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Characterization of pore size of trimethylol propane triacrylate (TMPTA) polymer foam by pulsed sputter coating and SEM analysis

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This paper describes the production and characterisation of low density polymeric foams used by the Atomic Weapons Establishment (AWE) Plasma Physics programme. Production and preparation of such foam samples for characterisation by scanning electron microscopy (SEM) are described. Examining non-conductive low density foam specimens by conventional SEM requires sputter coating with a very thin layer of gold to prevent overcharging the sample. This paper describes modifications to this process, which have illustrated the destructive effects of the sputtering process on these foams. Optimum conditions to minimise foam damage during sputtering have been determined. Low-vacuum SEM in conjunction with a charge cascade detector which enables non-conductive samples to be directly imaged has been used to reduce the damage to fragile foams. These results are compared with those taken of samples coated under optimum sputtering conditions. Using sputter coating time trials and an absorbed electron (AE) detector, it was revealed that the pore size of TMPTA foam was in the region of 0.1 μm, i.e. an order of magnitude lower than reported previously. Some proposed damage mechanisms are also discussed. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Low density unloaded and loaded foams (various high atomic number (Z) elements) [1] are made regularly in support of the AWE plasma physics experimental programme. The key requirements for the experimental campaigns were 50–200 mgcm^{-3} density foam. Foams as low as 3 mgcm^{-3} and as high as 800 mgcm^{-3} have been produced for research purposes [2]. Previously reported work on the fine structure of these foams which were characterised by scanning electron microscopy (SEM), showed pore size of about 1 μm, see Fig. 1, SEM was the only technique available that had the resolution required to image the foam cells.

It was standard practice to sputter coat the polymer foams with gold to prevent beam damage and to allow charge disipation to occur on the sample. SEM operated in secondary-electron mode was used to view the foam structure. SEM studies carried out on foams using this approach suggested that the pore size of Trimethylol Propane Triacrylate (TMPTA) was in the region of 1 μm. However, a wide range of pore structures had been observed over a period of years, which could not be explained by variations in foam production techniques. Other than production techniques two areas were considered as potential sources of damage to the cell structure. These sources were sputter coating and SEM beam damage. This paper is concerned with the former.

2. Foam filling of targets

Targets were foam-filled *in-situ* using an established in-situ polymerisation technique described in detail in [2]. Briefly, measured quantities of TMPTA (monomer) and N, N' azo-isobisbutyronitrile (AIBN) (initiator) were

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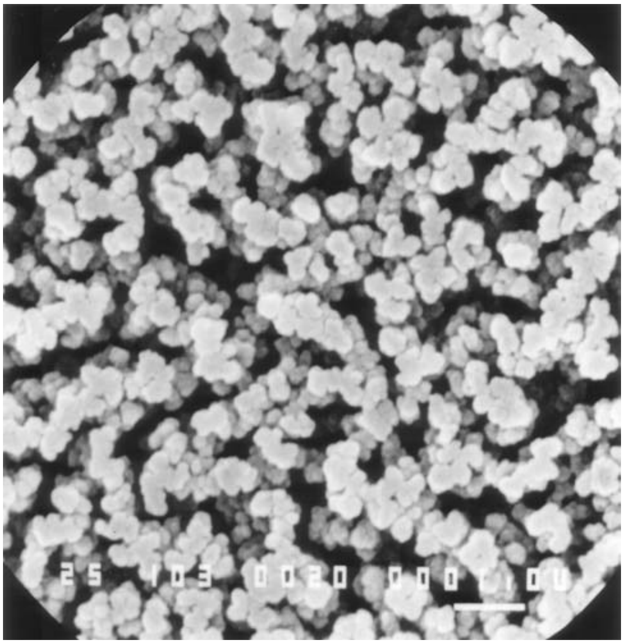

Figure 1 An SEM image of low density foam showing 1 μm pore size—sputter coated sample

dissolved in polyoxyethylene 4 lauryl ether (Brij 30) (solvent). This solution was then used to fill the cylindrical moulds (targets), typically 300–400 μm length and 300 μm diameter. The target containing monomer solution was then photo-initiated using an ORIEL 6000 medium pressure mercury lamp, equipped with fibre optic light guides to uniformly illuminate around the target. The solution in the target gelled in seconds and the target containing the wet gel was placed in methanol for solvent exchange. After the exchange, cylinders containing the wet foams were then transferred to a POLARON 3100 critical point dryer for removal and exchange of methanol with liquid CO_2 and subsequent drying. The cylinders containing the dried foams were then characterised at AWE.

