

Intermediate Processing of Polymer-Silica Hybrid Nanoparticles using X-ray Microtomography

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Abstract

For certain product applications in pharmaceutical, chemical and material sectors, sintering of powders while retaining grain sizes in the sub-micron range becomes a critical processing step. The key to nanosintering and compaction is to achieve densification by limiting coarsening and undesirable microstructural transformations. Densification commonly results in grain coarsening. Nanosintering brings on additional challenges as compared to sintering of micron-size powders due to high rate of agglomeration, high reactivity, grain coarsening and ultimate loss of nanofeatures. One of the most severe limitations is the apparent inability to retain initial micro structural features during consolidation and sintering. These limitations are mainly related to powder agglomeration and interparticle friction.

Polyviologens (PVs) are mainly used as potential templating agents in the hydrolytic sol-gel process. The resultant hybrid materials are amorphous aggregates of roughly spherical silica particles. Particle size range is between 100-300 nm and there is a large degree of agglomeration. Sol-gel process has become an important synthesis route for nanopowder applications over the last decade despite the fact that it has been around much longer than that.

In this paper, we describe an experimental system which has been designed to examine an assembly of nanoparticles in a wide range of process engineering applications. These applications include harvesting from solutions of nano-particles into green parts and subsequent sintering into finished components. The system is based on an X-ray microtomography with a spatial resolution down to 5 μm . The application of the microtomography technique to the study of thermally induced morphological changes in silica-polymer hybrid nanoparticles is described under different experimental conditions.

Introduction

The application of X-ray Computed Tomographic (CT) techniques to Non-Destructive Evaluation (NDE) of materials, outside of the medical field for which they were initially developed, is a rapidly expanding area of research. The expensive body sized medical CT machines have been replaced by relatively inexpensive bench-top sets. The typical spatial resolutions of 0.5mm for medical systems have also been improved down to 5 μm . These improvements are mainly due to the advancement in pixelated X-ray detectors and the simultaneous development of micro-focus X-ray tubes. For example, third generation

(cone-beam geometry, single source, two-dimensional detector) medical CT systems use 12 inch X-ray Image Intensifiers (detector pixel pitch of 0.5mm) and 1mm focal-spot size X-ray tubes in a proximity focused geometry. Compared to a modern NDE CT set which often use flat-panel pixelated CsI coated CMOS arrays (detector pixel pitch of 50 μ m) and X-rays tubes with a 5 μ m focal-spot size in a geometry which magnifies the sample on the detector. The use of improved detectors have the additional benefit of better contrast resolution and the signal digitisation is higher (XRIs are digitised to 8-bits, CMOS arrays are digitised to 12-bits). The use of NDE CT sets for use in the study of nano-powder assemblies is only just coming to fruition as the spatial and contrast resolutions are only just approaching the limits for which useful information can be obtained.

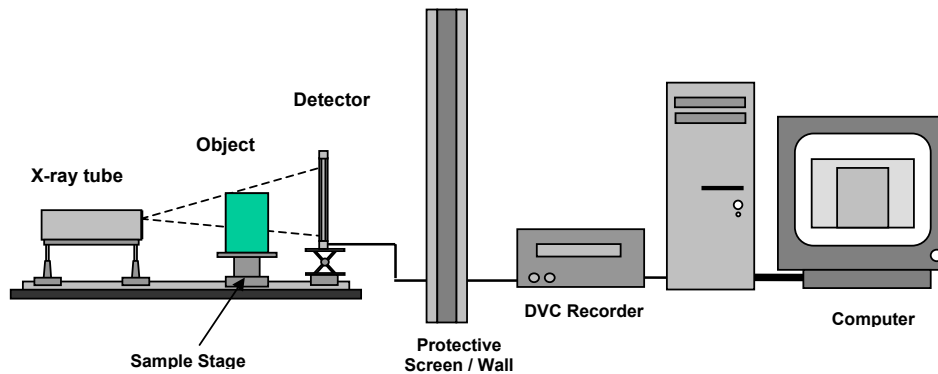


Figure1: Schematic diagram of the high-resolution X-ray CT set.

