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# Mechanical Properties of Glass Microspheres

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**Abstract**

Glass microspheres are used for both medical and industrial applications among others. It is of interest to develop simple experimental techniques to characterize the mechanical properties of different sets of glass microspheres.

In this study we performed the *Point Load Strength Tests* (PLST) on alumino-borosilicate and yttrium-aluminosilicate glass microspheres samples, with sizes between 50 and 200$\mu m$ obtained by the *In Flame Spherodization Method* (IFSM). We measured the breaking load of each microsphere within a set, and used *Weibull statistics* to determine the mechanical parameters values of each set of microspheres.

We found for 75$\mu m$ microspheres, that those made of alumino-borosilicate glass have a Weibull modulus of *4.0±0.1* and for the yttrium-aluminosilicate microspheres the Weibull modulus is *3.3±0.1*. Scale parameter values are *710±20* and *390±20MPa* respectively. These results show that the PLST technique and Weibull analysis together constitute a valuable tool for mechanical characterization of glass microspheres samples.



*Keywords*: glass microspheres; mechanical properties; Point Load Strength Test (PLST), Weibull Statistics.

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## 1. Introduction

Actually glass microspheres applications are as wide as medical applications, cancer radiotherapy treatment, drug delivery, proppants for the oil industry and even uses in the nuclear industry. Glass microspheres can be obtained from several methods, and the product properties will rely on the chosen production process. So it is of interest to develop a simple technique to analyze the mechanical behavior of sets of glass microspheres, and correlate the mechanical properties values obtained with the production process.

**Nomenclature**

| | |
|---|---|
| $T_G$ | vitreous transition temperature |
| $E$ | Young modulus |
| $\nu$ | Poisson modulus |
| $H_V$ | Vickers hardness |
| $\sigma_R$, $\sigma_\theta$ and $\sigma_\phi$ | radial stress, azimuthal stress and spherical stress |
| $R$ | sphere or microsphere radii |
| $F_0$ | external force applied on PLST |
| $a_c/R$ | contact length relation between the sphere and the compressing element on PLST |
| $\sigma_{brk}$ | maximum tensile stress at breakage |
| $F_{brk}$ | breakage external force |
| $P_f$ | failure probability of a loaded sample |
| $V$ | volume of a sample |
| $\sigma$ | tensile stress |
| $m$ | Weibull modulus |
| $\sigma_0$ | scale parameter |
| $i$ | order of tested microsphere |
| $n$ | total number of microspheres tested on a set |

### *1.1. Glass Microspheres Production - In Flame Spherodization Method*

To obtain glass microspheres, we used the In Flame Spherodization Method (IFSM). In this method, irregular glass particles are fed into a flame with a temperature well over the vitreous transition temperature ($T_G$). On their way, inside the flame and during a few milliseconds, the glass particles increase their temperature producing a simultaneous viscosity decrease adopting a spherical form due to the action of surface tension, Bortot (2012).
In Fig. 1 we show the IFSM scheme: here the irregular glass particles are slowly fed to the hot region of the flame through the Powder Feeder System which consists of a set of vibratory sieves, and then at the center zone of the flame the glass particles become spheroidized. Finally the obtained microspheres travel through the cool region of the flame (where the temperature is below $T_G$) into a cyclone system, which collects all the spheroidized particles.

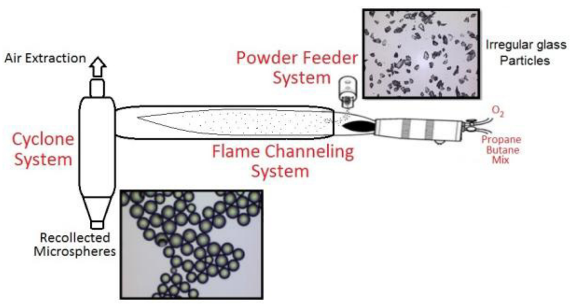


Fig. 1. IFSM scheme, we present pictures of irregular glass particles and glass microspheres.