3. Sample preparation & characterization

Characterization of foam samples for this work was carried out on a Hitachi S3200LV SEM. This instrument operates in two modes.

3.1. High vacuum SEM (HVSEM)

HVSEM is the conventional SEM technique and requires the sample to be conductive to earth to prevent charge build up. When used in this mode non-conductive samples such as polymer foams must be coated with a conductive layer. In this work this has been achieved by coating the sample in an Edwards S150A sputter coating equipment, typical coating parameters were originally a plasma current of 30 mA, at a distance of 6 cm for 5 minutes and an Ar pressure of 500 Pa. During this work other coating procedures were adopted to attempt to minimise possible damage due to the coating process. These involved coating the samples with shorter coating times and/or using a series of shorter coatings to give a thicker cumulative gold (Au) layer. It was speculated that sputter coating could damage the foam surface. In order to test this hypothesis, it was decided to apply different sputtering times and thereby establish whether it had an effect on the structure of the foam or the size of the pores. It will be shown later that the sputtering time had a profound effect on the structure and the resulting pore sizes. The first trial was conducted by randomly chosen samples and then coating them as outlined in Table I.

TABLE I Randomly chosen samples and Sputtering time

Sample	Sputter time (Seconds)	Comments
1	30	Dark Grey
2	90	Black
3	150	Dark Brown
4	270	Bronze
5	390	Gold

From the results of the first trial it was thought that after only 30 sec damage/change to the TMPTA was still taking place. Therefore, the next trial would see the samples coated for 5 sec with 120 sec 'cool off' period before the next 5 sec illumination. This coating cycle was used to provide 'cumulative' coating times as used above.

3.2. Low vacuum SEM (LVSEM)

In LVSEM a low pressure of gas is leaked into the specimen chamber and the presence of this gas prevents non-conductive samples charging in the following way. The low energy secondary electrons emitted from the surface of the sample efficiently ionise the ambient gas in the vicinity of the surface. Any charge build up due electron deposition on the surface then attracts the positive gas ions, which neutralise the charge build up. Therefore such samples no longer require a conduction path to earth and also no longer require to be Au coated. As the gas absorbs secondary electrons, a secondary electron detector can no longer be employed. Imaging is carried out using the higher energy back-scattered electrons. Images of foam surfaces can be taken with back-scattered electron detectors; however, due to the high electron energy they penetrate deep into the foam and can be re-emitted from below its surface confusing the signal from the actual surface. While a disadvantage in the measurement of foam surfaces, this large penetration distance has previously been employed to image high atomic number particulate dopants in such foams [1].

In order to produce high quality images of uncoated polymer foam surfaces an Environmental Secondary Electron Detector (ESED) was procured. This detector

