotchlite™ Glass Bubbles" by 3M Italia; in this case, use is made of the spheres indicated with the name "K37", with weight ratio of 0.25, corresponding to a volume fraction $f = 0.5153$. The mechanical properties of the used glass are: Young modulus $E_g = 70\,110$ MPa; Poisson coefficient $\nu_g = 0.23$. These values are not indicated in the data sheet available from the producer (3M Italia, 1993), and have been taken from the quoted paper of Huang and Gibson (1993), who apparently make use of microspheres of the same brand. However, there is a rather strong source of uncertainty with respect to the data values for this glass. For instance, Huang and Gibson indicate a density of their glass $\rho_g = 2.5$ g/cm^3, but in order to obtain internal consistency in the data provided in 3M Italia (1993), we need to use $\rho_g = 2.6$ g/cm^3. This may indicate that also the above-quoted values of the elastic moduli might be incorrect; we will comment on this later in this section. The average diameter of spheres type K37 is 50 μm, and their average wall thickness is 1.28 μm (data given in 3M Italia, 1993).

This syntactic foam has been produced and tested in Brescia. The details of the production and testing modalities (either uniaxial tension/compression or cyclic uniaxial loading) as well as of the equipment used (which has also been used to test the following syntactic foam types 2–4) can be found in the work of Bardella (1999).

It is quite important to note that the production modalities of this foam (resin and filler mixed "by hand" in carefully checked weight ratios, and both mixing and curing done under strong vacuum), hereafter denoted as "traditional", allowed us to obtain a foam with no unwanted voids; this is confirmed by the density measurements, always in agreement with the theoretical densities calculated from the component weight data.

This first type of syntactic foam has been tested at only one volume fraction, $f = 0.5153$. This material has been examined at the Scanning Electron Microscope, both before and after testing it, with the aim both of better understanding its internal structure and of understanding its fracture modalities. The second aspect is outside the scope of this work. The first one, however, deserves some comments.

The microstructure of this syntactic foam, that will be taken into account also to construct numerical models, whose results are commented in Section 6, is shown in Figs. 3 and 4, obtained by means of the Scanning Electron Microscope. Fig. 3 shows a polished section of an untested specimen; from our viewpoint, it is important to observe that the inclusions are distributed more or less randomly without local "lumps". This gives ground to the essential assumption of statistical homogeneity of the composite.

Fig. 4 shows the fracture surface of a specimen; here, one can observe how, at rupture of the composite, the hollow microspheres on the fracture surface are broken. This observation supports the other assumption underlying all the theories supporting this work, i.e., that perfect bond exists between matrix and filler. On the other side, the same observation contradicts a corresponding finding in the work by Hervé and Pellegrini, who report that, in their syntactic foam, at rupture, all the microspheres are intact, suggesting that detachment at the matrix–filler interface might be both a primary source of failure and an indication of damage occurring in the early stages of mechanical tests. We can only attribute this difference to different mechanical and/or geometrical characteristics of the materials used (indeed, the inclusions used by Hervé and Pellegrini are much thicker than those used by us).

Table 2 shows experimental results obtained by the authors on this syntactic foam in terms of elastic moduli both in uniaxial compression (subscript c) and uniaxial tension (subscript t).

The results indicate that the elastic properties of this material are practically deterministic, and that the elastic behavior is practically symmetric in tension and compression, if one neglects a tendency to be slightly stiffer in tension. The average values of the elastic moduli can be assumed to be $E \approx 3500$ MPa and $\nu \approx 0.335$.

The predictions obtained by applying Eqs. (A.25) and (A.28) to this material are the following: $E = 3300$ MPa, $\nu = 0.36$. The Young modulus is underestimated by 6%, while the Poisson coefficient is overestimated by the same amount. This performance can be considered acceptable, especially in the presence of several sources of uncertainty on the basic data. For instance, as said before, we do not know the exact value of the Young modulus of the glass used to produce the filler, and we have chosen the value suggested by Huang

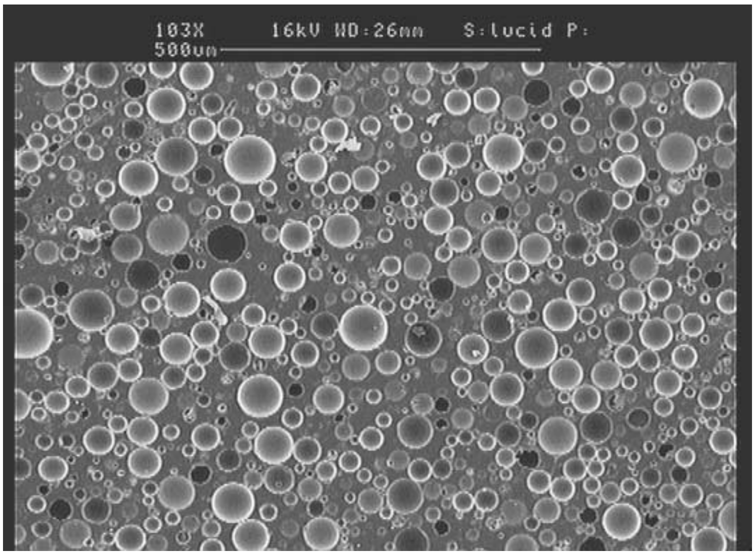

Fig. 3. SEM image of a polished section of a syntactic foam.

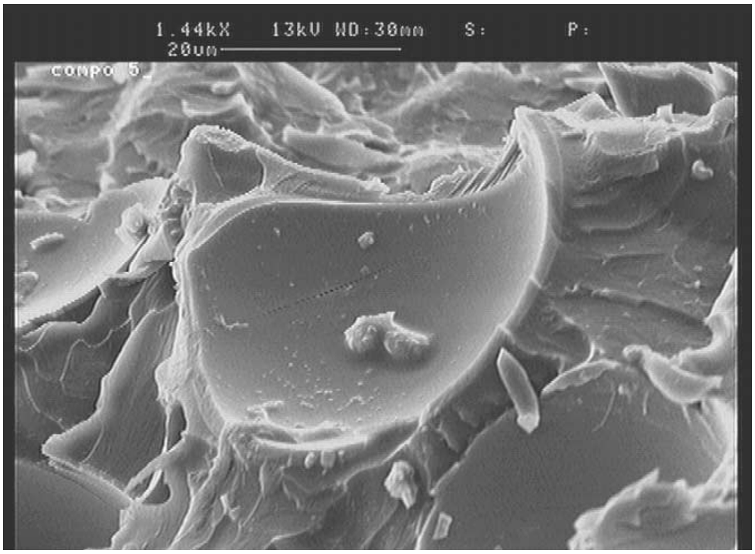

Fig. 4. SEM image of the fracture surface of a syntactic foam.

Table 2
Experimental results for syntactic foam type 1 (Bardella, 1997)

Syntactic foam	f	E_c [MPa]	ν_c [−]	E_t [MPa]	ν_t [−]	Test type	Velocity [mm/min]
DGEBA+K37	0.5153	3440	0.337			Compression	0.5
DGEBA+K37	0.5153	3460	0.336			Compression	0.5
DGEBA+K37	0.5153	3470	0.331			Compression	0.5
DGEBA+K37	0.5153	3450	0.345			Compression	1.0
DGEBA+K37	0.5153			3530	0.333	Tension	0.2
DGEBA+K37	0.5153			3530	0.333	Tension	0.2
DGEBA+K37	0.5153	3480		3480		Cyclic	–
DGEBA+K37	0.5153	3480		3530		Cyclic	–

and Gibson, who seem to have used the same glass spheres. However, as said, their value of the glass density does not agree with the data found in 3M Italia (1993), which suggests that our glass might be different from theirs. If we use, for the Young modulus of glass, the value $E_g = 77\,500$ MPa, as suggested in Brandt (1995) for a low alkali glass, we find, for the composite, $E = 3450$ MPa, practically the exact result.

4.2. Syntactic foam type 2

- Epoxy resin DGEBA as before, with a different hardener (type Laromin-C252, produced by BASF), but with the same elastic moduli;
- filler made by hollow glass microspheres type K37 as before with the same mechanical properties.

This foam differs from the first one because of the production modalities, hereafter indicated as "injection technique". Here, the resin is injected into a container filled with microspheres in such a way as to obtain the highest possible volume fraction of filler. In this way, however, it is inevitable to introduce also unwanted voids in the foam. In this case, both the volume fraction f of the filler and the volume fraction of these unwanted voids have been carefully measured by weighing the specimens, putting them into a muffle furnace and then taking weight of the dry glass; when the injection technique is adopted, unlike the case

Table 3
Experimental and analytical results for syntactic foam type 2

Syntactic foam	f	m	v	E_c [MPa]	ν_c [−]	E [MPa] (12)–(14)	ν (12)–(14)
DGEBA+K37 (silanized)	0.6058	0.3846	0.0096	3485	0.324	3333	0.347
DGEBA+K37	0.5835	0.3778	0.0387	3215	0.329	3128	0.341

with the traditional technique (i.e., the one used to produce the syntactic foam type 1), the exact weight fractions of microspheres and resin are unknown: this is the reason why one needs to burn the resin into a muffle furnace.

