KLA INSTRUMENTS

Young's Modulus of Glass Microspheres

Introduction

Microspheres have myriad uses in modern life. Hollow microspheres are used to lower the density of manufactured materials. In modern liquid chromatography, the analyte is forced through a column packed with glass microspheres, thus causing components of the analyte to separate based on the speed at which they can pass through the column. In electronic packaging, metalized polymer microspheres are packed together to created flexible, reliable connections. The glass microspheres tested in this work are incorporated into paints to enhance appearance and mar-resistance. In all these applications, knowing the mechanical properties of the microspheres is a critical aspect of design. With relatively minor changes in hardware and test procedure, the InForce 50 actuator becomes a general small-scale compression testing system. In this case, the actuator was fit with a flat-ended punch in order to set up a test condition that can be analyzed as a double-sided Hertzian contact [1]. For the test geometry illustrated in Figure 1, the Young's modulus, E, is related to the particle diameter, D, compression force, P, and the total compression distance, α, as[1]:

$$E = 3P(1 - v^2)/(D^{1/2}\alpha^{3/2}) \qquad \text{Equation 1}$$

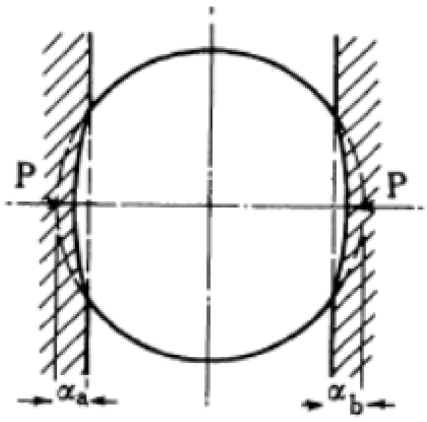

Figure 1. Compression of a sphere between two parallel platens, analyzed as a double-sided Hertzian contact [1]. In this work, the face of the flat punch is one platen, and the substrate is the other.

[1] Assuming infinitely stiff platens.

The oscillatory aspect of the InForce 50 [2] provides an experimental advantage in that one may use a derivative form of Equation 1 ($S = dP/d\alpha$), which reveals a more instantaneous relationship between properties and measured parameters:

$$E = 2S\,(1 - v^2)/\sqrt{\alpha D} \qquad \text{Equation 2}$$

In other words, the Young's modulus is related to the instantaneous stiffness S and the compression distance α. Not only is Equation 2 less sensitive to common measurement errors in the absolute values of P and α, it can reveal changes in modulus caused by increasing compressive strain. This is particularly important for polymer spheres because the compression process causes the polymer chains to stretch and become more closely packed, which can manifest as a true increase in modulus. In other words, the compressed polymer microsphere generally has a higher modulus than the original microsphere. Thus, Equation 2 is a better model, but it can only be used with testing instruments that superimpose an oscillatory force on the semi-static compression process.

To normalize results for particle size, we employ a simple definition of strain:

$$\epsilon = \alpha/D \qquad \text{Equation 3}$$

and report modulus for each microsphere at a specific value of strain.

Materials and Methods

All tests were performed with the KLA Instruments™ NanoFlip, which includes an InForce 50 actuator. The NanoFlip was chosen because its small size allows testing within an SEM chamber, and its superior positioning capability allows motion control with nanometer-scale precision. The actuator was configured with a tip extender and fitted with a conductive diamond frustum (Ψ = 60°, R = 5µm). The entire testing system was placed inside the main chamber of a Philips XL 30 Scanning Electron Microscope (SEM), shown schematically in Figure 2, to allow simultaneous imaging and testing.

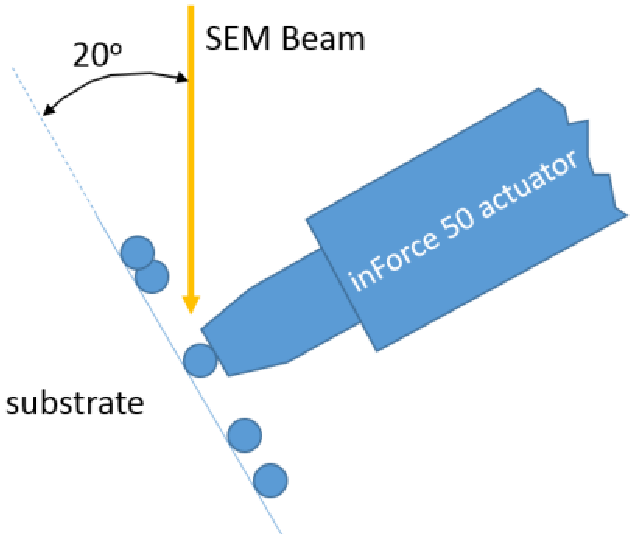

Figure 2. Schematic of test setup.

