JOURNAL OF MATERIALS SCIENCE 20 (1985) 1069–1078

# Hollow glass microsphere composites: preparation and properties

H. VERWEIJ, G. DE WITH, D. VEENEMAN
*Philips Research Laboratories, P.O. Box 80000, 5600 JA Eindhoven, The Netherlands*

Composites consisting of bonded hollow glass microspheres are promising for constructions in which materials are needed that combine a high Young's modulus with a low density. The elastic properties of ideally bonded hollow glass microsphere composites are predicted theoretically. Heat-treated castings of quartz glass microspheres approach the theoretical Young's modulus from below. The best result achieved was a Young's modulus of about 1 GPa with a strength of about 0.8 MPa at a density of about 180 kg m$^{-3}$. This was obtained with a casting of quartz glass microspheres, bonded with mono-aluminium phosphate. Composites made by pressing of appropriate microsphere/binder mixtures, followed by heating, had a density that was lower than for castings but had a Young's modulus far below the theoretical value.

## 1. Introduction

The present investigations were initiated by a request for new construction materials with a low density and a high Young's modulus. The requirements for the density pointed towards highly porous materials. These materials can be subdivided into simple foams and more complex composites such as hollow glass microsphere composites.

Organic materials generally have a Young's modulus that is an order of magnitude below that of inorganic materials, which makes them less suitable for the applications in mind. A well known inorganic foam is the so-called foam glass [1] with a Young's modulus of typically 1 GPa at a density of 130 kg m$^{-3}$. This material has a large average bubble size of up to 2 mm and must be machined to make complex shapes. This may be a disadvantage for mass production applications. Microsphere composites of complex shape can be prepared by casting or pressing microsphere/binder mixtures followed by heat treatment. This can be accomplished with relatively cheap techniques.

The present paper reports on the theory of elastic properties of hollow microsphere composites and on the preparation and mechanical properties of some specific hollow glass microsphere composites.

## 2. Theory

In microsphere composites two kinds of porosity may be present: an intergranular porosity $P_1$ and an intragranular porosity $P_2$. The total porosity is given by:

$$P = P_1 + P_2. \tag{1}$$

A reasonable estimate for the intergranular porosity, $P_1$, given random sphere packing is $P_1 \approx 0.4$. This estimate is based on both experimental and theoretical data; see for example [2].

The intragranular porosity, $P_2$, can be estimated from the average relative density of a thin-walled single hollow sphere, $\rho_s$, given by;

$$\rho_s = \frac{4\pi}{3}[R^3 - (R-d)^3] \Big/ \left[\frac{4\pi}{3}R^3\right] \approx 3d/R \tag{2}$$

where $R$ is the (outer) radius of the sphere and $d$ is the wall thickness. The single sphere porosity, $P_s$, is given by:

$$P_s = 1 - 3d/R. \tag{3}$$

In a microsphere composite only a fraction $f = (1 - P_1)$ is occupied by spheres so that the intragranular porosity, $P_2$, becomes:

$$P_2 = fP_s = (1 - P_1)(1 - 3d/R). \tag{4}$$

0022–2461/85 $03.00 + .12

The Young's modulus, $E$, of a porous material can be estimated using various models. The discussion of this subject as given below is necessarily brief. An extensive review of the microstructure dependence of mechanical properties can be found in [3].

A simple expression for $E$, based on load-bearing section arguments for a cubic pore symmetrically positioned inside a cube of solid material, reads:

$$E/E_0 = (1 - P^{2/3})/(1 - P^{2/3} + P), \qquad (5)$$

where $E_0$ is the Young's modulus of the cube material. Expression 5 satisfies the boundary conditions $E = E_0$ for $P = 0$ and $E = 0$ for $P = 1$ but generally leads to values for $E$ that are too high.

Another well-known expression, based on load-bearing section arguments for a packing of solid spheres, is given by:

$$E/E_0 = \exp(-b_1 P), \qquad (6)$$

where $b_1$ is a characteristic exponent that depends on the way the spheres are stacked. For a simple cubic packing with a coordination number of 6, the value of $b_1$ is about 6. In that case the dependence of $E$ on $P$ is reasonably described for $0 \leqslant P < 0.5$.

In a random sphere stacking a coordination number of 6 is also present [2]. This means that a value of 6 for $b_1$ could also be used for random-stacked microsphere composites, but it should be noted that Expression 6 is strictly valid only for intergranular porosity. Expression 6 does not hold for high porosities, but Rice [3, 4] has shown that a complementary relationship can be used based on a model with spherical pores in a solid matrix:

$$E/E_0 = 1 - \exp[-b_2(1 - P)], \qquad (7)$$

where $b_2$ is again a characteristic exponent with a value of about 0.5 for a simple cubic pore distribution. The validity range for Equation 7 is $0.5 \leqslant P \leqslant 1$.