Table 3 shows both the experimental results obtained for this foam, and the theoretical predictions, obtained using Eqs. (12) and (14) considering $N = 2$ (i.e., two different composite spheres: $\lambda = 1$ corresponds to the actual filler type K37, and $\lambda = 2$ corresponds to the voids). The symbols f, m and v refer to the same volume fractions already described in the previous section with reference to Huang and Gibson's foams.

Here, the analytical predictions of Young modulus underestimate the experimental ones roughly by 4%, a reasonably good result, considering the already mentioned sources of uncertainty on the initial data.

It is interesting to note that the first specimen was produced employing silanized microspheres; the filler can be silanized (i.e., subjected to a surface treatment with chemical agents (Tempesti, 1998)) to allow the improvement of the adhesion with the matrix. As one can see in Table 3, this technique, still under study, allows to produce a material with a void content v lower than that observable in the specimen produced with regular filler; it is then likely that the silanization helps also in reducing the content of unwanted voids, producing then a stiffer specimen, beside improving the ultimate behavior. Indeed, it is our opinion that most of the unwanted voids are entrapped at the interface between matrix and filler, i.e., where the resin, because of its viscosity, cannot fill all the spaces left between adjacent microspheres, interstices that are too narrow when the maximum volume fraction of filler is the goal, as in the case of the injection technique. Further, this fact can be indirectly proved in another way: current research on the nonlinear behavior of syntactic foams shows, by means of finite element simulations, that the uniaxial behavior of some types of syntactic foams, experimentally found to be weaker in compression than in tension, can be ascribed to the buckling of the hollow microspheres that are not completely surrounded by the matrix, i.e., those inclusions which are partially surrounded by unwanted voids.

4.3. Syntactic foam type 3

- Epoxy resin SP Ampreg 20™, produced by SP Systems, Montecatini Advanced Materials, with hardener "UltraSlow Hardener", produced by SP Systems, Montecatini Advanced Materials. The material properties of this epoxy resin are $E_r = 3700$ MPa, $\nu_r = 0.4$ (these data have been also measured in our laboratory by means of uniaxial tension or torsion tests); density $\rho_r = 1.15$ g/cm^3;
- the same microspheres described for the syntactic foam types 1 and 2, again of the type K37, with various volume fractions and granulometries.

This syntactic foam has been prepared in Brescia, and tested both in Brescia and in Milano. Its production modalities have been similar to those used for foam type 2, i.e., injection with no control both on the volume fraction of the filler and on the presence of unwanted voids. In this case, unfortunately, we did not measure the unwanted voids content. Therefore, the volume fractions used to obtain the analytical predictions are only theoretical, since they are based on the final density of the foam and the assumption of absence of unwanted voids. Of course, these volume fractions are overestimates of the actual volume fractions of filler, which, together with the neglect of the presence of unwanted voids, leads to a systematic overestimate of the Young modulus in the analytical predictions, as shown in Table 4.

Table 4
Experimental and analytical results for syntactic foam type 3

Syntactic foam	f^*	E_c [MPa]	ν_c [−]	E [MPa] (A.25)–(A.28)	ν (A.25)–(A.28)	Test location
SP+K37	0.665	3452	0.311	3889	0.332	Brescia
SP+K37	0.647	3465	0.320	3884	0.332	Brescia
SP+K37	0.659	3535	0.322	3887	0.332	Brescia
SP+K37	0.659	3455	0.319	3887	0.332	Brescia
SP+K37	0.678	3150		3893	0.33	Milano
SP+K37 sifted ($32 \leqslant \Phi \leqslant 45$)	0.585	3826	0.309	4395	0.344	Brescia
SP+K37 sifted ($32 \leqslant \Phi \leqslant 45$)	0.601	3847	0.305	4416	0.342	Brescia
SP+K37 sifted ($32 \leqslant \Phi \leqslant 45$)	0.623	3700		4446	0.340	Milano
SP+K37 sifted ($45 \leqslant \Phi \leqslant 63$)	0.704	2900		2999	0.321	Milano
SP+K37 sifted ($63 \leqslant \Phi \leqslant 90$)	0.626	3075	0.294	3740	0.335	Brescia
SP+K37 sifted ($63 \leqslant \Phi \leqslant 90$)	0.665	2942	0.269	3742	0.330	Brescia
SP+K37 sifted ($63 \leqslant \Phi \leqslant 90$)	0.633	3153	0.314	3740	0.334	Brescia

The results are divided into four rows. The first one refers to tests done both at Brescia and at Milano (Maier, 1998) on a syntactic foam made with K37 spheres as furnished by the producer, in the quoted volume fractions. Here the symbol f^* indicates that, as said, the volume fractions are derived from the wrong assumption of absence of unwanted voids.

The specimens tested in Milano are significantly less stiff than those tested by us in Brescia, even at comparable volume fractions. This indicates that the specimens tested in Milano contain more unwanted voids than those tested in Brescia. The theoretical predictions, as expected, are in excess up to 19% in the case of the material tested in Milano, and up to about +9% in the case of the tests done in Brescia.

This tendency of the theoretical predictions to overestimate the stiffness of the material is maintained throughout the cases reported in Table 4. The last three rows of this table refer to syntactic foams produced by the inclusion of microspheres taken from the K37 batch but sifted in order to obtain a controlled granulometry. The results refer to three growing diameter sizes: $32 \leqslant \Phi \leqslant 45$, $45 \leqslant \Phi \leqslant 63$ and $63 \leqslant \Phi \leqslant 90$ μm, where Φ indicates the diameter of one inclusion. The theoretical results, for all these cases, are always better when the volume fractions are smaller; for instance, for the case with $f^* = 0.585$ and $32 \leqslant \Phi \leqslant 45$ μm, the estimates have an error of +15%, whereas the tests done in Milano on the composite with the same granulometry, but with $f^* = 0.623$, find the analytical predictions to be in error of +20%. Again, this is a result of the uncertainty about the unwanted voids content, which increases when f^* increases. All the analytical results, however, are reasonable approximations of the experimental ones.

4.4. Syntactic foam type 4

- Epoxy resin SP Ampreg 20^{TM} with the same hardener as in foam type 3 with the same mechanical properties;
- same glassy hollow microspheres as in the preceding foams (type K37).

Table 5
Experimental and analytical results for syntactic foam type 4

Syntactic foam	f	m	v	E_c [MPa]	ν_c [−]	E [MPa] (12)–(14)	ν (12)–(14)
SP+K37 + voids	0.493	0.472	0.035	3324	0.344	3576	0.342
SP+K37 + voids	0.493	0.471	0.036	3339	0.336	3568	0.342
SP+K37 + voids	0.492	0.470	0.038	3340	0.339	3553	0.342
SP+K37 + voids	0.496	0.474	0.030	3399	0.333	3614	0.343
SP+K37 + voids	0.445	0.520	0.035	3411	0.344	3565	0.348
SP+K37 + voids	0.447	0.522	0.031	3392	0.343	3595	0.348
SP+K37 + voids	0.442	0.517	0.041	3358	0.344	3520	0.346
SP+K37 + voids	0.447	0.522	0.031	3389		3595	0.348
SP+K37 + voids	0.289	0.646	0.065	3309	0.363	3314	0.357
SP+K37 + voids	0.291	0.649	0.060	3341	0.362	3349	0.358
SP+K37 + voids	0.393	0.564	0.043	3407	0.349	3494	0.351
SP+K37 + voids	0.395	0.567	0.038	3477	0.349	3531	0.352
SP+K37 + voids	0.400	0.573	0.027	3426	0.345	3613	0.354
SP+K37 + voids	0.398	0.571	0.031	3424	0.350	3582	0.354

This foam, similar to the preceding foam type 3, has been produced by means of the traditional technique, and therefore the unwanted void content has been easily measured. The relevant results, both experimental and analytical, are summarized in Table 5.

The analytical results seem quite accurate for small volume fractions, and tend to lose some accuracy only for $f \geqslant 0.45$. In any case, the maximum errors are of about +7%, an acceptable result anyway.

4.5. Syntactic foam type 5

- Same resin and hardener as for material types 3 and 4;
- again, "Scotchlite^{TM} Glass Bubbles" produced by 3M Italia, but here of the type K1, with two different volume fractions. The spheres type K1 have an average diameter of 70 μm and an average wall thickness of 0.58 μm; they are thinner and lighter than the spheres type K37 used in all the previous foams.

This type of syntactic foam, tested only at the Politecnico of Milano, using machines and measurement techniques similar to those used by the authors to test the previous ones, contains unwanted voids in known volume fraction.

The relevant results, both experimental and analytical, are summarized in Table 6, where the experimental results are the average values of several tests done at the Politecnico of Milano (Maier, 1998).

