MODELING THE FORMATION OF POLYIMIDE MICROSPHERES

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High temperature polyimide microspheres have been developed from polyimide solid residuum by a simple inflation process. Microspheres have been fabricated from several polyimide precursors through the use of a circulating air oven. Microsphere formation and final physical property characterization have been limited to simple mechanical and thermal testing. The present paper focuses on developing an understanding of microsphere formation through simple geometric rules for an incompressible polymeric material and microscopic observations of precursor residuum inflation. Inflation kinematics of the hollow polyimide microspheres as a function of time and temperature is discussed.

KEY WORDS: Polyimides, Microspheres, Foams

1.0 INTRODUCTION TO POLYIMIDE FOAMS

The foam precursor was synthesized by mixing monomer reactant oxydiphthalic anhydride (ODPA) with a hydrogen bonded foaming agent in methanol (MeOH) at room temperature. After three hours of mixing at 60^0 C, this material was converted into ODP-dimethyl ester. It was then mixed with measured amounts of 3,4'-oxydianline (3,4'-ODA), and stirred for two hours to yield a homogeneous solution. A fine powder of salt-like foaming precursor was isolated from the solution by evaporation of the solvent to produce the polyimide precursor powder. The materials discussed in this paper were produced by Unitika Ltd of Japan (1).

Foams are produced from the polyimide precursor powder by a simple thermal cycle under ambient pressure conditions. While the mechanisms for particle inflation have not been studied in detail until the present paper, it is clear that the blowing agent is hydrogen bonded to the precursor particles and upon an increase in temperature, the polymer passes through its glass transition temperature and the particle is transformed into a hollow spherical geometry. When in a confined volume, the microspheres then grow together to produce the foam microstructure.

2.0 GEOMETRIC RELATIONSHIPS FOR INCOMPRESSIBLE POLYMER

The geometry of polymeric particle is idealized as a hollow microsphere of initial outer radius, b_0 and initial inner radius, a_0. Under the condition of constant volume of polymeric material, geometric relations can be developed that relate the microsphere radii, b and a, as a function of its initial dimensions.

$$\frac{b}{b_0} = \left[\frac{\left[1-(a_0/b_0)^3\right]}{\left[1-(a/b)^3\right]} \right]^{\frac{1}{3}}$$

[1]

$$\frac{a}{b_0} = \left(\frac{a}{b}\right)\left(\frac{b}{b_0}\right) = \left(\frac{a}{b}\right)\left[\frac{\left[1-(a_0/b_0)^3\right]}{\left[1-(a/b)^3\right]} \right]^{\frac{1}{3}}$$

[2]

2.1 Microsphere size as a function of a/b at a_0/b_0=0.1   Equations 1 and 2 give the ratio of the new outer radius to the initial outer radius, b/b_0 and the ratio of the new inner radius to the initial outer radius, a/b_0 as a function of the initial dimensions of the microsphere and reveal cubic relationships with the ratios of inner to outer diameter. These results are summarized in Figure 1 and Table 1 for an initial radius ratio of 0.1. Of particular note is the rate of growth of the new outer diameter, b as a function of the inner radius growth. Note, for example that an increase in the size of the inner radius ratio, a/b_0 from 0.1 to 0.523 corresponds to an increase in outer radius ratio, b/b_0 of only 1.0 to 1.045. Therefore, a change in inner radius of over 500% produces only a 5% change in external radius ratio.

Table 1: Results for a_0/b_0 = 0.1.

a/b	b/b_0	t/b_0	a/b_0
0.1	1.000	0.900	0.100
0.2	1.002	0.802	0.200
0.3	1.009	0.706	0.303
0.4	1.022	0.613	0.409
0.5	1.045	0.523	0.523
0.8	1.207	0.254	1.016
0.9	1.390	0.154	3.317
0.99	3.228	0.032	3.195
0.999	6.934	0.007	6.927

2.2 Wall thickness as a function of a/b and a_0/b_0   The microsphere wall thickness, t can be expressed as a function of the initial and final radius ratios as shown in Equation 3 and Figure 2.

$$\frac{t}{b_0} = \frac{b}{b_0}\left[1-\left(\frac{a}{b}\right)\right] = \left[\frac{\left[1-(a_0/b_0)^3\right]}{\left[1-(a/b)^3\right]} \right]^{\frac{1}{3}}\left[1-\left(\frac{a}{b}\right)\right]$$

[3]

From Table 1 it is also clear that the thickness ratio, t/b approaches zero as the ratio a/b approaches unity.