In the IFSM there is a temperature distribution inside the flame so each particle travels through a different thermal path, Bortot (2012). These different thermal paths produce differences in cooling rates for each spheroidized particle, which is the cause of different properties values among microsphere sets (different density values).
In Fig. 2 we present a picture of the Flame Channeling System, between the torch and the cyclone on Fig. 1. Inside both circular windows, we can observe the flame and different microspheres glowing tracks (one and four tracks respectively).

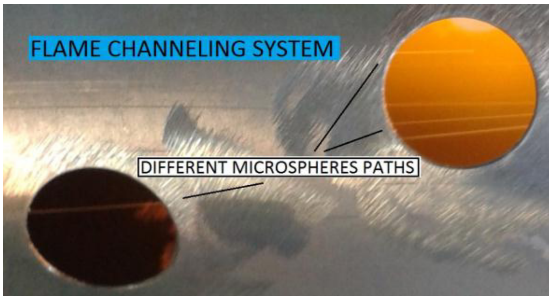


Fig. 2. Flame Channeling System. The flame and microspheres tracks are observed through two circular window holes.

### *1.2. Mechanical Characterization Technique*

The Point Load Strength Test (PLST) is an inexpensive method for strength estimation of brittle materials. An extensive theoretical analysis of PLST for isotropic spheres was made by Hiramatsu and Oka (HO) on 1966, reviewed by Chau et al. (1999). HO obtained the stress field ($\sigma_R$, $\sigma_\theta$ and $\sigma_\phi$) in a sphere of radius $R$ as a function of the elastic properties of both the compressed material and the compressor element ($E$, $\nu$), the external applied force ($F_0$) and the contact length relation ($a_c/R$).
In Fig. 3 we show (a) a sphere under uniaxial compression; and (b) a schematic stress field in the compressed sphere.

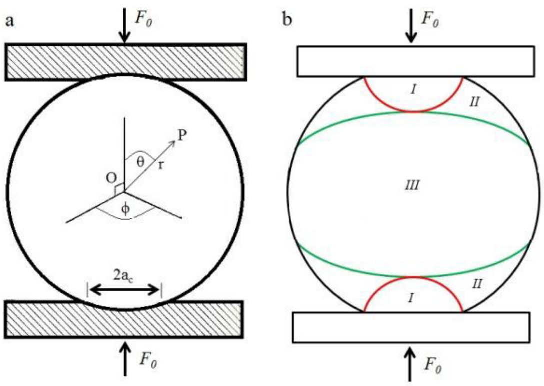


Fig. 3. (a) Sphere under uniaxial compression; (b) Schematic stress field diagram.

In Fig. 3 (b) we have a three zones map with different stress field conditions. At *zone I,* which corresponds to the contact zone between the sphere and the compressor element, we have a compression stress field. Then in *zone II,* which is ring shaped around the contact area, we have borderlines where $\sigma_\theta$ and $\sigma_\phi$ become into tensile stresses. Finally in *zone III*, the rest of the volume of the sphere, we have that $\sigma_\theta$ and $\sigma_\phi$ are always tensile stresses.

Under this stress field, brittle spheres fail because of tensile stresses. From the HO analysis the maximum tensile stress is located at the load axis, specifically at the center point of the sphere. However when the contact length relationship is less than 0.4; the maximum tensile stress moves through the load axis to a point near to the surface of the sphere (always in the zone III of Fig. 3 (b)), Shipway et al. (1993), Schönert (2004), Chen (2007).
Averaging these cases HO proposed, with reasonably accuracy, the relationship (1) to determinate the maximum tensile stress in a sphere at breakage.

$$\frac{\sigma_{brk}*\pi*R^2}{F_{brk}} = 0{,}7 \qquad (1)$$

where $F_{brk}$ is the breakage external force, and $\sigma_{brk}$ is the maximum tensile stress at breakage.