The analytical results overestimate the experimental ones by 16% in the first case, and by 8% in the second. It is difficult to precisely catch the source of these errors, scattered among different reasons. One possible explanation, however, lies in the brittleness of the very thin K1 spheres, broken in non-negligible percentage during the production process of the material. The real syntactic foam, in this case, is obviously

Table 6
Experimental and analytical results for syntactic foam type 5

Syntactic foam	f	m	v	E_c [MPa]	ν_c [−]	E [MPa] (12)–(14)	ν (12)–(14)
SP+K1 with voids	0.509	0.410	0.081	1610	0.347	1873	0.323
SP+K1 with voids	0.523	0.421	0.056	1835	0.322	1971	0.325

rather softer than what appears to the analytical model. This observation helps to explain also part of the error, illustrated in Fig. 2, arising when applying the homogenization technique to the foam of Huang and Gibson. Their foam makes use of spheres type K1 too, and therefore, in their case also, one should expect the analytical predictions to overestimate experimental results. More details about all the laboratory tests summarized here can be found in the work of Bardella (1999).

5. Influence of the variation of thickness of the inclusions

As already mentioned, and as visible also in Fig. 3, the ratio a/b, between the inner and the outer radius of the used microspheres, in reality, at least for this type of filler (glassy microspheres type K37 – see Section 4) can hardly be considered as constant, equal to an average value.

In order to evaluate the scatter of the ratios a/b for the filler used in the syntactic foams types 1–4, described in Section 4, we have sifted the K37 spheres using five sifts, thus obtaining five "monodispersed" sifted samples. We have then measured the density, ρ_λ, and the volume fraction, f_λ, of all the sifted samples, $\lambda = 1, \dots, 5$. The obtained results are shown in Table 7, in which the value of the ratio between the inner and outer radius of any sifted sample of filler, a_λ/b_λ, is computed assuming that the density of the glass is equal to 2.6 g/cm^3.

Let us recall that the average diameter of the K37 spheres is $\Phi = 50$ μm, and that the average ratio a/b is 0.9501 (data given in 3M Italy (1993)). Note that "average ratio a/b" means the ratio a/b of a fictitious hollow sphere that has the same effective density of the real filler, which then has to be computed as

$$\frac{a}{b} = \sqrt[3]{\sum_{\lambda=1}^{N} f_\lambda \left(\frac{a_\lambda}{b_\lambda}\right)^3}. \tag{15}$$

It is then apparent, from the results shown in Table 7, that there is some deviation, from the average values, both for the wall thicknesses and especially for the diameters of the hollow spheres.

Fig. 5 compares the results of the homogenization method, obtained by considering only the average values for the inclusions with those obtained considering $N = 5$ as shown in Table 7, for the case of syntactic foam type 1, as described in Section 4, considering the full range of filler volume fractions and assuming the absence of unwanted voids. The results are shown as relative errors, for both the shear and the bulk modulus, between the 5 and the 1 inclusion type solutions.

It is apparent that the differences between the values obtained using just the average values for the filler wall thickness, and those obtained from the more accurate data of Table 7, are in this case relatively small. The maximum difference is in fact of about 2%. This suggests that, for the morphology of these syntactic foams, and considering the difficulty of obtaining accurate information about the real values of the microsphere geometry, for all practical purposes it is sufficient to characterize the filler by means of its average values of the ratio a/b.

Table 7
Wall thickness gradation for filler K37

λ	Diameter [μm]	f_λ	ρ_λ [g/cm^3]	a_λ/b_λ
1	$\Phi \geqslant 90$	0.0906	0.2928	0.9610
2	$63 \leqslant \Phi \leqslant 90$	0.6481	0.3494	0.9530
3	$45 \leqslant \Phi \leqslant 63$	0.0551	0.2552	0.9661
4	$32 \leqslant \Phi \leqslant 45$	0.1737	0.4594	0.9372
5	$\Phi \leqslant 32$	0.0325	0.6920	0.9020

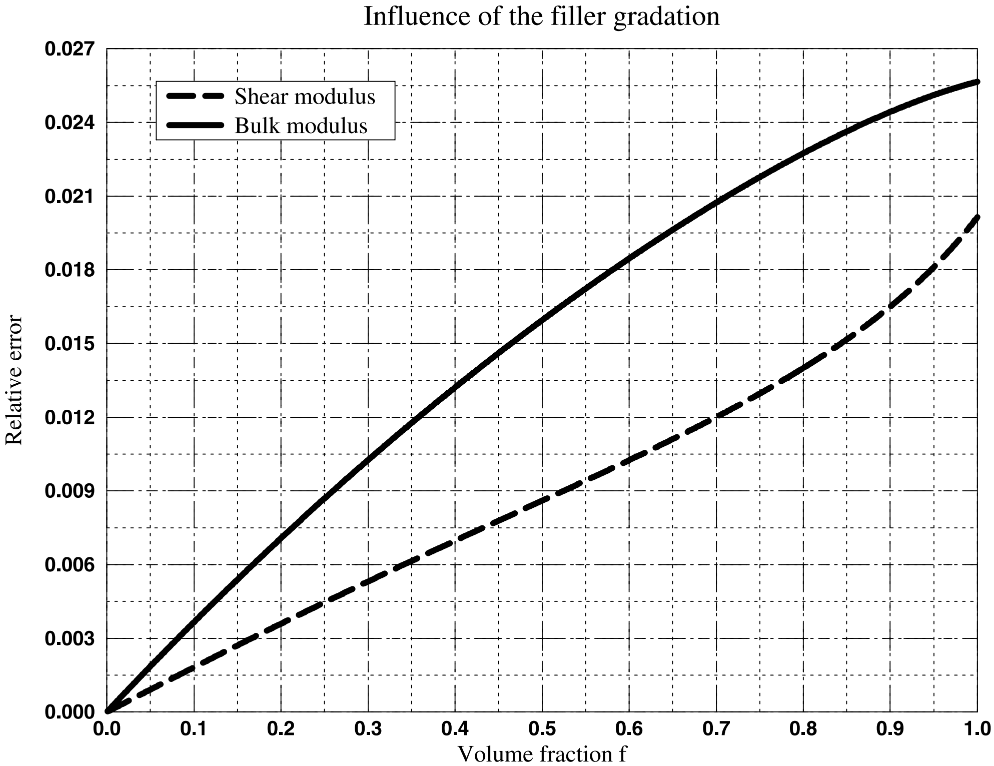

Fig. 5. Influence of filler gradation in epoxy resin DGEBA + hardener DDM + K37 microspheres: relative error between one sphere MRP solutions and five sphere MRP solutions. Syntactic foam as foam type 1 in Section 4.

This conclusion, however, may not always be valid, depending upon the actual gradation of the filler. To check this, we have considered a fictitious (and rather extreme) case, in which the filler has the following distribution of ratios between the inner and the outer radii:

$$a_\lambda/b_\lambda = 0.91,\ \ 0.92,\ \ 0.93,\ \ 0.94,\ \ 0.96,\ \ 0.97,\ \ 0.98,\ \ 0.99$$

each with equal volume fraction $f_\lambda = 1/8$; the average ratio a/b corresponding to this distribution is equal to 0.9508, roughly equal to that of the K37 filler.

Fig. 6 shows the relative error between the predictions of the single inclusion model and those of the multiple inclusion model for three types of matrix material: (i) an extremely stiff matrix ($E^{(m)} =$ 280 000 MPa), (ii) the DGEBA resin of syntactic foam types 1–4 of Section 4 ($E^{(m)} = 2800$ MPa) and (iii) an extremely compliant matrix ($E^{(m)} = 28$ MPa). Fig. 6a refers to the shear modulus, and Fig. 6b refers to the bulk modulus. In this way, we can appreciate the differences in the predictions of the two models for a range of ratios between the stiffness of the matrix and that of the inclusions.

It is apparent that now the two models, based on two very different RVEs, may yield significantly different results, with the "exact" elastic moduli always lower than those based on the average values of the wall thickness of the filler. Also, as obvious, the results of the two models tend to become coincident when the stiffness of the matrix becomes much larger than that of the inclusions. These results are obtained considering inclusions all made by the same material with a very large scatter in the wall thickness; of course, the same technique might turn useful also to take account of the presence of inclusions made by different materials.