2.3 Microsphere volume as a function of its initial radius ratio, a_0/b_0   It is significant to realize that for a large range of values of a_0/b_0, the volume of the microsphere available for growth is little changed. As shown in Equation 4 and Table 2, if a_0/b_0 is less than 0.4, the volume of the hollow microsphere is greater than 93% of the volume of the solid sphere. Therefore, a hollow microsphere of these dimensions has virtually the same volume available for inflation as that of a solid microsphere. Consider the non-dimensional volume of the hollow microsphere:

$$\frac{Volume}{b_0^3} = \frac{3}{4\pi}\left(\frac{b_0^3 - a_0^3}{b_0^3}\right) = 1 - \left(\frac{a_0}{b_0}\right)^3 \qquad [4]$$

Table 2: Non-dimensional Volume results as a function of a_0/b_0.

a_0/b_0	$1 - \left(\dfrac{a_0}{b_0}\right)^3$
0.0	1.000
0.1	0.999
0.2	0.992
0.3	0.973
0.4	0.936
0.5	0.875
0.6	0.784
0.7	0.657
0.8	0.488
0.9	0.271
0.99	0.030
0.999	0.003

2.4 Solid versus Hollow Microspheres

Tables 3 and 4 further illustrate the difference that the initial particle geometry, a_0/b_0 has on the final microsphere geometry for a constant volume process. Note that for an inflation ratio, a/b = 0.999, the wall thickness ratio, t/b is 0.007 for both the geometries presented while the maximum radius ratio, b_0/b is 6.936 for a_0/b_0 =0.0 and 6.627 for a_0/b_0 =0.5. Thus, the initial volume available is in the ratio of 0.875, while the maximum radius ratios differ by only 5%.

Table 3: Results for $a_0/b_0 = 0$.

a/b	b/b_0	t/b_0	a/b_0
0.0	1.000	1.0000	0.000
0.1	1.000	0.900	0.100
0.2	1.003	0.802	0.200
0.3	1.009	0.706	0.303
0.4	1.022	0.613	0.409
0.5	1.046	0.523	0.523
0.6	1.084	0.434	0.651
0.7	1.150	0.345	0.805
0.8	1.270	0.254	1.016
0.9	1.545	0.154	1.391
0.99	3.229	0.032	3.197
0.999	6.936	0.007	6.929

Table 4: Results for $a_0/b_0 = 0.5$:

a/b	b/b_0	t/b_0	a/b_0
0.5	1.000	0.500	0.500
0.6	1.037	0.415	0.622
0.7	1.100	0.330	0.770
0.8	1.215	0.243	0.972
0.9	1.478	0.148	1.330
0.99	3.088	0.031	3.058
0.999	6.634	0.007	6.627

3.0 MICROSPHERE GROWTH OBSERVATIONS

In order to evaluate the polyimide microsphere behavior when subjected to an increase in temperature from 27.5^0 C to 190^0 C the following measurements were undertaken.

3.1 Particle size distribution   In an attempt to determine the relationship between polymer particle size and microsphere size, size particle distribution within a typical polymer powder was measured by physical screening. Results presented in Table 5 show that almost 90% of the polymer powder particles ranged in size from 75 to 500 microns. These results show that the largest dimension of two-thirds of the particles falls in the range of 106-300 microns.

Table 5: Particle size distribution.

Particle size range, microns	Weight percent
0-75	11.6
75-106	17.2
106-180	28.1
180-300	39.4
300-500	03.5

3.2 Microsphere growth observations   It is instructive to examine the growth kinetics of a single microsphere in reverse time because the geometric formation of the microsphere from the single particle is quite complex. Here we can begin with the microsphere in its fully inflated state and measure its outer diameter, wall thickness and inner diameter. Table 6 shows data taken from the photographic images shown in Figures 3, 4, 5 & 6.