Following Rice [4] one may combine the models of Expression 6 and 7 to obtain an expression for hollow sphere composites. In that case the $E$ value of a material with intergranular porosity $P_1$ is predicted by Expression 6 with $P = P_1$ while $E_0$ in this expression is calculated from Equation 7 as the average Young's modulus of a hollow sphere with porosity $P_s$. The combined expression becomes:

$$\begin{aligned} E/E_0 &= \exp(-b_1 P_1)\{1 - \exp[-b_2(1 - P_s)]\} \\ &= \exp(-b_1 P_1)\left\{1 - \exp\left[-b_2 \frac{(1 - P)}{(1 - P_1)}\right]\right\} \end{aligned} \qquad (8)$$

using Equations 1, 4, 6 and 7.

Expression 8 satisfies the boundary condition for $P = 1$. Disadvantages of the model behind expressions 6, 7 and 8 are that it is semi-analytical and that some parameters have to be estimated. These problems can be avoided by using a model for calculating elastic properties without approximations. One of the most sophisticated models for quasi-homogeneous, isotropic materials is the three-phase model [5, 6]. This model uses two concentric spheres of materials 1 and 2 with respective radii $b$ and $a$, embedded in an infinite matrix of unknown effective properties. The radii are chosen such that $(a/b)^3$ equals the volume fraction of material 2. An expression for the bulk modulus $K$ and the shear modulus $G$ is derived on the assumption that the infinite matrix possesses the same average conditions of stress and strain and that all continuity conditions at the interfaces are fulfilled.

It can be proved that the solution for $K$ is also the solution for a material consisting of a composite sphere as mentioned above, surrounded by other composite spheres that completely fill the entire space. This is probably true for $G$ as well, but has not been proved. In our case material 2 is the pore phase. The Young's modulus, $E$, can be calculated from $K$ and $G$ in the usual way. The full expressions for $K$ and especially $G$ are rather lengthy, but have been described several times in the literature so that we omit them here. An interesting feature of the three-phase model is that it also yields correct estimates for $E$ if the pores are not spherical as long as the material remains (quasi) isotropic [6].

Hollow glass microspheres can be obtained with different compositions and in various sizes. As an example vitreous silica glass microspheres are based on a bulk material with a relatively high Young's modulus of 73 GPa [7] and a low density of 2200 kg m$^{-3}$ [8]. The estimated Young's modulus and density for a number of vitreous silica microsphere composites, based on the various expressions discussed, are given in Table I. In our opinion the three-phase model results (E4 in Table I) are the most trustworthy. The simple Expression 7 yields very similar results; the

TABLE I Estimated Young's moduli for various vitreous silica microsphere composites.

| $R$(μm) | $d$(μm) | $P$(%) | $\rho$(kg m$^{-3}$) | $E_1$(GPa) | $E_2$(GPa) | $E_3$(GPa) | $E_4$(GPa) |
|---|---|---|---|---|---|---|---|
| 80 | 1 | 97.7 | 50 | 1.1 | 0.84 | 0.1 | 0.6 |
| 80 | 2 | 95.5 | 99 | 2.2 | 1.6 | 0.2 | 1.3 |
| 40 | 1.5 | 93.2 | 149 | 3.4 | 2.4 | 0.4 | 1.9 |
| 20 | 1 | 91.0 | 198 | 4.6 | 3.2 | 0.5 | 2.6 |
| 20 | 2 | 82.0 | 396 | 9.6 | 6.3 | 0.9 | 5.7 |

$R$ = Average (outer) radius of the microspheres, $d$ = average wall thickness of the microspheres, $P = P_1 + P_2$ with $P_1$ = 0.4 and $P_2$ given by Expression 4, $\rho$ = density, calculated using a bulk density of 2200 kg m$^{-3}$, $E_1$ = estimated $E$ according to Expression 5, $E_2$ = estimated $E$ according to Expression 7 with $b_2 = 0.5$, $E_3$ = estimated $E$ according to Expression 8 with $b_1 = 6.0$ and $b_2 = 0.5$, $E_4$ = estimated $E$ according to the three-phase model. The Young's modulus of the bulk modulus was taken as 73 GPa and the Poisson ratio as 0.17 according to [7].

somewhat more elaborate Expression 8 gives relatively low $E$ values while the values of Equation 5 are very high.