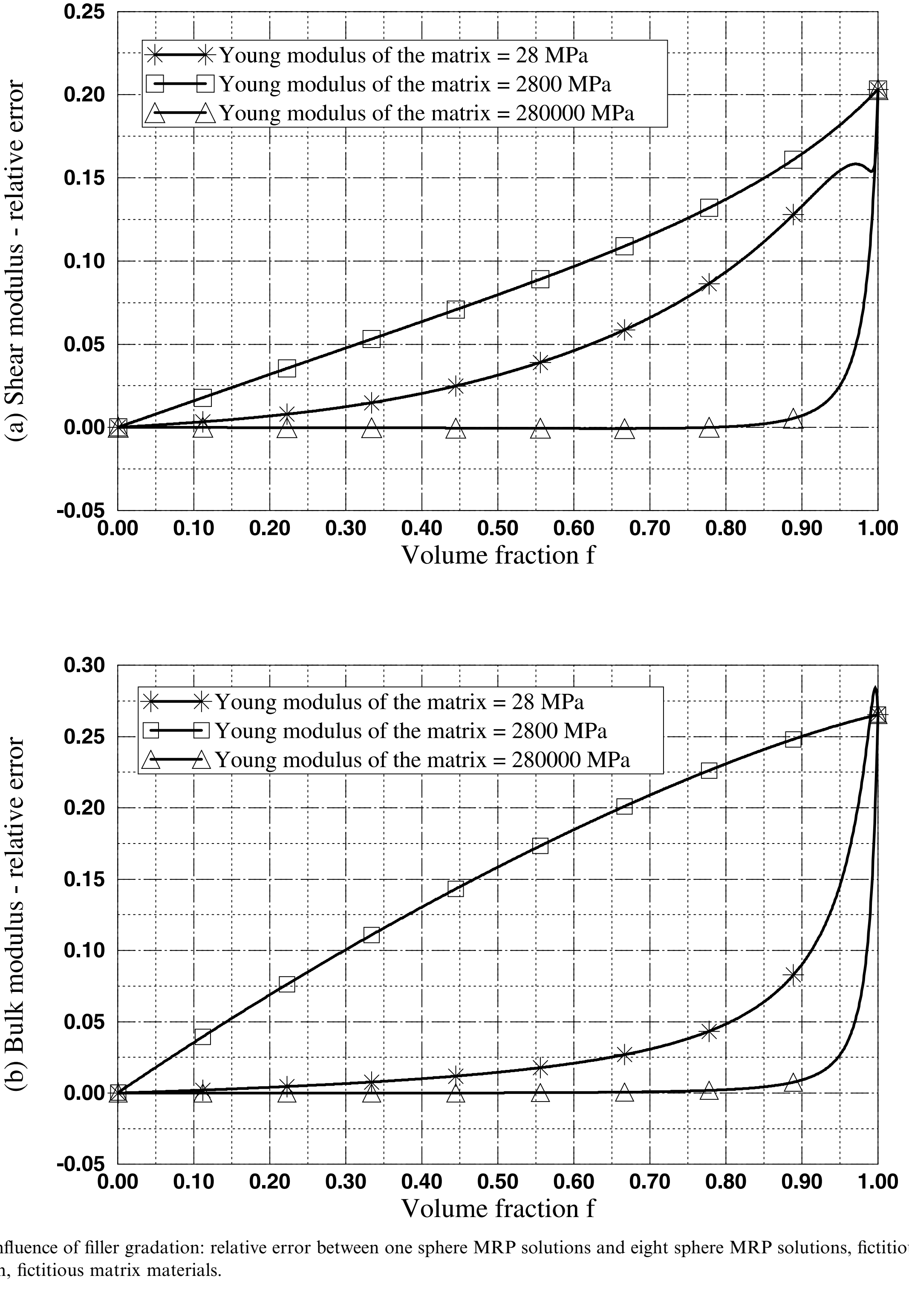

Fig. 6. Influence of filler gradation: relative error between one sphere MRP solutions and eight sphere MRP solutions, fictitious filler gradation, fictitious matrix materials.

6. Comparison with the predictions of numerical simulations

The effectiveness of estimates (A.25) and (A.28) has finally been checked against the results given by finite element simulations. The microstructure of the studied composite allows one to construct numerical models in terms of so-called "unit cells", which require a minimum computational effort and can therefore be used to test the validity of theoretical predictions over a wide range of base parameters.

Let us recall that, from the examination of the Scanning Electron Microscope images, shown and commented briefly in Section 4, one can draw two important conclusions:

1. The assumption of statistical homogeneity can be taken as valid for the study of this material; moreover, also the assumption of spatial periodicity of the microstructure may be invoked without introducing substantial errors.
2. The assumption of perfect bond between the two phases seems to be valid up to the rupture of the material, and, therefore, more so in the linear elastic range. This might not hold both for very small volume fractions, when a so-called "interphase" layer can appear around the outer surface of the inclusions, owing to an imperfect reticulation of the matrix, and for very high volume fractions, where the lack of matrix can lead to imperfect bonding. In both these extreme situations, one should expect experimental values of the elastic moduli systematically smaller than both the analytical and numerical predictions if these are based – as they indeed usually are – on the perfect bonding assumption.

From the computational viewpoint, the first observation allows us to simulate the results of uniaxial tests on cylindrical specimens by means of an axisymmetric unit cell, with appropriate boundary conditions enforcing the periodicity of the microstructure. Such model is shown in Fig. 7, where the mesh used to study one quarter of the unit cell, together with the deformed shape, is displayed. For a discussion of the unit cell calculations, as well as the relevant boundary conditions, see, for instance, Tvergaard (1982).

We have compared analytical with numerical results for a range of syntactic foams, similar to foam type 1 described in Section 4. The basic materials are the same; here we have extended the analysis to cover four choices of microspheres, taken from the standard catalog given by the producer (3M Italia, 1993). Table 8 shows the average details of the considered inclusions, as given in 3M Italia (1993).

The results of our analyses are shown in Figs. 8 and 9 in terms of the Young modulus and Poisson coefficient of the composite, respectively. Each figure includes four curves, computed analytically using Eqs. (A.25) and (A.28), on the basis of the moduli of the two phases and of the given average ratios a/b for the four different sets of spheres considered; numerical results are superimposed as filled symbols, corresponding to volume fractions of filler equal to 0.2, 0.3, 0.4, 0.5153 and 0.6. All the numerical results have been obtained using the finite element code ABAQUS (Hibbitt, Karlsson & Sorensen, 1998), employed in the linear elastic range and exploiting its "$*$MPC" and "$*$EQUATION" options, which allow one to prescribe the necessary periodicity boundary conditions on the external sides of the model.

The results in Fig. 8 confirm that the analytical estimates of the Young modulus predict with good accuracy all the essential features of the dependency from both the volume fraction and the inclusion geometry. The differences between the analytical and numerical results are always lower than about 7%, the numerical results being stiffer than the analytical for the light spheres (K1) and more flexible for the heavy spheres (K37).

It may be useful to recall that the axisymmetric unit cell, even in the case of real periodicity of microstructure, is an approximation of the three-dimensional solid because the unit cell model corresponds to a circular cylinder with a spherical inclusion, and no packing of circular cylinders fills the space. Therefore, the numerical results are in themselves affected by a slightly heavier approximation than that inherent into a

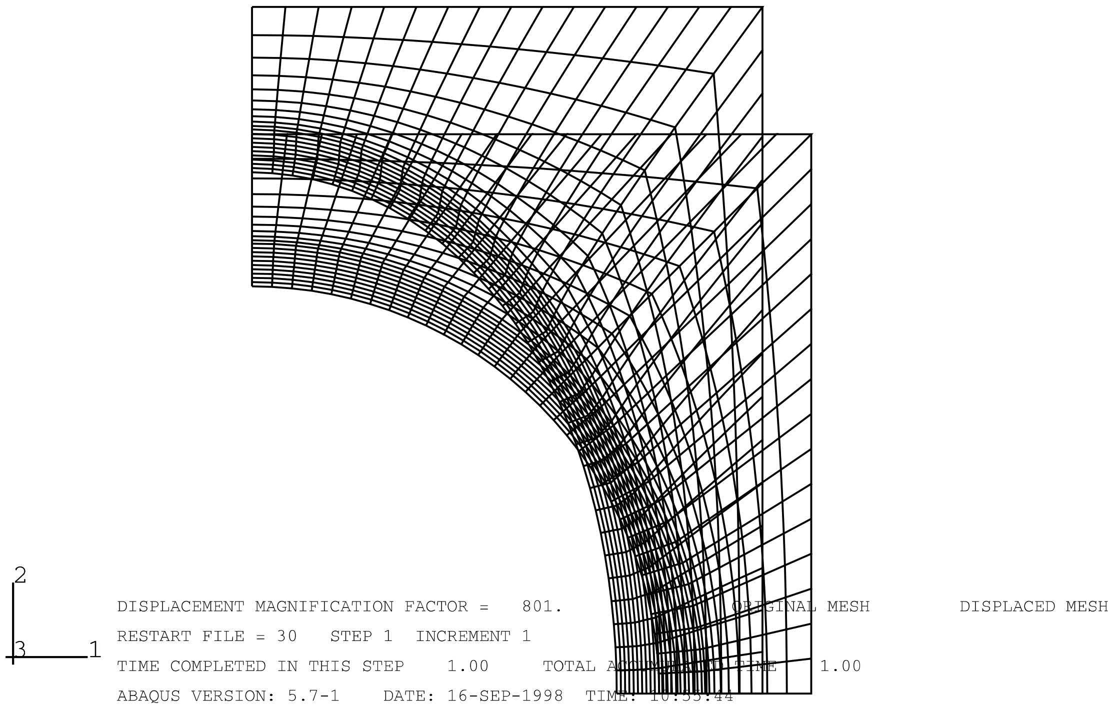

Fig. 7. Mesh and deformed shape for a unit cell finite element model (sphere type K37, $f = 0.30$).

Table 8
Average details of the considered microspheres (3M Italia, 1993)

Sphere type	Density [g/cm^3]	Median diameter [μm]	Wall thickness [μm]	a/b
K1	0.125	70.00	0.58	0.9836
K15	0.15	70.00	0.70	0.9802
S22	0.22	40.00	0.59	0.9709
K37	0.37	50.00	1.28	0.9501

finite element model. In consideration of this, the curves of Fig. 8 show an excellent agreement between analytical and numerical results.