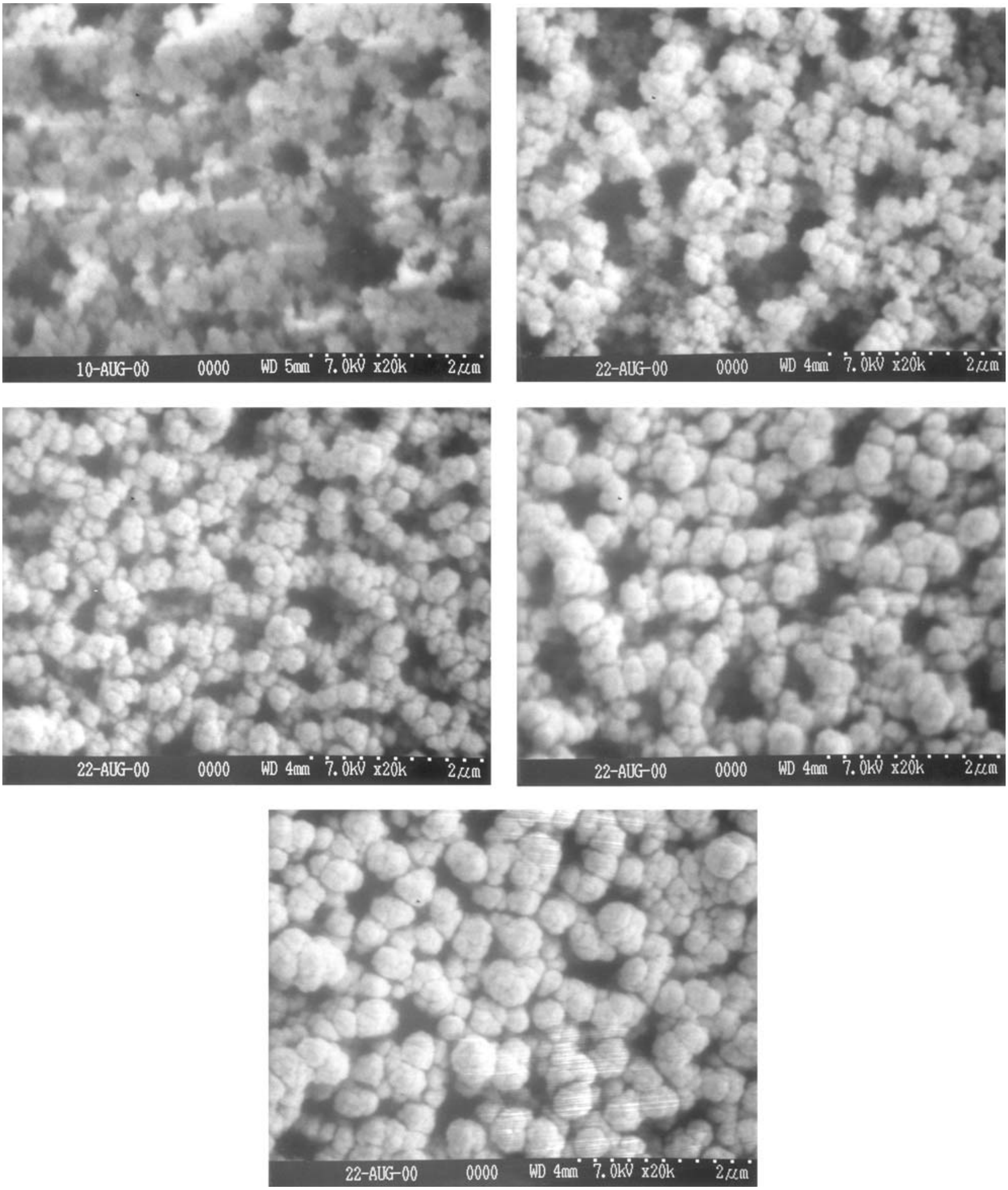

Figure 2 Gold coated foam for 30 sec, (a) Gold coated foam for 90 sec, (b) Gold coated foam for 150 sec, (c) Gold coated foam for 270 sec, (d) Gold coated foam for 390 sec

indirectly measures the secondary electron (SE) signal by measuring the ionization of the ambient gas in the environmental mode. This work describes the use and development of these techniques to minimize damage to the foam surface during characterization.

4. Results and discussion

During the coating trial the apparent foam pore size increased and at the same time the ‘nodes’ appeared to be enlarging with increasing deposition time. Earlier ‘contraction’ events seemed to have slowed down significantly