Table 6: Reverse growth kinetics of a single polyimide microsphere.

Time, min.	Temp,^{0}C	b, 10^{-3} m	t, 10^{-3} m	a, 10^{-3} m
16.26	190	0.2028	0.0064	0.1964
12.75	155	0.1752	0.0075	0.1677
12.35	151	0.1311	0.0161	0.1150
12.25	150	0.1030	0.0191	0.1964

Time, min.	Temp, ^{0}C	a/b	Volume, 10^{-12}m^3
16.26	190	0.968	3.20
12.75	155	0.957	2.77
12.35	151	0.877	3.07
12.25	150	0.814	2.10

Average Volume: 2.785 10^{-12} m^3

As time is observed in reverse from 16.26 minutes to 12.25 minutes, the diameter of the microsphere is seen to diminish from 202 microns to 103 microns, a reduction of approximately 50%. The wall thickness increases during this interval from 6.4 microns to 19.1 microns. The volume of the polymer within the microsphere appears to range from 2.10 to 3.20x 10^{-12} m^3, with an average volume of 2.87 x 10^{-12} m^3. This volume for an incompressible polymer would correspond to a solid particle initial radius of 88.2 microns or a diameter of 176 microns. For a_0/b_0 = 0.5, the hollow microsphere would have a diameter of 349 microns. Clearly, these measurements fall in the range reported above in Table 5.

3.3 Microsphere formation   Continuing to observe the microsphere formation in reverse time, it is instructive to examine the polymer particle as it transitions from microsphere to its irregular shape. Table 6 and Figures 7, 8 & 9 illustrate this phenomenon. Note that at time of 12.25 minutes (150 C^0), the particle has assumed a quasi-spherical shape, while at 11.75 minutes (145 C^0), the particle shape has become irregular. Indeed, as time is observed in reverse, from 11.75 minutes to 0, the particle appears to grow in planar dimensions. Table 7 shows that the approximate planar area of the particle grows from 7.3 to 11.3 x 10^{-9} m^2 as time is viewed from 11.75 to 0 minutes. In other words, the particle planar dimensions are seen to decrease with increasing time and temperature.

Table 7: Particle dimensional change.

Time, min.	Temp, °C	Max L, 10^{-3} m	Min L, 10^{-3} m	Area, 10^{-9}m^2
11.75	145	0.146	0.099	7.23
11.05	138	0.150	0.102	7.60
9.65	124	0.165	0.120	9.90
0.00	27.5	0.175	0.130	11.3

Time, min	Temp °C	Avg. L, 10^{-3} m	0.3xAvg. L, 10^{-3}m	Vol. 10^{-13} m^3
11.75	145	0.1225	0.0367	2.65
11.05	138	0.1260	0.0378	2.88
9.65	124	0.1257	0.0377	3.73
0.00	27.5	0.1229	0.0369	4.17

In the second matrix of data shown in Table 6, estimates of the particle volume are made. Here the average lateral dimension of the particle is multiplied by 0.3 in order to estimate the thickness dimension of the particle. Next the plan form area of the particle is multiplied by the estimated thickness in order to estimate the particle volume. The particle volume estimates ranged from 2.65 to 4.14 x 10^{-13} m^3. In contrast to the volume estimate of 2.87 x 10^{-12} m^3 taken from the microsphere geometries, the average particle volume estimate is only 3.36x10^{-13} m^3 or a factor of 8.5 difference – almost and order of magnitude difference. Clearly the simplifying assumption of constant volume throughout the process is not exact.

The data presented in Table 6 are compared to the geometric predictions in Figures 10 and 11. Here the initial radius ratio of 0.85 was chosen after comparing the experimental data to Equation 1 and arriving at an average value over the range 0.923-0.772. These figures show that the geometric relations for b/b_0, a/b_0 and t/b_0 are in reasonable agreement with the experimental results. And it is likely that the accuracy of the measurements had an adverse impact on the comparison. Indeed, the results confirm that for the microsphere observed, the constant volume approximation is approximate, even over the range in geometries wherein the microsphere has taken form. Clearly the observed deformations of the irregular shaped particle differ quite substantially from that of a constant volume, incompressible solid as well.