Using experimental data we can calculate the value of $\sigma_{brk}$ developed inside a tested microsphere, during a PLST experiment. Then to characterize a set of given glass microspheres, Weibull statistics allows us to analyze the data obtained from the corresponding set of PLST tests.
According to Weibull statistics the breakage of a brittle sample is a statistic event and is due to tensile local stresses developed at previously existent cracks inside the material. The largest crack determines the total resistance of the sample, Ashby (1998). Equation (2) shows the Weibull Statistics expression:

$$P_f(V) = 1 - e^{-(\frac{\sigma}{\sigma_0})^m} \qquad (2)$$

where $P_f$ is the failure probability of a sample with volume $V$ loaded with a tensile stress $\sigma$. In equation (2) $m$ is the *Weibull modulus* which is a material property and accounts for the fragility of the material (the lesser the value of $m$, the larger the fragility); and $\sigma_0$ is a *scale parameter* which represents the stress allowing to survive *37%* of the samples. The scale parameter is not a material property and decreases with larger sample volume because of the existence of larger cracks.

In summary, using the PLST technique and Weibull statistics we performed the mechanical characterization of sets of glass microspheres with given chemical composition and size ranges. We measured the breakage load on each microsphere within a set during the PLST tests, and with the HO solution we calculated the maximum tensile stress at breakage. Then using the Weibull statistics, we determined the Weibull modulus and the scale parameter which represent the mechanical characteristics of each set of microspheres.

## 2. Experimental Methods and Data Analysis

### *2.1. Glass Microspheres Samples*

We used an alumino-borosilicate glass (SG7 glass) with a percent weight composition 71.7 $SiO_2$; 8.4 $B_2O_3$; 8.6 $Al_2O_3$; 1 MgO; 2.7 CaO; 7.5 $Na_2O$; Audero et al. (1995), and yttrium-aluminosilicate glass (YAS glass) with composition 35 $SiO_2$; 45 $Y_2O_3$; 20 $Al_2O_3$; Bortot (2012).
In Table 1 we show several bulk properties of these glasses.

Table 1. Glass physicals properties.

| Physical properties | YAS glass, (Bortot,2012) | SG7 glass, (Audero et al., 1995) |
|---|---|---|
| vitreous transition temperature (°C) | 910 | 560 |
| density (gr/cm$^3$) | 3.37 | 2.3 |
| Young modulus (GPa) | 110 | 73 |
| Poisson modulus | 0.29 | 0.22 |
| Vickers hardness (kgf/mm$^2$) | 850 | 550 |

We obtained different sets of microspheres from SG7 and YAS irregular glass particles by the IFSM with a butane-propane-oxygen flame. Then we performed the mechanical characterization of sets of 40 SG7 glass microspheres, each set having diameters of 75, 100, 125, and $150\mu m$. Also we compared two sets of 40 YAS glass microspheres with diameters around $75\mu m$, with and without an annealing process at 950°C for 4 hours after IFSM.

### *2.2. Point Load Strength Test Device (PLST)*

We developed a sample holder device that was attached to an INSTRON Test Machine N°5567 to perform the PLST on each glass microsphere. The sample holder device consists of a compressor element and a container element made from cobalt steel "*Super70(18)*" (*18%* weight cobalt). The mechanical properties of the steel used are $H_V = 1210 kgf/mm^2$; $E_{stl} = 210 GPa$; $\nu_{stl} = 0.3$, Shipway (1993). The hardness of the cobalt steel prevents plastic deformation of the compressor and container elements when each PLST test is performed.
In Fig. 4 we show a lateral view scheme of the sample holder device.

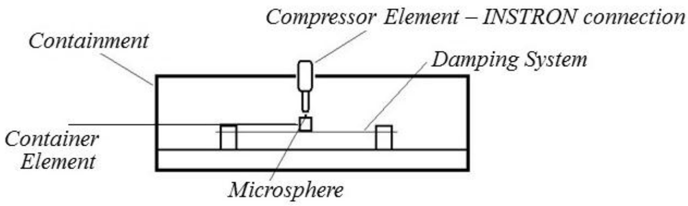


Fig. 4. Sample holder scheme, lateral view.

To perform the PLST on each microsphere we used a magnifying glass to determine the tested microsphere size and a needle to handle it individually. To measure the breakage load we used a dynamometer with an acquisition board attached to the INSTRON Test Machine.