Things are essentially the same also in terms of Poisson coefficient (Fig. 9), where, now, the numerical results underestimate the analytical ones for the light spheres and overestimate the analytical ones for the heavy spheres, with differences again up to $\pm 7\%$. The largest differences between the numerical and analytical results appear for the K1 spheres, at high volume fractions. At these volume fractions ($f \geqslant 0.6$), however, the spherical inclusions are close to their limit packing, and the numerical model inevitably includes several badly shaped elements; in this situation, a further loss of accuracy must therefore be expected in the numerical results. On the other hand, the analytical results also tend to become more and more inaccurate as the filler volume fraction becomes high. In any case, the results shown in Figs. 8 and 9 must be considered satisfactory; for a better understanding of the situation, Fig. 10 shows the numerical and analytical predictions in terms of bulk and shear moduli for the K1 microspheres only. Even if this is the case where the differences are the largest, the agreement is quite good.

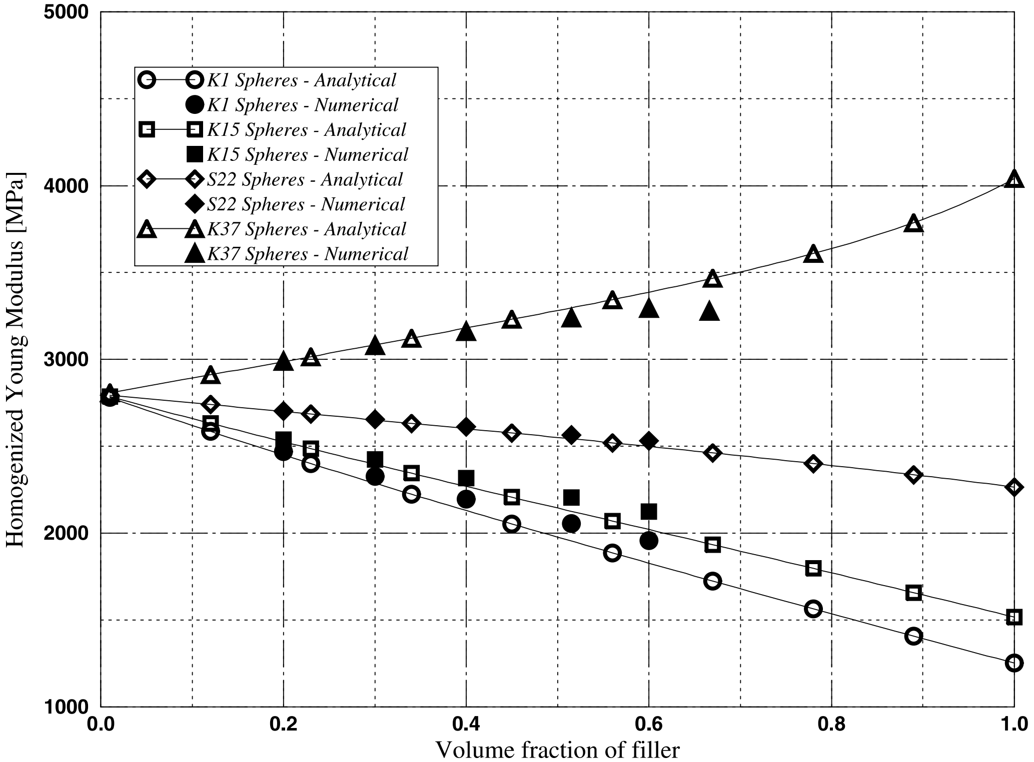

Fig. 8. Young modulus of syntactic foams: analytical vs numerical results.

7. Conclusions

We have illustrated the main features of the elastic behavior of special composite materials – syntactic foams – by comparing experimental, numerical, and analytical results. These last are obtained by using a homogenization technique particularly suited to deal with these materials, able to take account of both the presence of a void phase outside the filler and the actual distribution of wall thickness of the filler particles. The technique is based on analytical results obtained by Hervé and Pellegrini, and extends their homogenization technique using the MRP theory.

The comparison with both experimental and numerical results indicates that

- for the considered materials, the actual distribution of wall thickness of the microspheres seems to have little influence on the overall properties of the syntactic foam;
- the presence of unwanted voids has a significant effect on the elastic moduli of the composite;
- the Self-Consistent estimate, based on the three-phase model of Christensen and Lo (1979) and relevant extension by Hervé and Pellegrini (1995) gives results in good agreement with both experimental and numerical results.

Most of the experimental results have been obtained by us; unfortunately, we have been able to find only one work, in the literature, giving experimental results in a way complete enough to allow its proper use. Experimental results on syntactic foams are reported also in the works of Hervé and Pellegrini (1995) and Bunn and Mottram (1993). The paper by Hervé and Pellegrini, however, provides inconsistent information

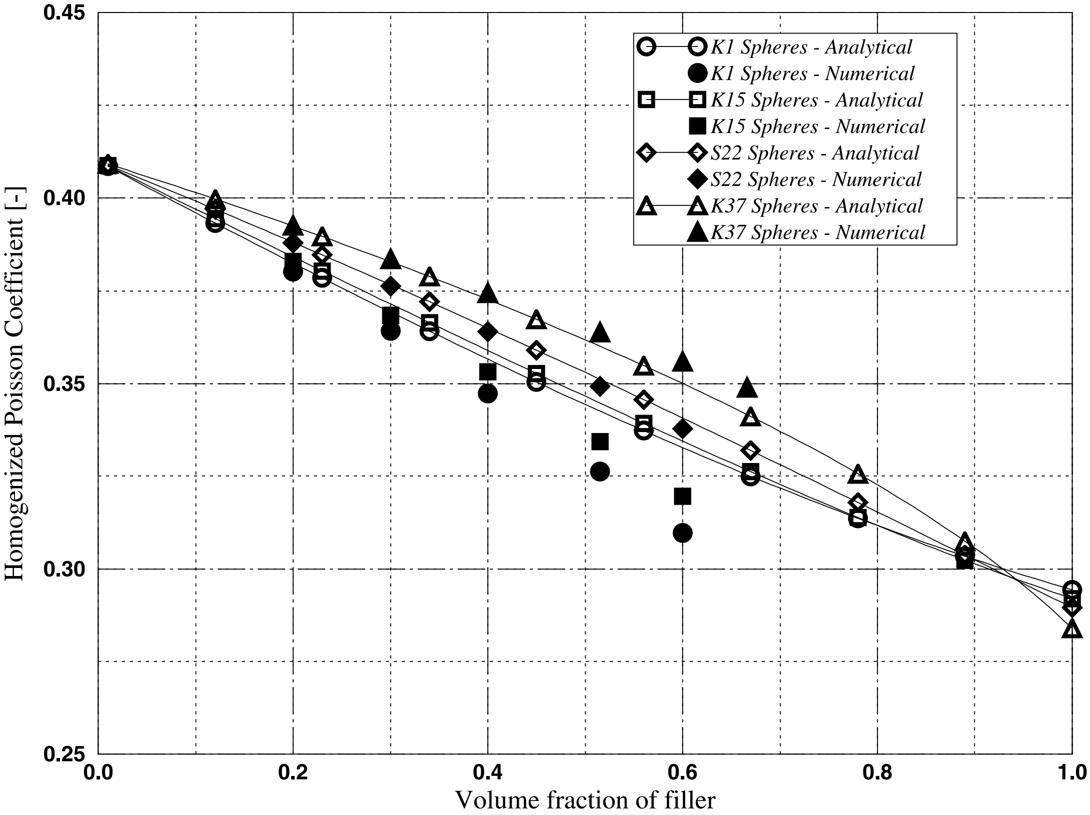

Fig. 9. Poisson coefficient of syntactic foams: analytical vs numerical results.

about the filler geometry, in that their indications about the filler density do not agree with their wall thickness data, which makes it impossible to reconstruct both their experimental results and analytical estimates.

The results of Bunn and Mottram (1993), concerning a syntactic foam made by phenolic microspheres, would have been a very useful test for checking the accuracy of the method illustrated in this paper since the elastic properties of the basic ingredients of that foam are very different from those tested by us. Unfortunately, we could not find, in the work of Bunn and Mottram (1993), sufficient data for applying the homogenization techniques.

The equations describing the homogenized values of the elastic moduli of the composite have a rather involved aspect, but they are simple in essence, and therefore can be relatively easily implemented into a computer code; the obtained results suggest that the developed method should provide an effective tool for designing syntactic foams. Finally, it is worth remarking that the technique illustrated in this work applies equally well to syntactic foams made by mixing fillers of different materials.

Work is in progress, experimental, theoretical and numerical, concerning the nonlinear behavior of these materials. The relevant results will be published in forthcoming papers.