4.0 RESULTS AND DISCUSSION

The results of this preliminary study provide an insight into the inflation kinetics of a polyimide foam wherein the polyimide particle contained trapped blowing agent and an increase in temperature resulted in the inflation of individual polyimide particles. A constant volume geometric analysis showed that the polymer volume available for the creation of microspheres is limited by the particle size, and inflation ratios (a/b) of 0.9 corresponded to a hollow sphere diameter of approximately 1.5 times the particle diameter for both hollow and solid particle geometries. It was also observed that the wall thickness of a microsphere of a polymer of constant volume achieves a value of approximately 0.15 times the equivalent solid particle radius at an inflation ratio of 0.9. Thus, one can estimate the diameter and wall thickness of microspheres by this simple rule.

The particle size distribution was measured and almost two-thirds of the particles were found to fall between 106-300 microns. The average observed volume in the microsphere phase was shown to correspond to a solid spherical particle of diameter equal to 176 microns.

Experimental data were presented for the inflation of a single polyimide particle containing blowing agent by raising the temperature at a rate of 10^0 C/min. from 27.5 to 190^0 C. By observing photographic images taken at known time and temperature intervals, the inflation kinetics could be separated into two phases. The first phase was found to be simple dimensional changes of a hollow microsphere with approximately constant polymer volume. The second phase was the transformation of the particle from an irregular shape to a microsphere. In this phase, the particle appeared to shrink as time and temperature were increased. Indeed, the estimated volume of the irregular polymer precursor particle appeared to be an order of magnitude less than that of the final microsphere.

The assumption of conservation of volume throughout the particle transformation and inflation processes has been shown to be an approximation, and the need for a more rigorous treatment of the multiple stages of this process is clearly evident.

5.0 REFERENCES

1. Hou, T.H., Weiser, E.S., Siochi, E.J. and St Clair, T.L., <u>Proceedings of SAMPE Annual Conference</u>, 1999, pp 1792-1807.

6.0 NOMENCLATURE

a_0 = initial inner radius
b_0 = initial outer radius
a = inner radius
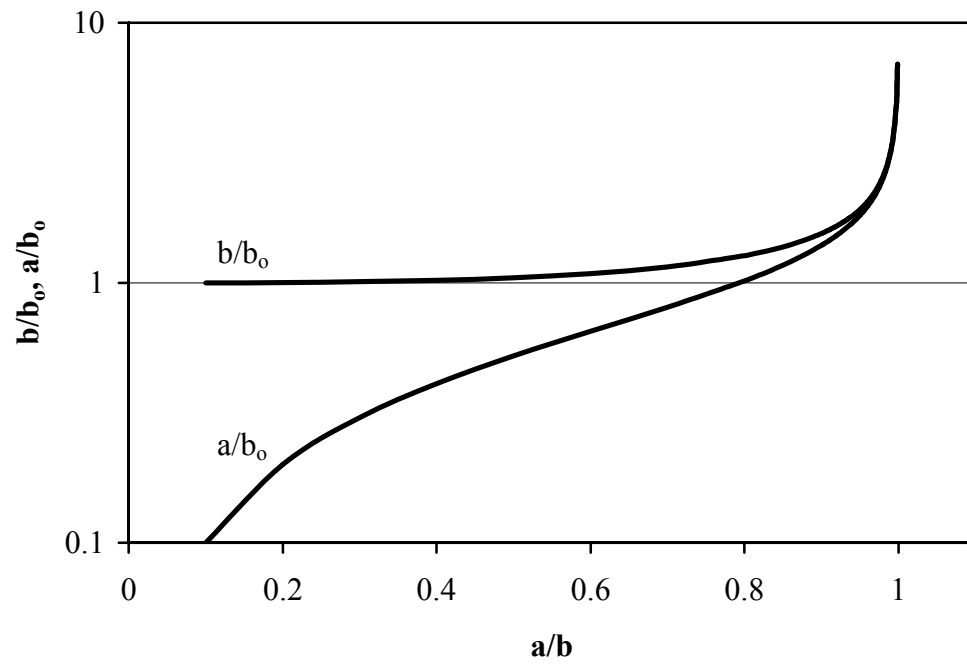b = outer radius
t = wall thickness