The values of $R$ and $d$ in Table I include sizes that are typical of commercially available glass microspheres. Glass microspheres other than vitreous silica microspheres are generally made of oxide glasses [9] with Young's moduli somewhat lower and densities somewhat higher than those of vitreous silica [8]. This may result in theoretical Young's moduli of down to 50% of the corresponding moduli for vitreous silica composites. It can be concluded that theoretically hollow glass microsphere composites may have a Young's modulus nearly equivalent to that of many organic polymer materials with a density an order of magnitude lower.

## 3. Experimental details

### 3.1. Microspheres

For the experiments we used Emerson & Cuming SI quartz glass bubbles and 3M C15/250 soda–lime–borosilicate (SLB) glass bubbles. Their properties are given in Table II. The properties of the SI microspheres were specified by the manufacturer. The properties of the SLB microspheres were measured in our laboratory by standard methods. The SI microspheres were chosen for their strength and chemical inertness and for the high Young's modulus of the bulk material. The 3M bubbles were chosen for their low powder bulk density. The intergranular porosity, $P_1$, was about 0.4 for both microsphere powders.

TABLE II Properties of hollow glass microspheres.

| Property | Type | |
|---|---|---|
| | E & C SI | 3M C15/250 |
| True particle density (kg m$^{-3}$) | 254 | 142 |
| Powder tap density (kg m$^{-3}$) | 152 | 85 |
| Average particle diameter (μm) | 80 | 50 |
| Average wall thickness (μm) | 1.5 | 0.5 |
| Glass transition temperature (°C) | 980 | 545 |

### 3.2. Inorganic binder solutions

The microspheres were bonded using inorganic binder solutions. Most experiments were performed with diluted solutions of $Al(H_2PO_4)_3$, mono-aluminium phosphate (MAP), in water. MAP is a well known bonding agent for various ceramic materials [10–13]. If a MAP solution is heated it loses water and a number of complex hydrates are formed. These hydrates decompose to an amorphous substance with formula $Al_2O_3 \cdot 3P_2O_5$ at temperatures above 300° C [14–16]. This substance is non-hygroscopic and may react with the material to be bonded, meanwhile forming more complex vitreous or crystalline compounds. A slight reaction with the material can be expected to favour the bonding properties.

Attempts were made to use 3 wt% NaOH in water, diluted waterglass, $SiO_2$ suspensions (Dupont, Ludox AS) and AlO(OH) (Boehmite) suspensions for bonding. The $SiO_2$ and AlO(OH) suspensions gave no bonding at all. The NaOH and waterglass solutions gave severe chemical reactions, especially with the soda–lime–borosilicate (SLB) microspheres, and caused too much shrinkage when the compacts were fired. This shrinkage caused breakdown of composites with dimensions of more than a few centimetres.

### 3.3. Composites made from castings of microsphere slurries

Hollow microsphere/MAP slurries were cast in PTFE (M/S Release-agent MS-122) coated stainless steel or perspex moulds. These moulds consisted of a divided ring and perforated bottom and top plates; the inner diameter was 170 or 60 mm with a height of 20 to 50 mm. The bottom and top plates were covered with 35 $\mu$m polyester sieve cloth (Monolen) to prevent the microspheres from filling and escaping through the perforation holes. Excess liquid was allowed to leak away and the mould with the slurry was held at 50° C for 3 days, followed by the same period at 90° C. The dry compacts were released from the mould and were heated at a rate of $50°\,C\,h^{-1}$ to top level, followed by a constant period and cooling at $50°\,C\,h^{-1}$ to ambient. The top level was varied between 300 and 900° C; the level time was varied between 1 and 24 h. The MAP concentration in the binder solution was also varied between 2 and 16%. Optimum processing and best results were obtained with a solution/microsphere weight ratio of about 3.

## 3.4. Composites made by pressing of microsphere flakes

At low solution/microsphere ratios the viscosity of the mixture becomes too high for casting. In that case the mixture can be prepared as flakes for pressing green microsphere compacts. Microspheres and solution were mixed with an S-shaped stirrer, after which the mixture was broken up into flakes by means of a wing stirrer. The flaky mass was pressed to discs of 60 mm diameter and 10 to 20 mm thickness in a perspex die with a pressure of 0.02 to 0.15 $kg\,cm^{-2}$. The green compacts could easily be released from the die. The SI compacts were fired at $50°\,C\,h^{-1}$ to 50° C and held constant at that temperature for 72 h. Then they were fired at $50°\,C\,h^{-1}$ to 90° C, 24 h constant; $50°\,C\,h^{-1}$ to 600° C, 3 h constant; $50°\,C\,h^{-1}$ to ambient.