Solid microspheres made from recycled soda-lime glass (mean diameter of 4µm) were acquired from Prizmalite Industries, Inc.[2] Microspheres were dispersed on a glass microscope slide using ethanol. All tests were performed using the test method **InSEM Dynamic Spherical Compression**. This test method operates in individual mode, allowing the user to execute one test at a time. The following steps were performed for each test:

1. Guided by a video stream from the SEM, the moving platen (the flat face of the diamond frustum indenter) was centered over the target particle, approximately 2µm above the top of the particle.
2. The diameter of the particle was measured using a high-quality SEM image[3].
3. The moving platen approached the particle at a velocity of 50nm/s until contact was detected.
4. The particle was loaded at a rate of 0.1mN/s while simultaneously oscillating the moving platen with an amplitude of 2nm and a frequency of 100Hz. Loading was terminated when the total compression exceeded 1500nm or the applied force exceeded 50mN.
5. The particle was unloaded over the course of 1s.

During the approach, loading, and unloading, fast-scan video[4] from the SEM was automatically acquired and synchronized with the mechanical data by the InView software.

Results and Discussion

Figure 3 shows the SEM images of the first microsphere, before and after testing (other microspheres exhibit similar deformation). Clearly, the test causes both plastic yield, as indicated by the flattened shape, as well as fracture. Although the goal of this work is to measure Young's modulus, future efforts will focus on measuring yield strength by means of a similar test.

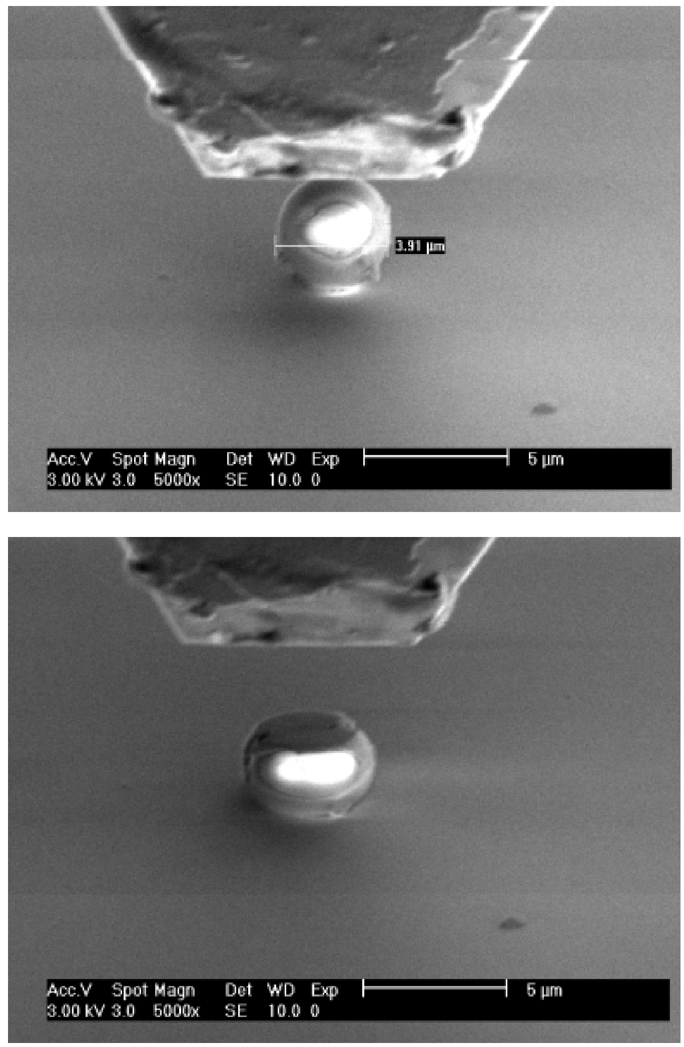

Figure 3. Microsphere (a) before testing, and (b) after plastic yielding and fracture.