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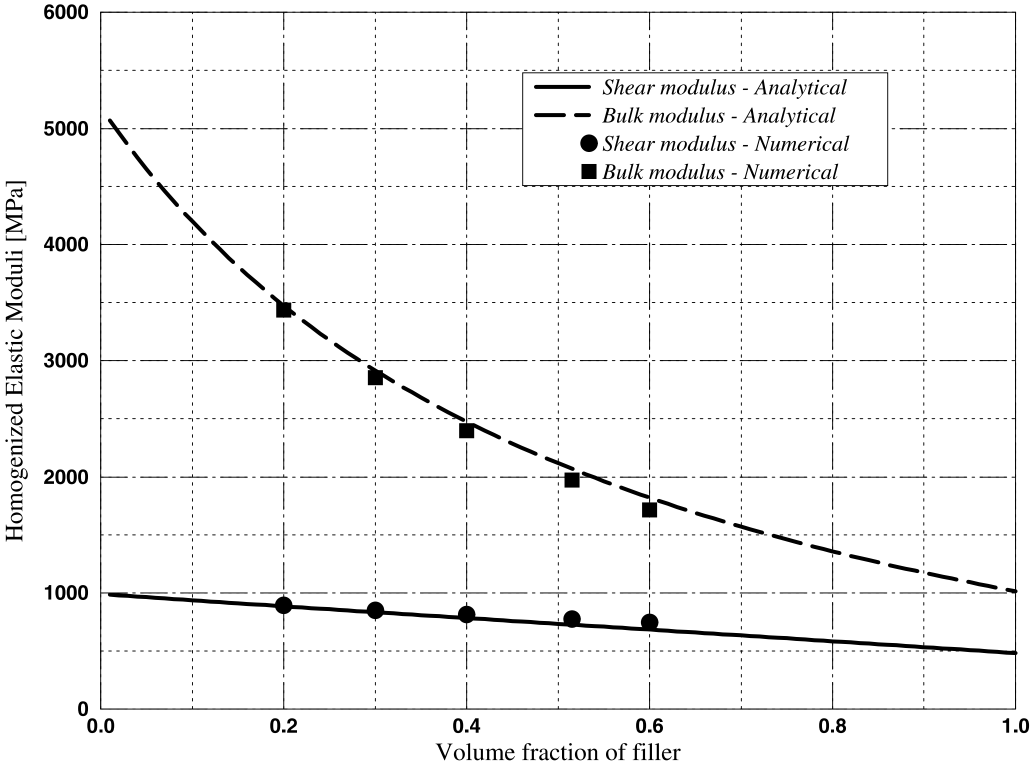

Fig. 10. Bulk and shear moduli of a syntactic foam: analytical vs numerical results for filler K1 microspheres.

element code ABAQUS has been run at the Department of Civil Engineering, University of Brescia, Italy, under an academic license. The authors wish to thank Professor Ezio Tempesti, of the Department of Chemistry and Physics for Engineering and for Materials of the University of Brescia, for allowing access to the Applied Chemistry Laboratory and for providing the raw materials for experiments. Finally, thanks are due to Dr. Michel Palumbo, Mr. Luca Martinelli, Mr. Modestino Savoia, Mr. Gianmarco Calò, Mr. Ivan Guizzetti and Ms. Serenella Raffelli both for their help in the preparation of the laboratory specimens and their assistance in the experimental work, and to Dr. Leonardo Lauri for his help with the Scanning Electron Microscope.

Appendix A

Here we summarize both some details needed to practically use Eqs. (12) and (14), and the relevant results pertaining to the simple case of a single type of composite sphere. These last results have been obtained for the first time by Hervé and Pellegrini (1995) for a much more general case than that of a syntactic foam, and, therefore, their formulae are rather involved. For this reason, we feel it might be worth reporting here explicit results for the syntactic foam case, the specific subject of this work.

First, we write down the system of equations corresponding to the boundary conditions of the four-phase model of Fig. 1, i.e., vanishing of tractions at the inner surface of the inclusion ($r = a$), continuity of both tractions and displacements at the two interfaces ($r = b$ and $r = c$), and the applied strain field at infinity.

For the case of shear boundary conditions, the full set of equations, in the unknown coefficients $I_1,\ldots,I_4$, $M_1,\ldots,M_4$, $S_1,\ldots,S_4$, is as follows:

$$2I_1 - 8I_2 + C_1^{(i)}I_3 + C_3^{(i)}I_4 = 0, \tag{A.1}$$

$$40I_2 + C_2^{(i)}I_3 + C_4^{(i)}I_4 = 0, \tag{A.2}$$

$$I_1 + \frac{a^5}{b^5}I_2 + \frac{b^2}{a^2}I_3 + \frac{a^3}{b^3}I_4 = M_1 + \frac{a^5}{b^5}M_2 + \frac{b^2}{a^2}M_3 + \frac{a^3}{b^3}M_4, \tag{A.3}$$

$$-5\frac{a^5}{b^7}I_2 + \alpha_2^{(i)}\frac{1}{a^2}I_3 + \left(\alpha_{-3}^{(i)} - 5\right)\frac{a^3}{b^5}I_4 = -5\frac{a^5}{b^7}M_2 + \alpha_2^{(m)}\frac{1}{a^2}M_3 + \left(\alpha_{-3}^{(m)} - 5\right)\frac{a^3}{b^5}M_4, \tag{A.4}$$

$$G^{(i)}\left(2I_1 - 8\frac{a^5}{b^5}I_2 + C_1^{(i)}\frac{b^2}{a^2}I_3 + C_3^{(i)}\frac{a^3}{b^3}I_4\right) = G^{(m)}\left(2M_1 - 8\frac{a^5}{b^5}M_2 + C_1^{(m)}\frac{b^2}{a^2}M_3 + C_3^{(m)}\frac{a^3}{b^3}M_4\right), \tag{A.5}$$

$$G^{(i)}\left(40\frac{a^5}{b^7}I_2 + C_2^{(i)}\frac{1}{a^2}I_3 + C_4^{(i)}\frac{a^3}{b^5}I_4\right) = G^{(m)}\left(40\frac{a^5}{b^7}M_2 + C_2^{(m)}\frac{1}{a^2}M_3 + C_4^{(m)}\frac{a^3}{b^5}M_4\right), \tag{A.6}$$

$$M_1 + \frac{a^5}{c^5}M_2 + \frac{c^2}{a^2}M_3 + \frac{a^3}{c^3}M_4 = S_1 + \frac{a^5}{c^5}S_2 + \frac{a^3}{c^3}S_4, \tag{A.7}$$

$$-5\frac{a^5}{c^7}M_2 + \alpha_2^{(m)}\frac{1}{a^2}M_3 + \left(\alpha_{-3}^{(m)} - 5\right)\frac{a^3}{c^5}M_4 = -5\frac{a^5}{c^7}S_2 + \left(\alpha_{-3}^{(s)} - 5\right)\frac{a^3}{c^5}S_4, \tag{A.8}$$

$$G^{(m)}\left(2M_1 - 8\frac{a^5}{c^5}M_2 + C_1^{(m)}\frac{c^2}{a^2}M_3 + C_3^{(m)}\frac{a^3}{c^3}M_4\right) = G^{(s)}\left(2S_1 - 8\frac{a^5}{c^5}S_2 + C_3^{(s)}\frac{a^3}{c^3}S_4\right), \tag{A.9}$$

$$G^{(m)}\left(40\frac{a^5}{c^7}M_2 + C_2^{(m)}\frac{1}{a^2}M_3 + C_4^{(m)}\frac{a^3}{c^5}M_4\right) = G^{(s)}\left(40\frac{a^5}{c^7}S_2 + C_4^{(s)}\frac{a^3}{c^5}S_4\right), \tag{A.10}$$

$$S_1 = \gamma. \tag{A.11}$$

In all the preceding equations $G^{(m)}$, $G^{(i)}$ and $G^{(s)}$ indicate the shear moduli of the matrix, the inclusion and the surrounding medium, respectively, and coefficients $\alpha_2^{(\zeta)}$, $\alpha_{-3}^{(\zeta)}$, $C_1^{(\zeta)}$, $C_2^{(\zeta)}$, $C_3^{(\zeta)}$ and $C_4^{(\zeta)}$ are defined as follows:

$$\begin{aligned} &\alpha_2^{(\zeta)} = -2\frac{7-10\nu^{(\zeta)}}{7-4\nu^{(\zeta)}}, \qquad \alpha_{-3}^{(\zeta)} = 2\frac{4-5\nu^{(\zeta)}}{1-2\nu^{(\zeta)}}, \\ &C_1^{(\zeta)} = \frac{14+4\nu^{(\zeta)}}{7-4\nu^{(\zeta)}}, \qquad C_2^{(\zeta)} = 4\frac{7-4\nu^{(\zeta)} - (7-10\nu^{(\zeta)})(2+\nu^{(\zeta)})}{(7-4\nu^{(\zeta)})(1-2\nu^{(\zeta)})}, \\ &C_3^{(\zeta)} = 2\frac{1+\nu^{(\zeta)}}{1-2\nu^{(\zeta)}}, \qquad C_4^{(\zeta)} = \frac{-24}{1-2\nu^{(\zeta)}}, \end{aligned} \tag{A.12}$$

where index ζ becomes i, m and s in the various regions of the four-phase model.