Pressed SLB compacts were dried by keeping them for 24 h at ambient, followed by heating at $5°\,C\,h^{-1}$ to 75° C, 16 h constant and natural cooling. The dried SLB compacts were subsequently fired at $50°\,C\,h^{-1}$ to top level, 3 h constant; $50°\,C\,h^{-1}$ to ambient.

Optimum processing and best results were obtained with a 4 wt% MAP solution and a solution/microsphere weight ratio of 1.75 for SI compacts and for SLB compacts with a 12 wt% MAP solution and a solution/microsphere weight ratio of 1.

To investigate anisotropy caused by pressing, a number of small strips with dimensions of 5 mm × 10 mm × 45 mm were pressed in the directions of the 5 and 45 mm edges.

## 3.5. Heat treatment

The green compacts were fired in a 210 mm × 210 mm × 300 mm chamber furnace with vertical SiC elements at both sides (Blue M). The chamber was provided with an SiC or heat-resistant stainless steel encapsulation for temperature homogenization. The temperature at the compact was controlled by means of a direct digital cascade control system with two completely adaptive software PID controllers and software setpoint programming. The temperature stability at top level was within 0.1° C with an absolute accuracy of ± 2° C. Setpoint program conformity was within ± 2° C in all cases.

## 3.6. Density of the fired composites: special attempts to decrease the final density

The density of the fired compacts was measured on machined bars with dimensions of 10 mm × 10 mm × 30 mm or 3 mm × 9 mm × 45 mm by simple weighing and dividing by the calculated volume. Crack-free samples showed negligible shrinkage.

Some preliminary attempts were undertaken to decrease the final density of the compacts by increasing the viscosity of the binder solution, by foaming or by filling with PMMA (polymethyl metacrylate) spheres that were depolymerized by heat treatment.

The viscosity of the binder solution was increased by adding methyl cellulose, gelatine or bioagar. It appeared however that a high viscosity of the binder solution resulted in serious processing problems and had almost no effect on the final density.

Foaming was achieved by adding $H_2O_2$ to the binder solution, followed by heating or by the addition of polyvinyl alcohol, Teepol or Lissapol N foaming agents and vigorous stirring or syphoning. The resulting foams proved to be highly unstable and showed considerable inhomogeneity so that no further attempts were made to decrease the final density of the compacts by foaming.

Filling with PMMA spheres followed by depolymerization was the most successful special technique used to decrease the final density. Green compacts that contained SI microspheres and PMMA spheres in weight ratios between 1:1 and

1:5 were made by casting and vacuum filtration. The compacts were dried at 50 and 90° C, and then heated for 24 h at 230° C. At this temperature the PMMA spheres depolymerized and evaporated, leaving spherical intergranular cavities in the microsphere compacts. Composites were made by firing for 3 h at 600° C; final densities below $100\,\mathrm{kg\,m^{-3}}$ were obtained. Unfortunately these composites showed marked inhomogeneity and inferior properties so that no further experiments with PMMA filling were conducted.

### 3.7. Measurement of mechanical properties

The compressive strength of SI microsphere composites was measured on machined bars using an Overload S200 testing machine. The compressive force was applied on one of the 10 mm x 10 mm planes with a cross-head speed of $0.1\,\mathrm{mm\,min^{-1}}$. Normally the specimens did not show catastrophic failure but crumbled near the top plane, while the compressive strength remained approximately constant.

The compressive strength was found to be about 15 MPa and did not show a strong dependence on processing. The compressive strength of microsphere composites is apparently mainly determined by the intrinsic properties of the spheres.

The Young's modulus, $E$, and bending strength, $S$, were determined on 3 mm x 9 mm x 45 mm (H x W x Y) machined bars on the same testing machine in a three-point bending set-up, using a span, $L$, of 36 mm. The force, $F$, was applied on the middle of one of the 9 mm x 45 mm planes with a cross-head speed of $0.1\,\mathrm{mm\,min^{-1}}$ using a bar with a radius of 2 mm. The deflection, $D$, of the strips was monitored by an inductive displacement sensor (Tesa, type 32.10802) with a spherical tip (radius 2 mm). The tip had a load force of 10 g and was placed against the centre of the other 9 mm x 45 mm plane.

During the measurement the force, the deflection and the time were recorded by an Apple II + computer system and the data were stored on floppy disc for further processing. Most $F$–$D$ curves were linear until catastrophic failure occurred. Preliminary experiments on microsphere composites, bonded with an organic binder, revealed non-linear behaviour that could be ascribed to plastic deformation of the bonding phase.