The superimposed oscillation applied during loading (1nm, 100Hz) yields a continuous measure of stiffness as each microsphere is compressed. From this continuous measure of

[2] Prizmalite Industries, Inc. 380 Lexington Avenue, 17th Floor, New York NY 10168. Product name P2011SL Glass Microspheres; Lot Number PS130803A.

[3] 16.7ms/line, 2904 lines/frame.

[4] 1.68ms/line, 484 lines/frame.

stiffness, modulus is calculated according to Equation 2. Figure 4 shows this calculation of modulus as a continuous function of strain for all tests. As expected, the measured modulus is more consistent from test to test at larger strains. This is because inaccuracies in the compression distance (which arise primarily from imperfections in the shapes of the contacting surfaces) become relatively unimportant as the overall compression distance increases. All particles fail at a strain just above 0.3%. Thus, we report the measured modulus at a lesser strain around 0.20% (between the "X" and the green circle in Figure 4).

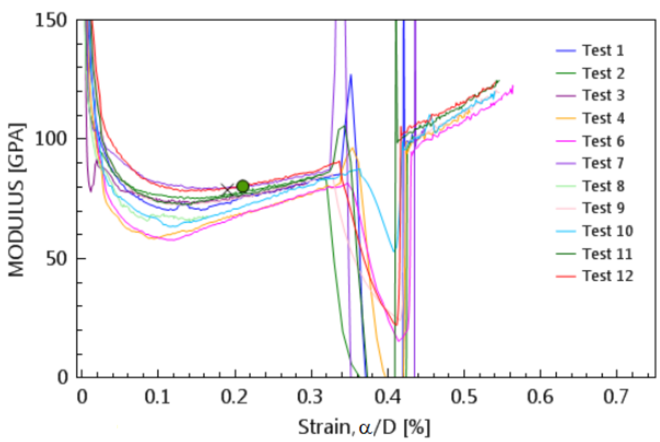

Figure 4. Modulus as a function of compressive strain for 12 microspheres. Failure is obvious at strains just greater than 0.3%.

Figure 4 illustrates a very practical advantage of the superimposed oscillation: simplicity in testing. It is not necessary to know much about the sample or its expected behavior in order to plan a good test. The superimposed oscillation gives properties as a continuous function of strain (or load, or depth) and the experimenter is free to decide, after the fact, the ideal conditions for reporting properties—in this case, just prior to fracture. The InView software makes these advantages available to the experimenter by allowing changes in data analysis after testing is complete.

Table 1 summarizes the measurements of diameter and modulus for all microspheres. Even for this very small (and not random) sampling, the mean diameter is close to that reported by the manufacturer (4μm), and the measured modulus of 73.6GPa is within the expected range for soda-lime glass (72-74GPa [3]).

Table 1. Diameter and Young's modulus for soda-lime glass microspheres.

Microsphere	Diameter (um)	E @ 0.2% strain (GPa)
1	3.91	74.44
2	4.31	77.16
3	5.44	75.57
4	3.12	68.20
5	4.34	71.36
6	2.79	67.31
7	3.55	80.01
8	7.40	67.29
9	2.89	75.24
10	2.92	70.75
11	2.89	76.38
12	2.92	79.80
Median	**3.34**	**74.84**
Mean	**3.87**	**73.63**
Std. Deviation	**1.32**	**4.32**

Conclusions

The KLA Instruments NanoFlip nanoindenter is used as a general micro-scale compression tester in order to measure the Young's modulus of glass microspheres of about 4μm in diameter. The test is interpreted with a double-sided Hertzian model in order to achieve a value for Young's modulus. The dynamic aspect of this testing system, which measures elastic stiffness as a continuous function of compression, reduces sensitivity to imperfections in the shapes of the contacting bodies, thus allowing an accurate measurement of Young's modulus (73.6 ± 4.3GPa).

References

[1] M. J. Puttock, E. G. Thwaite. "Elastic Compression of Spheres and Cylinders at Point Contact and Line Contact." National Standards Laboratory Technical Paper No. 25. CSIRO, Melbourne, (1969).

[2] Oliver, W.C. and Pharr, G.M., "An Improved Technique for Determining Hardness and Elastic Modulus Using Load and Displacement Sensing Indentation Experiments, Journal of Materials Research 7(6):1564- 1583 (1992).

[3] "Soda-lime Glass." https://en.wikipedia.org/wiki/Soda-lime_glass.

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