Figure 1 shows the experimental apparatus used for high-resolution X-ray CT. The detector is a Hamamatsu C7942 flat-panel CMOS array (2400 x 2400 pixels at a 50 μ m pixel pitch with a CsI-coating) and a Hamamatsu L6731-01 micro-focus X-ray tube (Mo target 80kVp, 100 μ A, 5 μ m focal-spot size). The sample stage is a computer controlled rotational stepper motor with a resolution of 0.01 $^\circ$. The ring-artefact commonly associated with third generation scanners (caused by the repeated use of the same detector elements in each projection) is minimised by mechanically translating the detector sideways by a random integer number of pixels for each projection. The sample is rotated through 360 $^\circ$ in a number of steps determined by the Nyquist sampling theorem (typically, number of steps = $\pi/2$ * number detector elements). The projection data is then stored and at a later stage reconstructed using a Feldkamp based three-dimensional back-projection routine on the Beowulf parallel-processing cluster into a three-dimensional data set of the linear attenuation coefficients. This can then be processed using a variety of signal-processing methods to extract useful information from the data.

The normal rotational stage can be replaced by a beryllium or carbon fibre windowed environmental chamber as shown in Figure 2. The samples can then be heated (up to 1000K) and compressed (up to 6kPa) under partial pressure (1 atm to below 10 $^{-6}$ mbar).

X-ray micro-tomography is an ideal tool for imaging nano-powder assemblies but does not have the resolution to image individual nano-particles. Nevertheless, it provides valuable non-destructive evaluation of harvesting of nano-particle assemblies from various synthesis routes. The formation of the assembly can be studied as the suspension medium is

evaporated and information regarding the packing density and large area defects can be obtained. The samples can then be mechanically tested and desirable properties can be linked to the formation and structure of the final assembly. The drying process can then be adapted allowing the evolution of better harvesting techniques. One of the most severe limitations is the apparent inability to retain initial microstructural features during consolidation and sintering. These limitations are mainly related to powder agglomeration and interparticle friction. In some nanopowders, particle coarsening proceeds rapidly without shrinkage by evaporation-condensation mechanism during sintering.



Figure 2: Picture of environmental vacuum chamber

Self Assembled Organic-Inorganic Silica Hybrids from Polyviologens

Although biological systems (e.g. diatoms) form silica structures at room temperature and neutral pH, industrial synthesis of silica based materials typically require high temperature and pH. Polyviologens are used as potential templating agents in the hydrolytic sol-gel process, electrochemical processes, microelectronics, functional thin films, electrodes in biosensing systems, detection systems, in electrochromic (term refers to a material which changes colour when subjected to an electrochemical potential), in membranes etc. Variations in the alkylene spacer length and the associated counter ion appear to have little, if any, effect upon the rate of polymerisation as measured by the colorimetric molybdosilicate method. The resultant hybrid materials are amorphous aggregates of roughly spherical particles. Particle size range is about 100nm to 300nm. There is a large degree of agglomeration.

The hybrid particles are produced by a catalytic silica precipitation reaction, using bipyridinium polymers ('polyviologens; PVs) as catalyst. A slightly modified version of the procedure reported by Marvel and Sekera [6] was used for the synthesis of 1,4-butane ditosylate. Pyridine (20 ml) and 1,4-butanediol (2.019 g, 1.98 ml, 22.4 mmol) were added to a 100 ml round bottom flask equipped with a magnetic stirrer. The flask is cooled to 0°C and *p*-toluenesulfonyl chloride (8.701 g, 45.6 mmol) added in portions over 5 minutes, taking care to ensure that the temperature does not rise above 15°C. The mixture is stirred for 3 hours below 20°C before addition of hydrochloric acid (15 ml) in ice-cold water (50 ml). The ester that crystallises is collected on a chilled Buchner funnel and sucked as dry as possible. Recrystallisation from methanol yielded a crystalline white powder, which was then dried under vacuum for 24 hours. The purity of the monomer was checked by ¹H NMR spectroscopy and elemental analysis. Equimolar amounts of 4,4-bipyridyl and 1,4-butane ditosylate were stirred in dry acetonitrile at 80°C for 120 h under an atmosphere of nitrogen according to the previously reported procedure