All measurements were done in normal air. The Young's modulus of the samples was calculated from the slope, $\Delta F/\Delta D$, of the linear part of the $F$–$D$ curve according to [17]:

$$E = \frac{L^3}{4WH^3} \times \frac{\Delta F}{\Delta D}.$$

The slopes were calculated by linear regression. The bending strength, $S$, was calculated from the failure load according to [17]:

$$S = 3FL/2WH^2.$$

There were some indications that machining of the test strips had an effect on the properties, but no clear trends could be observed.

## 4. Results and Discussion

### 4.1. Microsphere composites made by casting

The best composites were obtained by casting SI microsphere/MAP solution slurries to discs, followed by a heat treatment. Scanning electron microscopy (SEM) photographs of an SI microsphere composite, prepared by casting with a 4 wt % MAP solution are given in Fig. 1.

The composites made by casting showed a slight inhomogeneity, revealed by cutting test strips from the top, the middle and the lower flat-faced side of the discs. The best SI composite strips had a Young's modulus of about 1 GPa and a strength of about 0.8 MPa at a density of about $180\,\mathrm{kg\,m^{-3}}$.

The influence of top-level temperature on $\rho$ and $E$ and SI microsphere composite, prepared by casting and bonded with a 4 wt % MAP solution is given in Fig. 2.

The occurrence of the maximum in $E$ is probably connected with an increase of the efficiency of MAP bonding at lower temperatures, followed by a degradation of the SI microspheres at higher temperatures. This degradation is caused by crystallization of the microspheres. Cristobalite starts to form at temperatures of between 600 and 700° C and causes a complete breakdown of the microspheres at higher temperatures. These phenomena were checked by X-ray diffraction and SEM (see Fig. 3).

The maximum in density at 700° C can be explained by the complete transformation to relatively coherent cristobalite microspheres at that temperature; the decrease at higher temperatures is caused by an expansion process that occurs with the breakdown of the cristobalite microspheres.

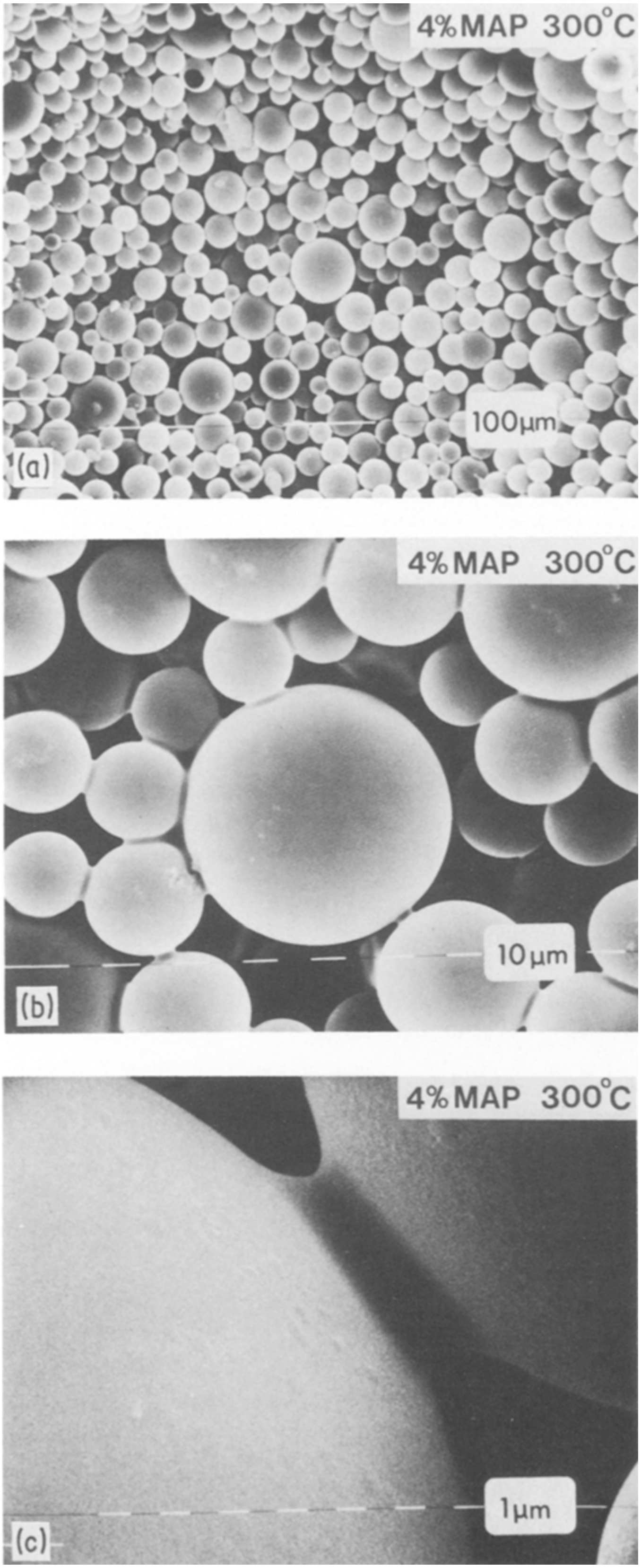

*Figure 1* SEM photographs of an SI microsphere casting, bonded with 4 wt% MAP and fired at 300° C for 3 h.