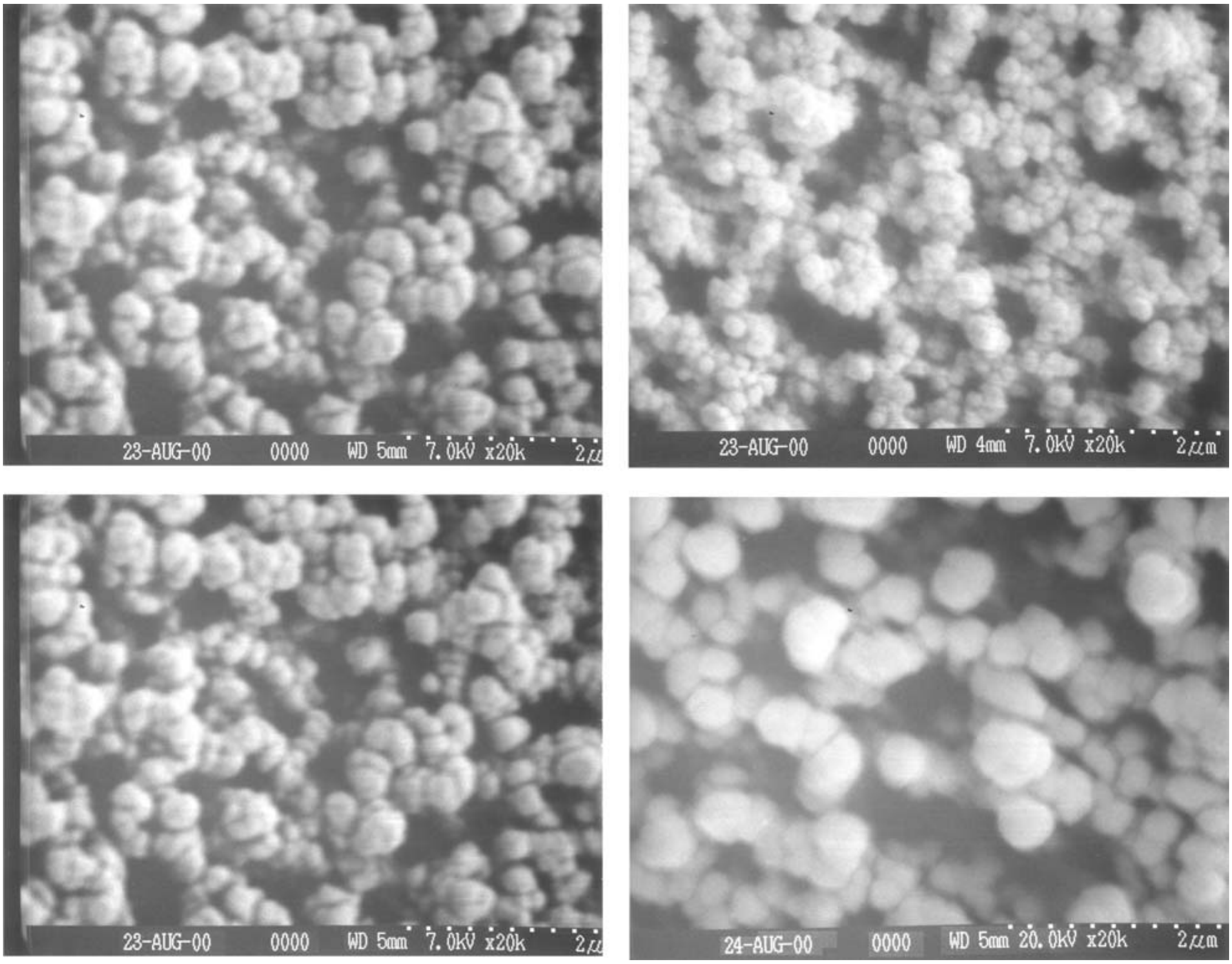

Figure 3 (a) Gold coated foam for 90 sec, (b) Gold coated foam for 150 sec, (c) Gold coated foam for 270 sec, (d) Gold coated foam for 390 sec

or even stopped from approximately 150 sec onwards. However, due to the continuing Au deposition these earlier 'contraction' events seemed to be reversed.

It is apparent that there was a difference between 30 s (Fig. 2) and 90 s (Fig. 2a), in that the 'nodes' appear to be enlarging whilst the spacing between the 'polymer strands' remain similar. When comparing 90 s (Fig. 2a) and 150 s (Fig. 2b), the 'nodes' could be seen to be enlarging further and the 'polymer strands' appeared to be moving apart. For the rest of the samples 150 s, 270 s and 390 s (Fig. 2b–d respectively), the enlarging trend of the 'nodes' continued. The distance between 'polymer strands', however, started to decrease. This happened to such an extent that in the final sample the 'polymer strand' distance was the same as or even slightly less than the ones seen in 90 s.

The evidence from above showed that the TMPTA foam was contracting during the first 150 s of coating (by various processes mentioned above). At the same time gold was depositing on the polymer and hence giving the appearance of the 'nodes' enlarging with increasing deposition time; with the pores apparently shrinking. The 'contraction' events seem to have slowed down significantly from 150 s to the end of the procedure (390 sec), in doing so extenuates the deposition/build up of gold on the 'nodes'. This happened to such an extent that the structure of TMPTA appeared to have reversed its previous 'contraction' events and in doing so led to an inference of the TMPTA pore size being on the order of 1 μm as previously believed.