7.0 FIGURES

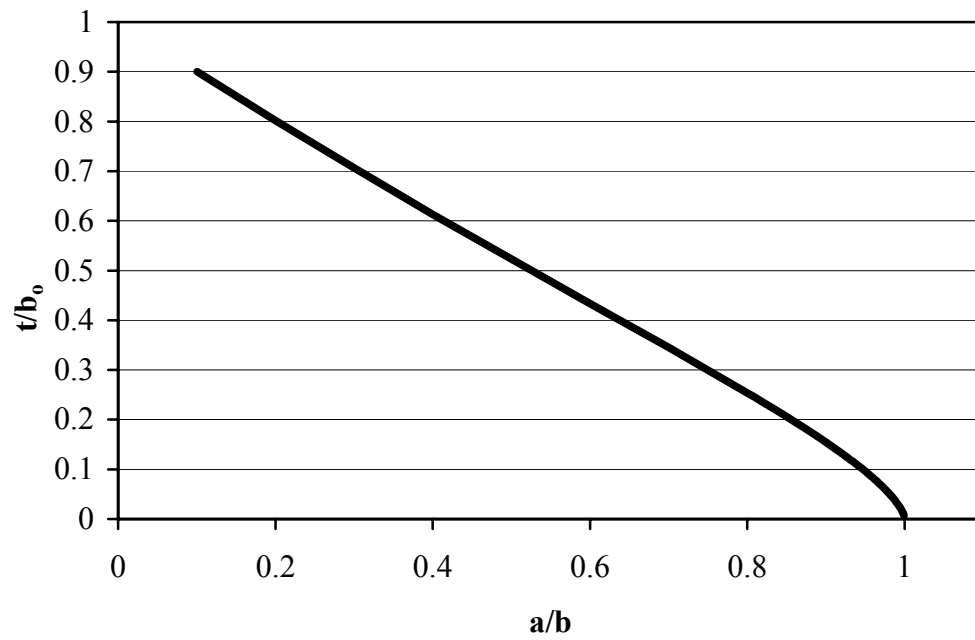**Figure 1 Microsphere size as a function of a/b at $a_0/b_0 = 0.1$**

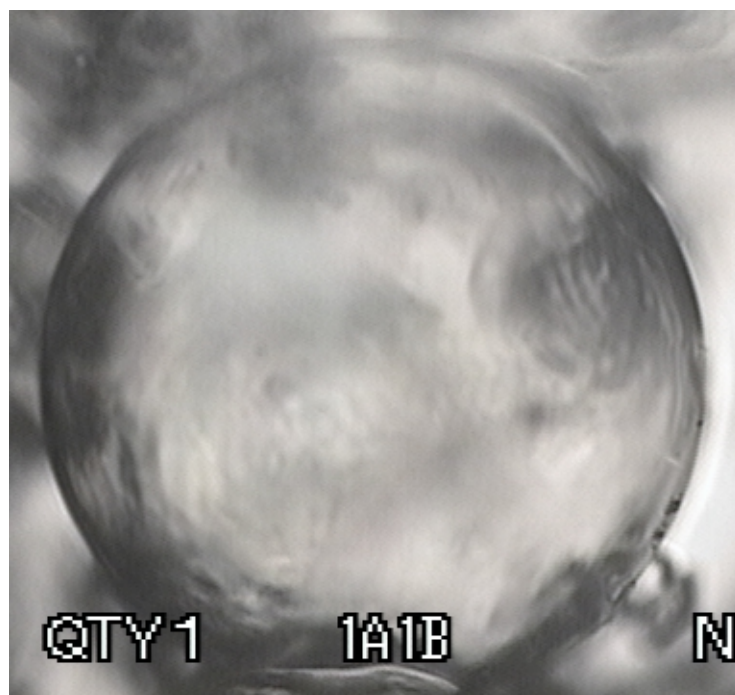**Figure 2 Microsphere wall thickness as a function of a/b at $a_0/b_0 = 0.1$**