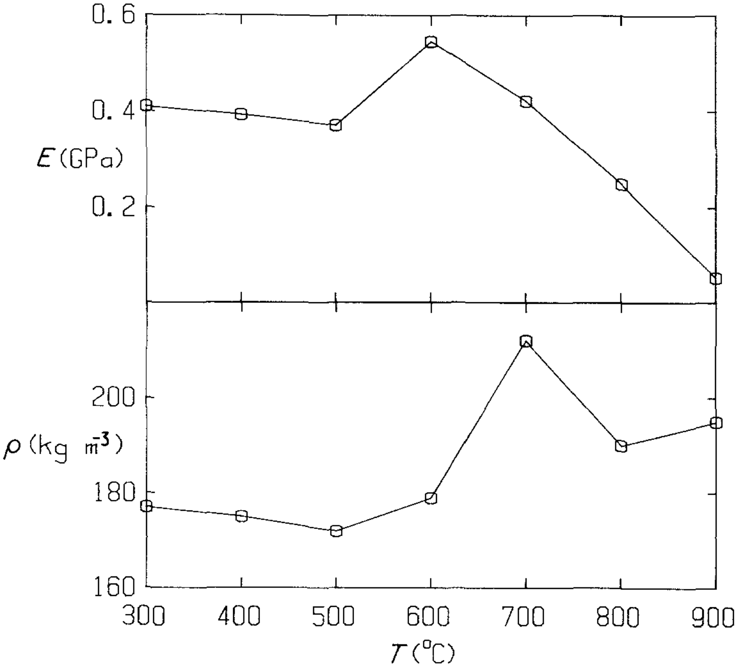

*Figure 2* Influence of the top-level temperature on $\rho$ and $E$ for SI microsphere castings, bonded with 4 wt% MAP and fired for 3 h on top-level.

The density appeared to be roughly constant with time for firing at 600° C (Fig. 4). This indicates that the bonding phase does not lose any more water with increasing firing time. Young's modulus (Fig. 4) and strength showed a tentative maximum at about 3 h firing time, probably due to the completion of bonding phase settling and continuing crystallization of the microspheres.

Density increases gradually with the initial MAP concentration for composites fired for 3 h at 600° C (Fig. 5). At low MAP concentrations it is completely determined by the microspheres but at high concentration the contribution of the binder phase to the density becomes noticeable. The Young's modulus shows a maximum at 4 wt% (Fig. 5). This may be ascribed to a competition between improving bonding efficiency and increasing contribution of the binder phase with increasing MAP concentration. The binder phase is expected to have a significantly lower Young's modulus than vitreous silica, resulting in lower overall $E$-values for the composites. A decrease in $E$ due to microcracking as a result of thermal expansion coefficient differences between the phases is also conceivable.

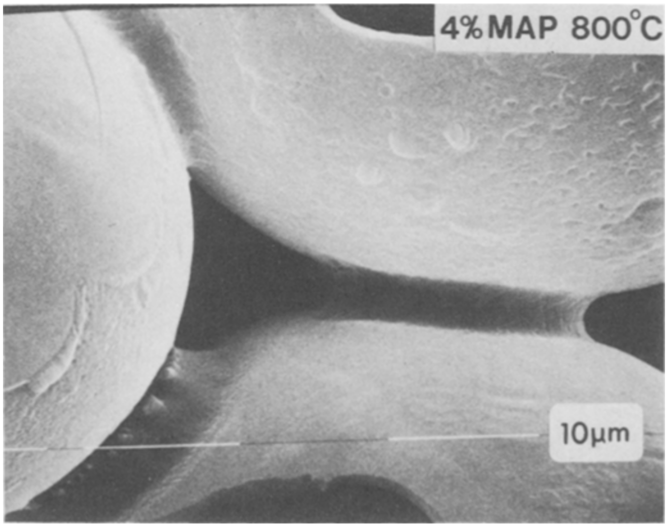

*Figure 3* SEM photograph of an SI microsphere casting, bonded with 4 wt% MAP and fired at 800° C for 3 h.