### *2.3. Data Analysis*

#### *2.3.1. Tensile Strength*

From the HO solutions we obtained the expression (3) for the maximum tensile stress at the microsphere breakage:

$$\sigma_{brk} = \frac{-F_{brk} * \left[1 - \left(\frac{3}{2} * (1 + cos(\theta_0)) * cos(\theta_0) * \frac{35 + 10 * \nu}{42 + 30 * \nu}\right)\right]}{2 * \pi * R^2} \tag{3}$$

where $\theta_0 = \arcsin(a_c/R)$, by elastic theory $a_c = \sqrt[3]{(3/4) * k * F_0 * R}$ and
$k = \left((1 - \nu_{gls})/E_{gls}\right) + ((1 - \nu_{stl})/E_{stl})$; where *gls* indicates a glass bulk property and *stl* indicates a steel property.

Expression (3) is similar to expression (1) but allows incorporating bulk mechanical properties of the sample and the components of the sample holder device.

#### *2.3.2. Maximum Likelihood Method (MLM)*

We used the Maximum Likelihood Method (MLM) to calculate the Weibull parameters values ($m$ and $\sigma_0$). The mathematical expression for the Weibull parameters in MLM are (4) and (5), Dongfang et al. (2004).

$$\frac{n}{m} + \sum_{i=1}^{n} ln(\sigma_{brk_i}) - \frac{\sum_{i=1}^{n} \sigma_{brk_i}{}^{m} * ln(\sigma_{brk_i})}{\sum_{i=1}^{n} \sigma_{brk_i}{}^{m}} = 0 \quad (4)$$

$$\sigma_0 = (\frac{1}{n} * \sum_{i=1}^{n} \sigma_{brk_i}{}^{m})^{1/m} \quad (5)$$

where $\sigma_{brk_i}$ is the breakage tensile stress on the i-th tested microsphere; and $n$ is the total number of tested microspheres on a set.

## 3. Experimental Results

### *3.1. Alumino-borosilicate glass microspheres*

In Fig. 5 we show (a) the failure probability at different stress values for sets of SG7 microspheres with diameters (D) of 75, 100, 125, and 150$\mu m$; (b) the Weibull modulus as a function of microsphere size; and (c) the scale parameter as a function of microsphere diameter.
In Table 2 we show the values of Weibull modulus and the scale parameters for each set of microspheres.