[7] for the synthesis of poly(butylviologen ditosylate) (PBV-OTs). The resulting polymer was dried under vacuum at 80 °C for 24 h. The structure of PBV-OTs is depicted in Figure 3.

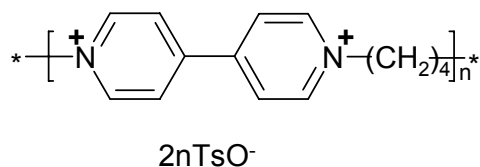


Figure 3: Structure of PBV-OTs.

The method used for silica precipitation was that employed by Coradin and Livage [8]. Sodium silicate solution (0.5 ml) was added to the buffer solution (150 ml) in a 250 ml conical flask. The mixture was stirred for 10 minutes before a solution of polymer (15×10^{-5} M) in buffer (15 ml) was added. After 2 hours, the reaction mixture was centrifuged and the recovered solids dried under a flow of air at room temperature.

Polyviologens (bipyridinium polymers) are effective catalysts for the polymerisation of silicic acid at room temperature and neutral pH [5]. Variations in the alkylene spacer length and the associated counter ion appear to have little, if any, effect upon the rate of polymerisation. The resultant silica-PV hybrids are amorphous aggregates of roughly spherical particles of approximately 100 nm diameter. Particle sizing by scanning electron microscopy (SEM) shows that there are also occasional monolith structures which are much larger and do not appear to consist of an aggregate of spherical particles. We have shown previously that calcination of related silica-PV hybrids can lead to formation of mesoporous silica [7]. The effect of thermal treatment on the hybrid structures formed in the current work was studied by microtomography.

Experimental Procedure

The powder was put into a crucible with 7mm inside diameter and 20mm height. It was placed onto a temperature controlled heating system already fitted onto the rotating sample holder. The X-ray microtomography tube was operated at 65kV and 101 μ A and 900 projections were taken as the sample was rotated via a stepper motor. The geometrical magnification of the sample projection onto the detector resulted in a linear pixel resolution of 7.9 μ m. Two sets of experiments were carried out:

- The sample was heated up to 555 °C starting from 40 °C at a rate of 1°C/min under ambient conditions.
- The sample was heated up to 555 °C starting from 40 °C at a rate of 1°C/min under 2.1 MPa compaction and kept at 555 °C for further 15 minutes.
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The collected projections were fed into the reconstruction algorithm and Figure 4 shows a centrally reconstructed slice.