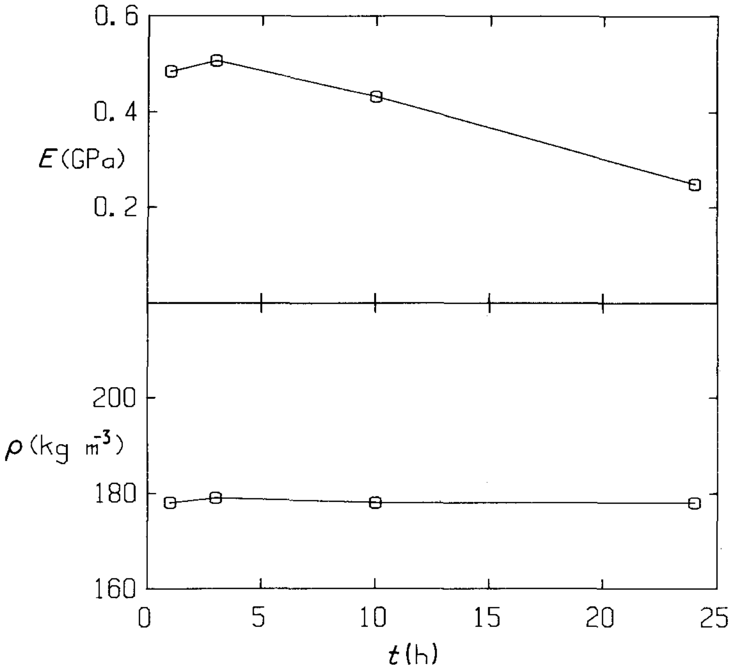

*Figure 4* Influence of top-level time at 600° C on $\rho$ and $E$ for SI microsphere castings bonded with 4 wt% MAP.

The values of Figs. 2 and 5 are typical and are obtained in a single series of experiments. The reproducibility between different series of experiments is within ± 50% for $E$ and ± 10% for $\rho$. The reproducibility in the same series is ± 5% for $E$ and $\rho$.

Casting of SLB microsphere composites was not successful. The castings showed considerable cracking during drying or subsequent heat treatments. This is probably caused by too vigorous chemical reactions of the acid MAP solution with the SLB microspheres.

## 4.2. Microsphere compacts made by pressing

Pressing of microsphere/MAP solution masses, followed by firing, generally resulted in composites that were more homogeneous than composites

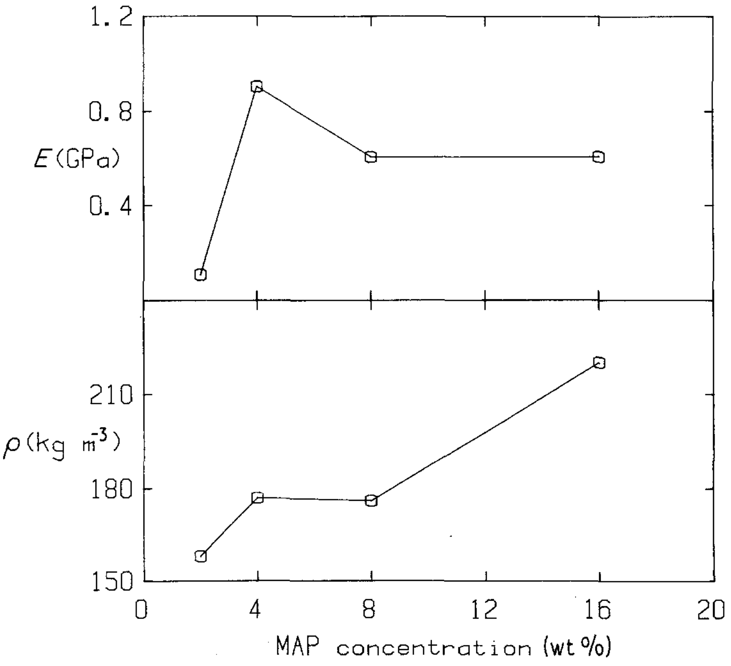

*Figure 5* Influence of the MAP concentration in the binder solution on $\rho$ and $E$ for SI microspheres castings, fired for 3 h at 600° C.

made by casting. The final density of SI microsphere composites made by pressing was generally lower than that of the corresponding castings. The bending strength was of the same order of magnitude but the Young's modulus was lower by a factor of about 4.

Unlike the casting method, pressing proved to be a suitable method for making soda–lime–borosilicate (SLB) microsphere composites. This can be explained as an effect of the chemical reaction between the microspheres and the MAP solution. The quantity of MAP solution in casting slurries is much larger than in the pressing masses. The relatively resistant SI microspheres are attacked much less by the acid solution than SLB microspheres. In SLB casting slurries the kinetics of the reaction is apparently such that breakdown of the SLB composites occurs during drying and heat treatment.