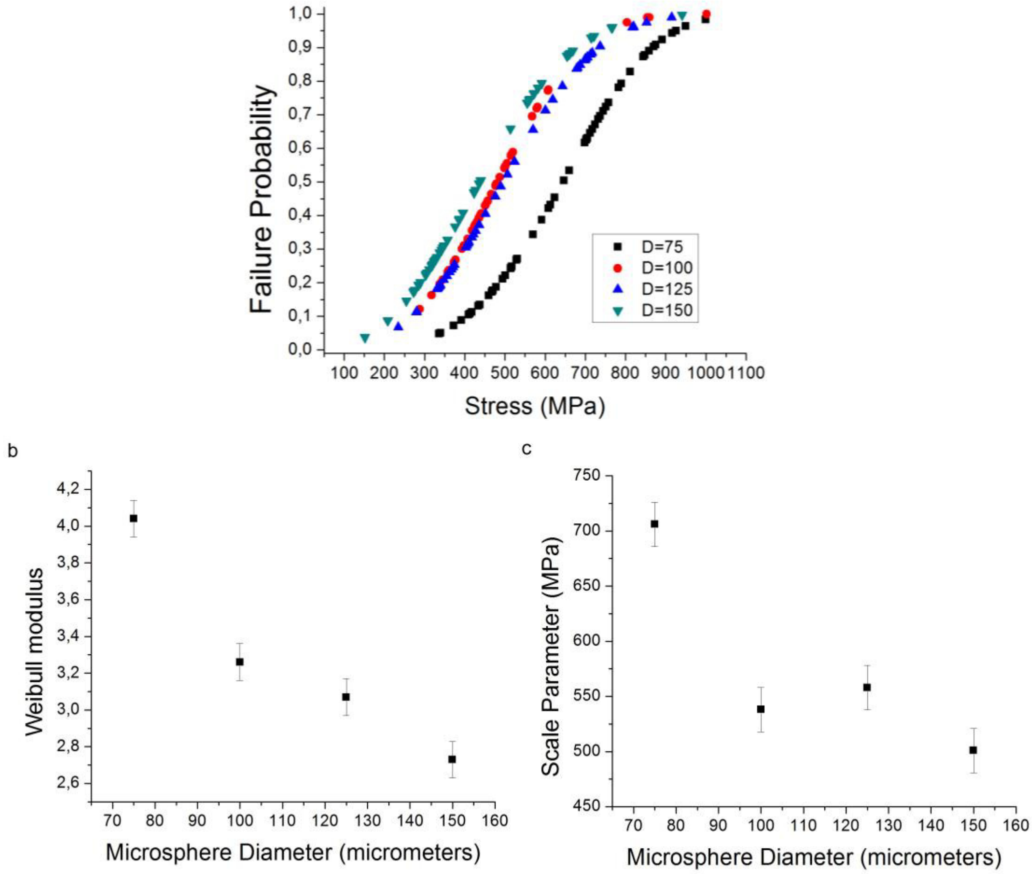


Fig. 5. (a) Probability of failure at different stresses for SG7 microspheres with diameters (D) of 75, 100, 125 and 150$\mu m$; (b) Weibull modulus as a function of microsphere diameter; (c) scale parameter as a function of microsphere size.

Table 2. Weibull modulus and Scale parameter values for sets of SG7 microspheres of different size.

| Microspheres diameter ($\mu m$) | Weibull modulus | Scale parameter (MPa) |
|---|---|---|
| 75 | 4.0±0.1 | 710±20 |
| 100 | 3.3±0.1 | 540±20 |
| 125 | 3.1±0.1 | 560±20 |
| 150 | 2.7±0.1 | 500±20 |

The Weibull modulus decreases with larger microsphere diameters; this result evidences an increase on the material fragility on larger size microspheres.

The Scale parameter decreases with larger diameters according to the Weibull theory. However the different Weibull modulus values of different sets of spheroidized particles do not allow us to correlate both parameters.

*3.2. Yttrium-aluminosilicate glass microspheres*

In Fig. 6 we show the failure probability at different stress values for sets of 75$\mu m$ YAS microspheres, the red solid dots refers to a set of annealed microspheres after the IFSM.

In Table 3 we present the Weibull modulus and the scale parameter values for each set of microspheres.

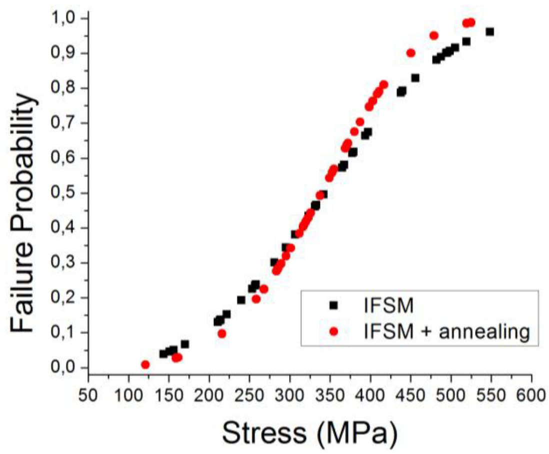


Fig. 6. Probability of failure as a function of the applied stress for 75$\mu m$ YAS microspheres. The red solid dots refer to annealed microspheres after the IFSM.

Table 3. Weibull modulus and scale parameter values for sets of 75$\mu m$ YAS microspheres.

| YAS microspheres (75$\mu m$) | Weibull modulus | Scale parameter (MPa) |
|---|---|---|
| IFSM | 3.3±0.1 | 390±20 |
| IFSM+ annealing process | 4.3±0.1 | 370±20 |

The Weibull modulus of annealed microspheres was *30%* higher than for the not annealed microspheres, and the scale parameter values were the same on both sets. These results mean that there is a decrease on the microspheres fragility with no change on their resistance to breakage, because the annealing process.

### *3.3. Comparison of mechanical characteristics for different composition glass microspheres*

In Fig. 7 we present (a) the failure probability at different stress values for a set of $75\mu m$ YAS glass microspheres and a set of $75\mu m$ SG7 glass microspheres, both without annealing process; (b) the same data for probability of failure as a function of stress shown in (a), but each stress value was normalized with its scale parameter ($\sigma_0$).