Figure 3   Polyimide microsphere at 190 ^{0}C

Figure 4   Polyimide microsphere at 155 ^{0}C

Figure 5 Polyimide microsphere at 151 ^{0}C

Figure 6 Polyimide particle at 150 ^{0}C
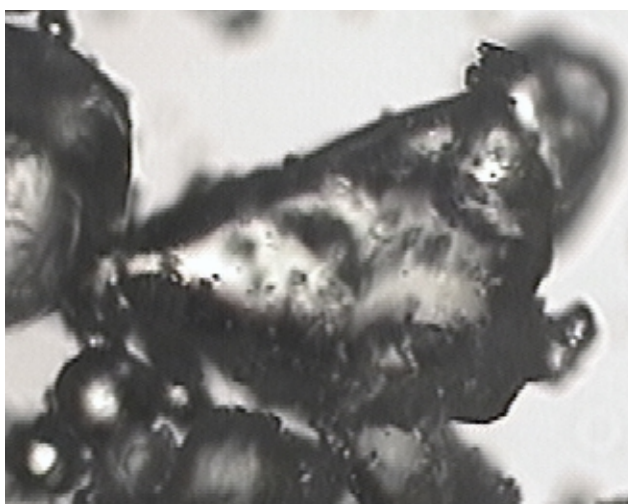
Figure 7 Polyimide Particle at 145 ^{0}C
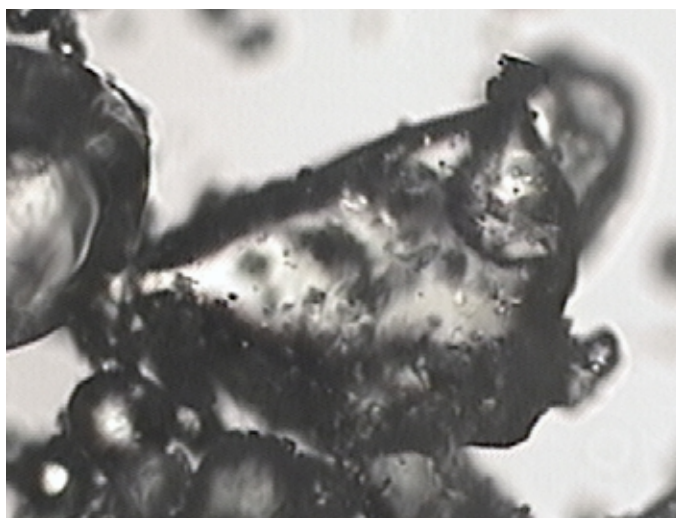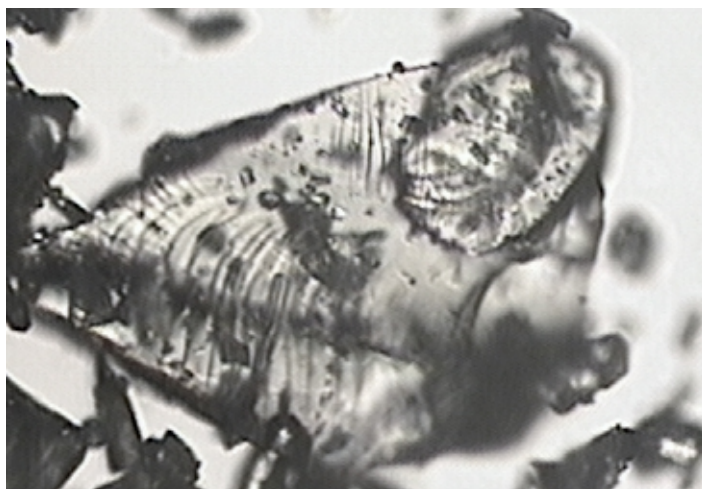
Figure 8 Polyimide particle at 138 ^{0}C