For the case of volumetric boundary conditions, the set of equations, in the unknown coefficients J_1, J_2, P_1, P_2, T_1, T_2, is as follows:

$$3K^{(i)}J_1 - 4G^{(i)}J_2 = 0, \tag{A.13}$$

$$3K^{(\mathrm{i})}J_1 - 4G^{(\mathrm{i})}J_2\frac{a^3}{b^3} = 3K^{(\mathrm{m})}P_1 - 4G^{(\mathrm{m})}P_2\frac{a^3}{b^3}, \tag{A.14}$$

$$J_1 b + J_2\frac{a^3}{b^2} = P_1 b + P_2\frac{a^3}{b^2}, \tag{A.15}$$

$$3K^{(\mathrm{m})}P_1 - 4G^{(\mathrm{m})}P_2\frac{a^3}{c^3} = 3K^{(\mathrm{s})}T_1 - 4G^{(\mathrm{s})}T_2\frac{a^3}{c^3}, \tag{A.16}$$

$$P_1 c + P_2\frac{a^3}{c^2} = T_1 c + T_2\frac{a^3}{c^2}, \tag{A.17}$$

$$T_1 = \theta. \tag{A.18}$$

These two systems of equations need to be solved for each type of composite sphere λ, for $\lambda = 1, \ldots, N$.

Finally, to evaluate the effective elastic moduli by Eqs. (12) and (14), one needs to compute the following averages:

$$\bar{\varepsilon}_{12}^{(\mathrm{m})} = M_1 + \left(1 + \frac{1}{5}\alpha_2^{(\mathrm{m})}\right)\frac{c^5 - b^5}{a^2(c^3 - b^3)}M_3, \tag{A.19}$$

$$\bar{\varepsilon}_{12}^{(\mathrm{i})} = I_1 + \left(1 + \frac{1}{5}\alpha_2^{(\mathrm{i})}\right)\frac{b^5 - a^5}{a^2(b^3 - a^3)}I_3, \tag{A.20}$$

$$\bar{\varepsilon}_{12}^{(\mathrm{CS})} = M_1 + \left(1 + \frac{1}{5}\alpha_2^{(\mathrm{m})}\right)\frac{c^2}{a^2}M_3 + \frac{1}{5}\alpha_{-3}^{(\mathrm{m})}\frac{a^3}{c^3}M_4, \tag{A.21}$$

$$\bar{\varepsilon}_{kk}^{(\mathrm{m})} = 3P_1, \tag{A.22}$$

$$\bar{\varepsilon}_{kk}^{(\mathrm{i})} = 3J_1, \tag{A.23}$$

$$\bar{\varepsilon}_{kk}^{(\mathrm{CS})} = 3\left(P_1 + P_2\frac{a^3}{c^3}\right). \tag{A.24}$$

In the case $N = 1$, one recovers the results of Hervé and Pellegrini for the situation they denote by $n = 3$ (i.e., a three-layered composite sphere, i.e., a syntactic foam). We write here the corresponding solution in a somewhat simpler way. The bulk modulus estimate is unique (it does not depend on the stiffness of the surrounding medium), and had already been obtained by Lee and Westmann (1970); the result is as follows:

$$K_0^{\mathrm{est}} = K^{(\mathrm{m})}\frac{\delta\left(1 + \frac{b^3}{c^3}\beta\right) + \kappa\left(1 - \frac{b^3}{c^3}\right)\beta}{\delta\left(1 - \frac{b^3}{c^3}\right) + \kappa\left(\beta + \frac{b^3}{c^3}\right)}, \tag{A.25}$$

where

$$\beta = \frac{4G^{(\mathrm{m})}}{3K^{(\mathrm{m})}}, \qquad \delta = \frac{4G^{(\mathrm{i})}}{3K^{(\mathrm{m})}}\left(1 - \frac{a^3}{b^3}\right), \qquad \kappa = \frac{4G^{(\mathrm{i})}}{3K^{(\mathrm{i})}} + \frac{a^3}{b^3}. \tag{A.26}$$

The shear modulus general estimate (that depends on $G^{(\mathrm{s})}$ through all the unknown coefficients of system (A.1)–(A.12)) is the following:

$$G_0^{\text{est}} = \frac{G^{(\text{m})}\left(\frac{c^3-b^3}{c^3}M_1 + \left(1+\frac{1}{5}\alpha_2^{(\text{m})}\right)\frac{c^5-b^5}{a^2c^3}M_3\right) + G^{(\text{i})}\left(\frac{b^3-a^3}{c^3}I_1 + \left(1+\frac{1}{5}\alpha_2^{(\text{i})}\right)\frac{b^5-a^5}{a^2c^3}I_3\right)}{M_1 + \left(1+\frac{1}{5}\alpha_2^{(\text{m})}\right)\frac{c^2}{a^2}M_3 + \frac{1}{5}\alpha_{-3}^{(\text{m})}\frac{a^3}{c^3}M_4}. \tag{A.27}$$

In the case of the Self-Consistent estimate, one should replace the unknown value G_0^{est} for $G^{(\text{s})}$ in system (A.1)–(A.12), which makes the problem implicit and nonlinear. However, in the case of a single composite sphere, it is possible to obtain a relatively simple quadratic equation whose solution gives directly the desired result, $G_0^{\text{est}} = G_0^{\text{SC}}$:

$$\left(40H_1\frac{a^5}{c^5}\right)\left(\frac{G_0^{\text{SC}}}{G^{(\text{m})}}\right)^2 + \left(2F_4 - F_2 - 8(F_1+3F_3)\frac{a^5}{c^5}\right)\left(\frac{G_0^{\text{SC}}}{G^{(\text{m})}}\right) + \frac{F_2F_3 - F_1F_4}{H_1} = 0, \tag{A.28}$$

whose coefficients F_1, F_2, F_3, F_4 and H_1 are defined as follows. First define

$$C_1 = \frac{21}{5}\frac{b}{a} - 6v^{(\text{i})}\frac{b^3}{a^3} + \frac{3}{20}(7+5v^{(\text{i})})\frac{a^4}{b^4}, \tag{A.29}$$

$$C_2 = \frac{2}{5}(7-5v^{(\text{i})})\frac{b}{a} + (5-4v^{(\text{i})})\frac{a^2}{b^2} - \frac{9}{5}\frac{a^4}{b^4}, \tag{A.30}$$

$$C_3 = \frac{21}{5}\frac{b}{a} - (7-4v^{(\text{i})})\frac{b^3}{a^3} - \frac{1}{10}(7+5v^{(\text{i})})\frac{a^4}{b^4}, \tag{A.31}$$

$$C_4 = \frac{2}{5}(7-5v^{(\text{i})})\frac{b}{a} + 2(1-2v^{(\text{i})})\frac{a^2}{b^2} + \frac{6}{5}\frac{a^4}{b^4}, \tag{A.32}$$

$$C_5 = \frac{42}{5} + 6v^{(\text{i})}\frac{b^2}{a^2} - \frac{6}{5}(7+5v^{(\text{i})})\frac{a^5}{b^5}, \tag{A.33}$$

$$C_6 = \frac{4}{5}(7-5v^{(\text{i})}) - 4(5-v^{(\text{i})})\frac{a^3}{b^3} + \frac{72}{5}\frac{a^5}{b^5}, \tag{A.34}$$

$$C_7 = \frac{21}{5} - (7+2v^{(\text{i})})\frac{b^2}{a^2} + \frac{2}{5}(7+5v^{(\text{i})})\frac{a^5}{b^5}, \tag{A.35}$$

$$C_8 = \frac{2}{5}(7-5v^{(\text{i})}) + 2(1+v^{(\text{i})})\frac{a^3}{b^3} - \frac{24}{5}\frac{a^5}{b^5}. \tag{A.36}$$

Then,

$$D_1 = \big(C_5(C_4-C_2) + C_6(C_1-C_3)\big)\frac{b}{a} - 2\frac{G^{(\text{m})}}{G^{(\text{i})}}(C_1C_4 - C_2C_3), \tag{A.37}$$

$$D_2 = \big((C_2C_5 - C_1C_6)(7-4v^{(\text{m})}) + 6(C_3C_6 - C_4C_5)v^{(\text{m})}\big)\frac{b^3}{a^3} - 6\frac{G^{(\text{m})}}{G^{(\text{i})}}v^{(\text{m})}(C_1C_4 - C_2C_3)\frac{b^2}{a^2}, \tag{A.38}$$

$$D_3 = (C_5(2C_2+3C_4) - C_6(2C_1+3C_3))\frac{a^4}{b^4} + 24\frac{G^{(\text{m})}}{G^{(\text{i})}}(C_1C_4 - C_2C_3)\frac{a^5}{b^5}, \tag{A.39}$$

$$D_4 = \left((C_4C_5 - C_3C_6)(5 - 4\nu^{(m)}) + 2(C_1C_6 - C_2C_5)(1 - 2\nu^{(m)})\right)\frac{a^2}{b^2} + 4\frac{G^{(m)}}{G^{(i)}}(5 - \nu^{(m)}) \times (C_1C_4 - C_2C_3)\frac{a^3}{b^3}, \tag{A.40}$$