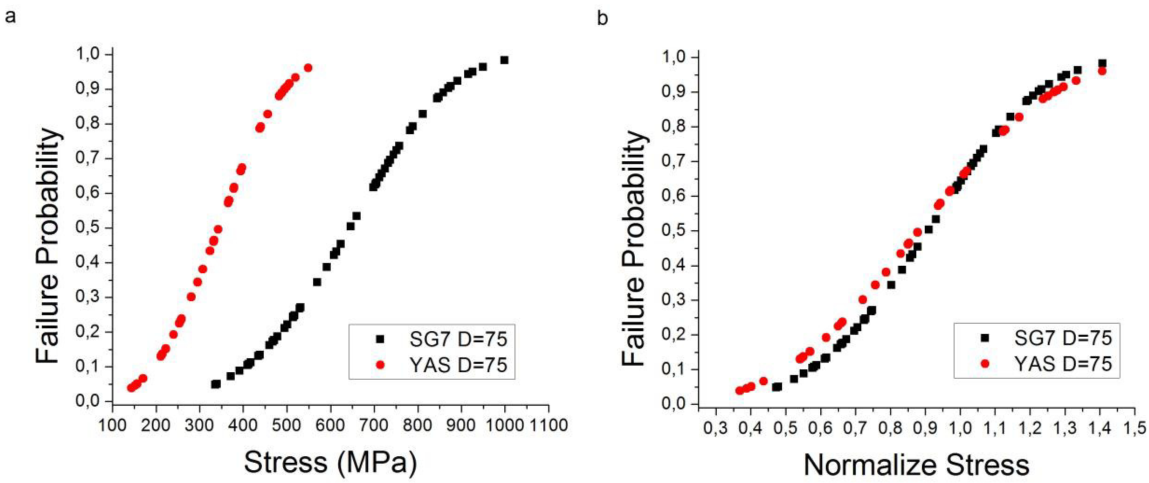


Fig. 7. (a) Probability of failure at different stress values for set of $75\mu m$ SG7 glass microspheres and a set of $75\mu m$ YAS glass microspheres, both without annealing process; (b) Probability of failure at different stress normalizes with the scale parameter of each set of $75\mu m$ microspheres.

The set of SG7 glass microspheres breaks at higher stresses than the set of YAS glass microspheres. This result shows that SG7 microspheres have more resistance to breakage than YAS microspheres.
The normalized curves show a higher Weibull modulus for SG7 glass microspheres which demonstrates that SG7 glass microspheres are less fragile than YAS glass microspheres.

## 4. Discussion and Conclusions

We developed a simple technique for the mechanical characterization of glass microspheres with different sizes and compositions. We characterized sets of SG7 glass microspheres with several diameters, a set of $75\mu m$ YAS glass microspheres and finally a set of $75\mu m$ annealed YAS glass microspheres.

Particularly for sets of alumino-borosilicate glass microspheres (SG7) we obtained a decrease in the fragility for larger size microspheres. This can be understood since different size spheres have different thermal histories in the IFSM, thus different glass properties. Moreover, the cooling process originates internal tensions in the microspheres because of the external surface layer cools faster than the internal volume. This effect can increase the fragility of bigger microspheres ($150\mu m$).
We expect that the Weibull modulus has to reach an asymptotic value with the volume increase, since for larger diameters a larger fraction of its volume will have the same glass transition temperature ($T_G$) and a similar cooling process.

A *30%* decrease on the fragility was obtained after an annealing process for the $75\mu m$ yttrium alumino-silicate (YAS) microspheres set without change on their resistance to breakage. This result can be understood because of the partial healing during the annealing process of internal flaws generated in the IFSM.

Finally, when comparing the mechanical properties of sets of microspheres with different compositions and the same size, we obtained that SG7 glass microspheres are less fragile than YAS glass microspheres. Also SG7 glass microspheres exhibit a higher resistance to breakage.
The fragility difference can be explained because the glass transition temperature ($T_G$) necessary for the spherodization process in SG7 glass is lower than YAS glass, so less internal flaws or tensions remained after the cooling process.

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