For pressing masses the drying times are much shorter and less MAP solution is present. This probably results in a rapid completion of the chemical reaction of the SLB microspheres so that the compacts remain intact during heat treatment. The best result for pressed SI compacts was a Young's modulus of about 0.15 GPa at a density of about 150 kg m$^{-3}$. Some indications for anisotropy due to pressing were found on non-machined, as-pressed strips. The best result for SLB composites was a Young's modulus of about 0.2 GPa at a density of 121 kg m$^{-3}$, with a top-level temperature between 200 and 600° C and a top-level time of 3 h.

The Young's modulus of the composites made by pressing is generally far below theoretical predictions. The reason of this effect is not very clear; pressing anisotropy may play a role as the theory is only strictly valid for isotropic media. The microspheres may have been microcracked during pressing or the number of real bonding necks may be too low due to the low solution concentration.

## 5. Final remarks

Hollow glass microsphere composites with good mechanical properties are obtained by casting slurries of quartz glass microspheres mixed with a 4 wt% mono-aluminium phosphate (MAP) solution, followed by heat treatment. The highest experimental values remain below the theoretical values predicted in Section 2. The best machined samples had a Young's modulus and strength of about 1 GPa and 0.8 MPa respectively at a density of about 180 kg m$^{-3}$ (porosity 92%); the three-phase model predicts a Young's modulus of 2.4 GPa for a hollow quartz glass microsphere composite with the same density. The discrepancy may be ascribed to oversimplifications in the theory but also to non-ideal bonding of the microspheres, contribution from the binder phase to the elasticity and to the presence of microcracks.

Pressing of MAP solution/microsphere mixtures resulted in relatively homogeneous products that were crack-free after firing. SI composites made by pressing had a density of about 150 kg m$^{-3}$, slightly below that of the castings. The Young's modulus and the bending strength were significantly lower than for castings.

Crack-free SLB microsphere composites could only be made by the pressing method with a lowest density of 105 kg m$^{-3}$ but in most cases they showed inferior mechanical properties.

Complex shapes with good mechanical properties and details of for example 2 mm × 20 mm × 80 mm have been made in our laboratories by machining quartz glass micosphere castings bonded with MAP and by moist-pressing of granulated glass micosphere/MAP mixtures.

## Acknowledgement

The authors are indebted to J. E. D. Parren for the mechanical property measurement and to A. J. Zwartjens for help with the preparation of the samples.

## References

1. J. S. MORGAN, J. L. WOOD and R. C. BRADT, *Mater. Sci. Eng.* **47** (1981) 37.
2. H. E. EXNER, "Grundlagen von Sintervorgänge" (Gebr. Bornträager, Berlin, 1978).
3. R. W. RICE, in "Treatise on Materials Science and Technology", vol. 11, "Properties and Microstructure" (Academic Press, Inc, New York, 1977) pp. 199–381.
4. *Idem, J. Amer. Ceram. Soc.* **59** (1976) 536.
5. R. M. CHRISTENSEN, "Mechanics of Composite Materials" (John Wiley & Sons, New York, 1979).
6. J. R. WILLIS, in "Mechanics of Solids", edited by H. G. Hopkins and M. J. Sewell (Pergamon, Oxford, 1982) p. 653.
7. S. SPINNER, *J. Amer. Ceram. Soc.* **45** (1962) 394.
8. H. SCHOLZE, "Glass" (Springer Verlag, Berlin, 1977).
9. B. RYAN and B. TARDY, in "Handbook of Fillers and Reinforcements for Plastics", edited by H. S. Katz and J. V. Milewski (van Nostrand Reinhold, New York, 1978) pp. 317–30.

10. V. KÖHNE and W. PEEK, "Spechsaal für Keramik. Glas. Email. Silikate" **100** (1967) 830.
11. *Idem, ibid.* **101** (1968) 507.
12. W. D. KINGERY, *J. Amer. Ceram. Soc.* **33** (1950) 239.
13. *Idem, ibid.* **35** (1952) 61.
14. J. E. CASSIDY, *Ceram. Bull.* **56** (1977) 640.
15. M. J. O'HARA, J. D. DUGA and H. D. SHEETS, *ibid.* **51** (1972) 590.
16. J. H. MORRIS, P. G. PERKINS, A. E. A. ROSE and W. E. SMITH, *J. Appl. Chem. Biotechnol.* **28** (1978) 756.
17. S. TIMOSHENKO, "Strength of Materials", 3rd edn (van Nostrand Rheinhold Princeton, NJ 1955).

*Received 9 April*
*and accepted 10 May 1984*