$$D_5 = \left(C_7(C_4 - C_2) + C_8(C_1 - C_3)\right)\frac{b}{a} - \frac{G^{(m)}}{G^{(i)}}(C_1C_4 - C_2C_3), \tag{A.41}$$

$$D_6 = \left((C_2C_7 - C_1C_8)(7 - 4\nu^{(m)}) + 6(C_3C_8 - C_4C_7)\nu^{(m)}\right)\frac{b^3}{a^3} + \frac{G^{(m)}}{G^{(i)}}(7 + 2\nu^{(m)})(C_1C_4 - C_2C_3) \times \frac{b^2}{a^2}, \tag{A.42}$$

$$D_7 = \left(C_7(2C_2 + 3C_4) - C_8(2C_1 + 3C_3)\right)\frac{a^4}{b^4} - 8\frac{G^{(m)}}{G^{(i)}}(C_1C_4 - C_2C_3)\frac{a^5}{b^5}, \tag{A.43}$$

$$D_8 = \left((C_4C_7 - C_3C_8)(5 - 4\nu^{(m)}) + 2(C_1C_8 - C_2C_7)(1 - 2\nu^{(m)})\right)\frac{a^2}{b^2} - 2\frac{G^{(m)}}{G^{(i)}}(1 + \nu^{(m)}) \times (C_1C_4 - C_2C_3)\frac{a^3}{b^3} \tag{A.44}$$

then again,

$$H_1 = \frac{D_3D_6 - D_2D_7}{D_1D_7 - D_3D_5}\frac{c}{a} - 6\nu^{(m)}\frac{c^3}{a^3} + 3\frac{D_2D_5 - D_1D_6}{D_1D_7 - D_3D_5}\frac{a^4}{c^4}, \tag{A.45}$$

$$H_2 = \frac{D_3D_8 - D_4D_7}{D_1D_7 - D_3D_5}\frac{c}{a} + (5 - 4\nu^{(m)})\frac{a^2}{c^2} + 3\frac{D_4D_5 - D_1D_8}{D_1D_7 - D_3D_5}\frac{a^4}{c^4}, \tag{A.46}$$

$$H_3 = \frac{D_3D_6 - D_2D_7}{D_1D_7 - D_3D_5}\frac{c}{a} - (7 - 4\nu^{(m)})\frac{c^3}{a^3} - 2\frac{D_2D_5 - D_1D_6}{D_1D_7 - D_3D_5}\frac{a^4}{c^4}, \tag{A.47}$$

$$H_4 = \frac{D_3D_8 - D_4D_7}{D_1D_7 - D_3D_5}\frac{c}{a} + 2(1 - 2\nu^{(m)})\frac{a^2}{c^2} - 2\frac{D_4D_5 - D_1D_8}{D_1D_7 - D_3D_5}\frac{a^4}{c^4}, \tag{A.48}$$

$$H_5 = 2\frac{D_3D_6 - D_2D_7}{D_1D_7 - D_3D_5} + 6\nu^{(m)}\frac{c^2}{a^2} - 24\frac{D_2D_5 - D_1D_6}{D_1D_7 - D_3D_5}\frac{a^5}{c^5}, \tag{A.49}$$

$$H_6 = 2\frac{D_3D_8 - D_4D_7}{D_1D_7 - D_3D_5} - 4(5 - \nu^{(m)})\frac{a^3}{c^3} - 24\frac{D_4D_5 - D_1D_8}{D_1D_7 - D_3D_5}\frac{a^5}{c^5}, \tag{A.50}$$

$$H_7 = \frac{D_3D_6 - D_2D_7}{D_1D_7 - D_3D_5} - (7 + 2\nu^{(m)})\frac{c^2}{a^2} + 8\frac{D_2D_5 - D_1D_6}{D_1D_7 - D_3D_5}\frac{a^5}{c^5}, \tag{A.51}$$

$$H_8 = \frac{D_3D_8 - D_4D_7}{D_1D_7 - D_3D_5} + 2(1 + \nu^{(m)})\frac{a^3}{c^3} + 8\frac{D_4D_5 - D_1D_8}{D_1D_7 - D_3D_5}\frac{a^5}{c^5}, \tag{A.52}$$

and finally,

$$F_1 = \left((H_1 - H_3) \frac{H_6 H_1 - H_5 H_2}{H_1 H_4 - H_3 H_2} + H_5 \right) \frac{c}{a}, \tag{A.53}$$

$$F_2 = \left((2H_1 + 3H_3) \frac{H_6 H_1 - H_5 H_2}{H_1 H_4 - H_3 H_2} - 3H_5 \right) \frac{a^4}{c^4}, \tag{A.54}$$

$$F_3 = \left((H_1 - H_3) \frac{H_8 H_1 - H_7 H_2}{H_1 H_4 - H_3 H_2} + H_7 \right) \frac{c}{a}, \tag{A.55}$$

$$F_4 = \left((2H_1 + 3H_3) \frac{H_8 H_1 - H_7 H_2}{H_1 H_4 - H_3 H_2} - 3H_7 \right) \frac{a^4}{c^4}. \tag{A.56}$$

The significant root of Eq. (A.28) for G_0^{SC} is positive (i.e., greater than the value of the shear modulus of the void), and lower than the highest value between the shear modulus of the matrix, $G^{(m)}$, and the shear modulus of the inclusion, $G^{(i)}$.

References

Bardella, L., 1997. Comportamento a rottura di un materiale composito in resina polimerica e microsfere cave in vetro. Tesi di Laurea, Università di Brescia, Facoltà di Ingegneria (In Italian).

Bardella, L., 1999. Mechanical behaviour of syntactic foams: experimental results and estimates of the effective elastic moduli. Technical Report N. 14/1999, Department of Civil Engineering, University of Brescia, Italy.

Bardella, L., Genna, F., 2000. Elastic design of syntactic foamed sandwiches obtained by filling of three-dimensional sandwich-fabric panels. Int. J. Solids and Structures 38, 307–333.

Bornert, M., Hervé, É., Zaoui, A., 1994. Self-Consistent approaches and strain heterogeneities in two-phase elastoplastic materials. Applied Mechanics Review 47 (1), S66–S76.

Bornert, M., Stolz, C., Zaoui, A., 1996. Morphologically Representative Pattern-based bounding in elasticity. Journal of the Mechanics and Physics of Solids 44, 307–331.

Brandt, A.M., 1995. Cement-based Composites. Materials, Mechanical Properties and Performance. E & FN SPON, London.

Budiansky, B., 1965. On elastic moduli of some heterogeneous materials. Journal of the Mechanics and Physics of Solids 13, 223–277.

Bunn, P., Mottram, J.T., 1993. Manufacture and compression properties of syntactic foams. Composites 24 (7), 565–571.

Christensen, R.M., Lo, K.H., 1979. Solutions for effective shear properties in three phase sphere and cylinder models. Journal of the Mechanics and Physics of Solids 27, 315–330.

Hashin, Z., 1962. The elastic moduli of heterogeneous materials. Journal of Applied Mechanics 29, 143–150.

Hervé, É., Pellegrini, O., 1995. The elastic constants of a material containing spherical coated holes. Archives of Mechanics 47 (2), 223–246.

Hibbitt, Karlsson and Sorensen, Inc., 1998. ABAQUS User's and Theory Manuals. Release 5.8, Pawtucket, USA.

Hill, R., 1965. A Self-Consistent mechanics of composite materials. Journal of the Mechanics and Physics of Solids 13, 213–222.

Huang, J.S., Gibson, L.J., 1993. Elastic moduli of a composite of hollow spheres in a matrix. Journal of the Mechanics and Physics of Solids 41, 55–75.

3M Italia, 1993. Scotchlite™ glass bubbles. Informazioni di prodotto. Private communication (In Italian).

Lee, K.J., Westmann, R.A., 1970. Elastic properties of hollow-sphere-reinforced composites. Journal of Composite Materials 4, 242–253.

Love, A.E.H., 1944. A Treatise on the Mathematical Theory of Elasticity. Dover Publications, New York.

Maier, G., 1998. Analisi delle proprietà chimiche, fisiche e micromeccaniche di un materiale composito in sandwich di schiuma sintattica e fibra di vetro preimpregnata. Studio del comportamento meccanico di un materiale composito a sandwich di schiuma sintattica e fibra di vetro. Private communication (In Italian).

Nielsen, L.E., Landel, R.F., 1994. Mechanical Properties of Polymers and Composites, second ed. Marcel Dekker, New York.

Tempesti, E., 1998. Analisi delle proprietá chimiche, fisiche e micromeccaniche di un materiale composito in sandwich di schiuma sintattica e fibra di vetro preimpregnata. Studio del comportamento meccanico di un materiale composito a sandwich di schiuma sintattica e fibra di vetro. Private communication (In Italian).

Tvergaard, V., 1982. On localization in ductile materials containing spherical voids. International Journal of Fracture 18 (4), 237–252.

Zaoui, A., 1997. Structural morphology and constitutive behaviour of microheterogeneous materials. In: Suquet, P., (Ed.), Continuum Micromechanics, CISM Lecture Notes 377, Springer, Berlin, pp. 291–347.