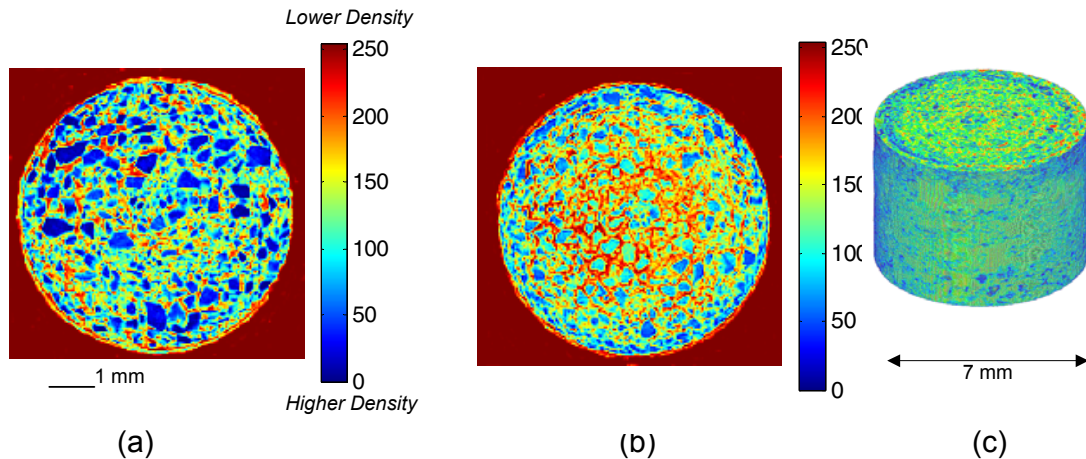


Figure 4: Reconstructed central slices for the sample sintered a) without compaction b) under compaction c) 3-D reconstruction.

It is obvious from Figure 4a that there are a large number of rather big and dense clusters present in the sample sintered under ambient conditions without compaction. Figure 4b shows the centrally reconstructed slice for the sample sintered under compaction. In this sample, clusters are smaller and less dense than the ones shown in Figure 4a.

In order to carry out morphological size changes induced under these different experimental conditions, the reconstructed slices given in Figures 4a and 4b were converted into binary images by using a thresholding technique and these are given in Figure 5. It is clear that shape, size and number of clusters have been influenced by sintering under compaction. There is less number of clusters compared to sintering without compaction.

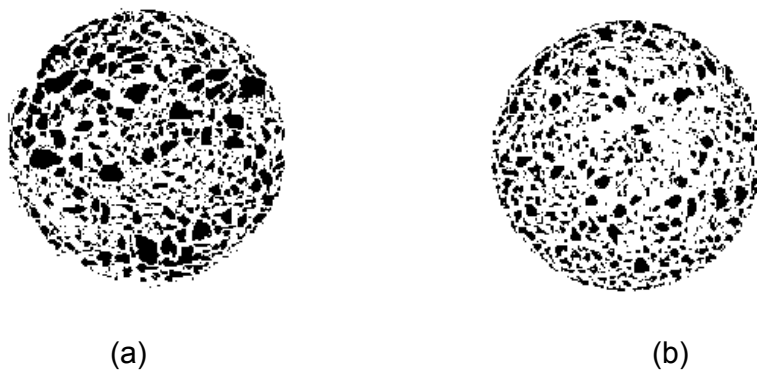


Figure 5: a) Thresholded image of centrally reconstructed slice shown in Figure 4a b) Thresholded image of centrally reconstructed slice shown in Figure 4b

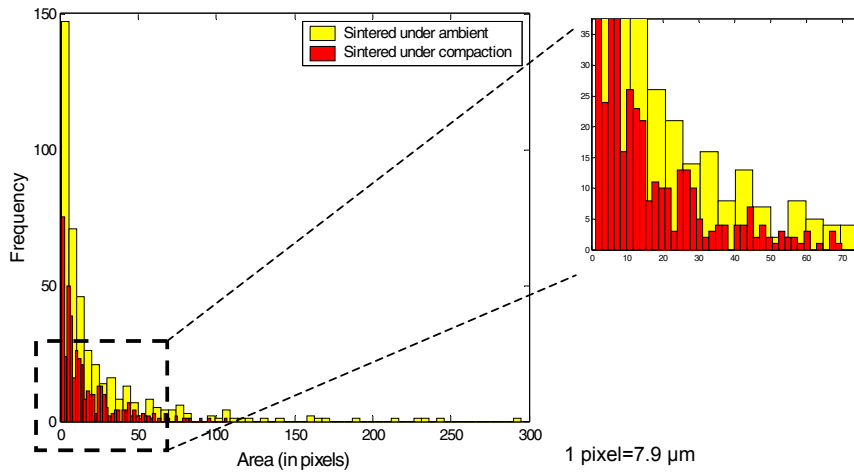


Figure 6: Agglomerate size distribution under two different conditions.