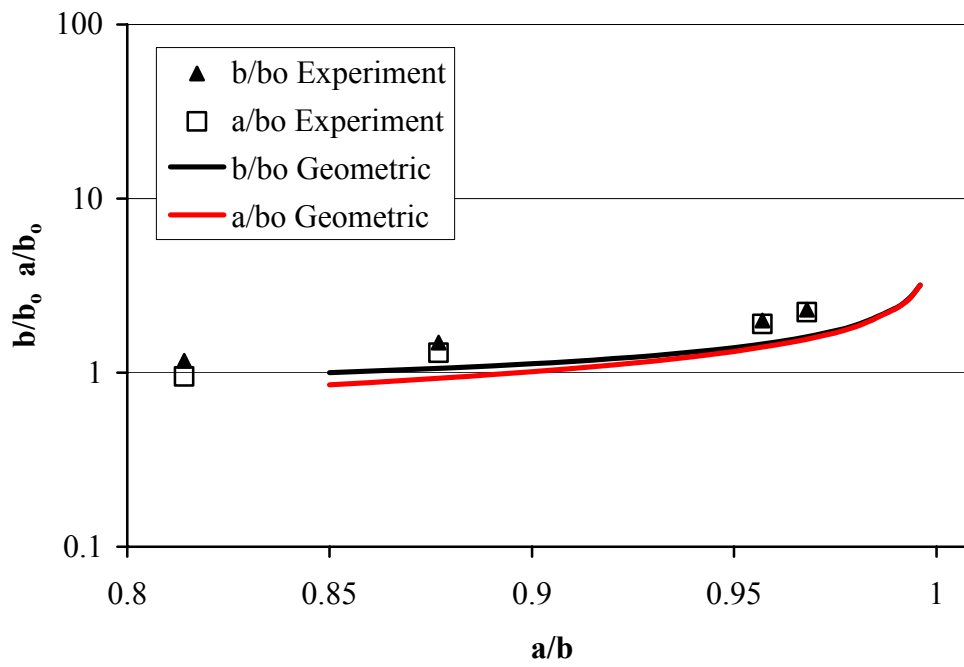**Figure 9 Polyimide particle at 27.5 ^{0}C**

Figure 10 Experimental results for microsphere size as a function of a/b at a_0/b_0 =0.85.
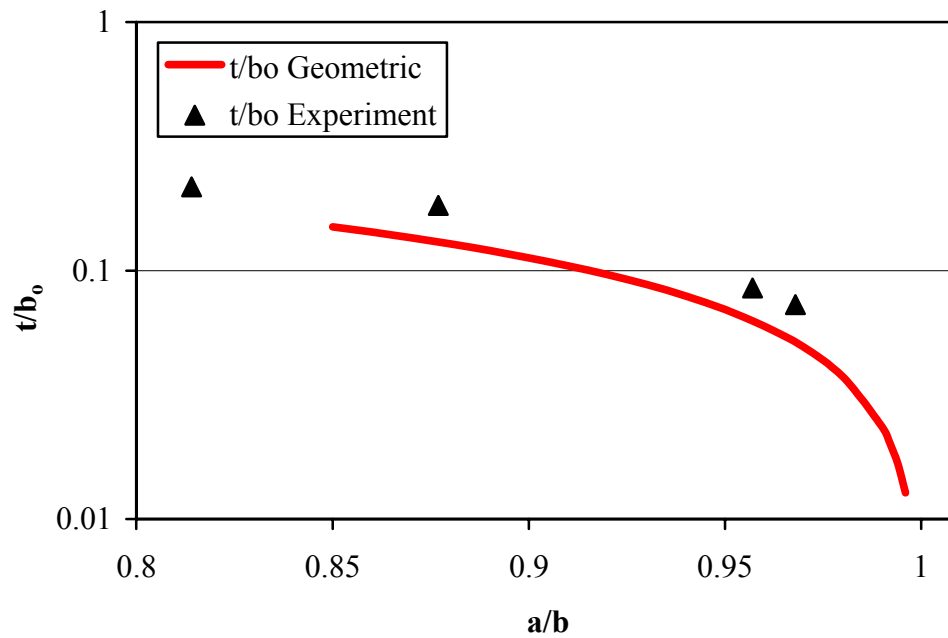

Figure 11 Experimental results for microsphere wall thickness as a function of a/b at a_0/b_0 =0.85.