Figure 6 shows the size histogram of the clusters under two different conditions. The size range of the clusters is narrower when sintered under compaction. This is an encouraging processing step for this hybrid polymer-silica nanosystem as keeping the agglomeration to minimum and narrowing its size range is one of the important factors in nanosintering. Table 1 gives some of the parameters related to the cluster size range. The maximum cluster area for the sample sintered under compaction is nearly one third of the sample sintered without compaction. The mean value of the cluster size is nearly halved as well.

Table 1: Cluster information under two different conditions. (1 pixel=7.9 μm)

	Number of Clusters	Maximum Cluster Area (in pixels)	Mean Cluster Area (in pixels)
Sintered	423	295	28.81
Sintered and Compacted	418	107	16.31

Figure 7 shows a simplified shape analysis of the clusters where every cluster was compared to an ellipsoid. The cluster area was scanned internally and two axes were calculated as major and minor axes. For circular shapes, both of these axes would be equal and their ratio or slope of the plot of these axes would be equal to one. As it can be seen, there are more circular clusters when sintered under compaction and narrower size range distribution is also evident from this figure.

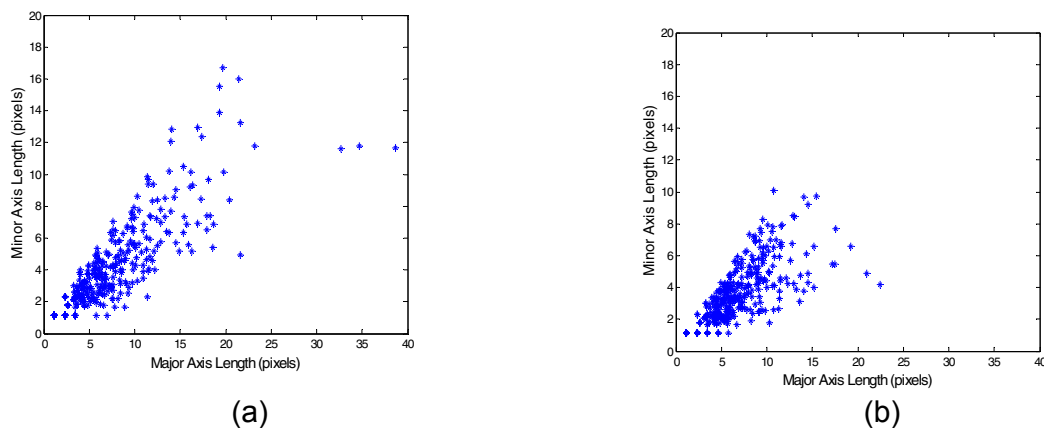


Figure 7: Shape analysis of the clusters for the samples sintered a) without compaction. b) under compaction. (1 pixel=7.9 μm)

Conclusions

The dynamic morphological changes that take place in this silica-polymer hybrid system have been examined using a high resolution X-ray microtomography system developed. The x-ray microtomography system has a current resolution of $5\mu\text{m}$ and developments are under way to reduce this further. When the sample is sintered under compaction, there is significantly smaller degree of particle agglomeration with a smaller size distribution and these clusters are less dense compared to the sample sintered without compaction. One can see that sintering under compaction decreases the cluster size and the number of clusters. It is evident that ultra fine and nano particles are prone to form clusters in the micron-size region during compaction and sintering and prevention of clustering requires innovative processing steps that current research is concentrating on. We can look into changes of clusters dynamically and examine the final microstructural features. Unlike other commercially available imaging techniques which are usually surface techniques, X-ray microtomography allows us to see through the sample and allow us to reconstruct 3-D internal structure of the sample. We can also follow dynamic morphological changes that take place during sintering and compaction of ultra fine powder systems by using a high resolution x-ray microtomography placed in a specially constructed environmental chamber where we can carry out experiments under controlled vacuum conditions.

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