As mentioned previously, evidence from the coating trial described above indicates that changes to the pore size/structure had taken place even during the first 30 sec of the coating process. Therefore, the next logical step was to decrease this time still further. It was decided to break down the initial coating time into six segments of 5 sec with 120 sec of "cool off" period between the 5 sec pulses.

A random sample was chosen and coated using the above procedure. The sample was then examined using the SE detector with the SEM in high vacuum mode. This coating and characterisation process was repeated to give a cumulative coating time of 390 s. When looking at the images produced with increasing coating time, a very

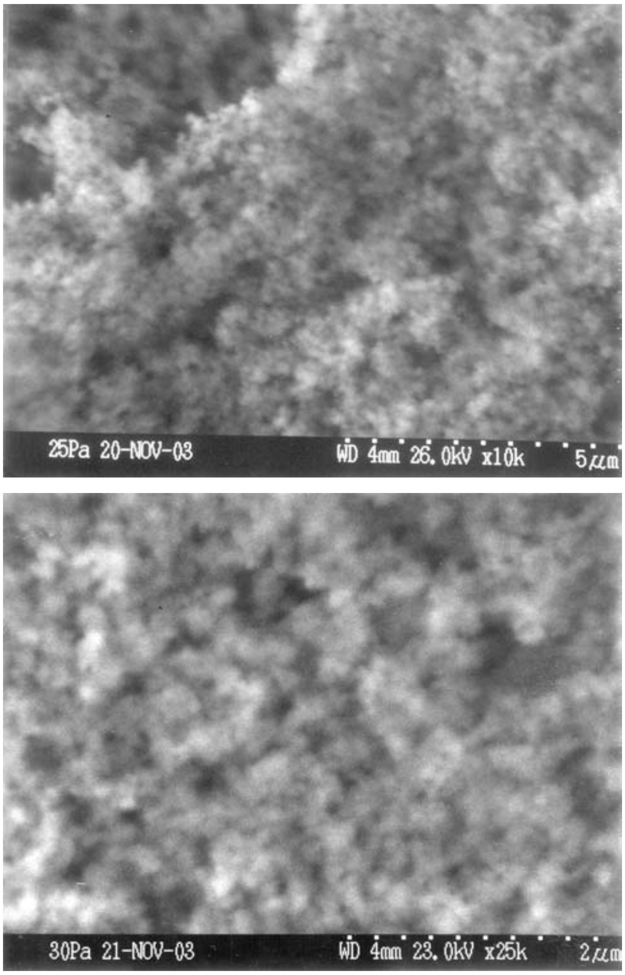

Figure 4 (a) Uncoated foam–magnification × 10 K, (b) Uncoated foam–magnification × 25 K

similar pattern to the first coating trial can be seen; see Fig. 3a (90 s), Fig. 3b (150 s), Fig. 3c (270 s) and Fig. 3d (390 s). The 'nodes' appear to enlarge and the distance between the 'polymer strands' increases with the length of coating time.

It was evident from the above coating trials that damaged processes were taking place. The samples were gold coated to remove the charge build up imparted by e-beam, a practice that is used routinely in SEM analysis. Ideally it is preferable to look at these foams uncoated since this would be a more accurate representation of the foam structure. Since the original coating trails, an ESED was used to facilitate SEM imaging of the uncoated sample. The ESED was operated with the SEM in its low vacuum mode, that is, air is allowed into the chamber to a pressure of 1–240 Pa. Instead of using the backscattered electrons from the sample the ESED detects (via, the gas amplification process) the weakly emerging SE/air ionisation events arriving back at the sample/stage [3]. This allowed the interrogation of the foam sample without altering the original foam structure. However, damage due to the incident electron beam/sample interaction may still be present [4, 5].

It was evident from first sputter trial (unpulsed 30 sec), that when comparing the two ESED images with the images of the coated samples it was apparent that the uncoated sample exhibits very different appearance, structure and pore size (although viewed at slightly different magnification). It was suggested by this experiment that even at a sputter time of 30 s the foam experiences some effect/change. These differences may be due to several factors. Possible reasons could be thermal or mechanical stress. Plasma processes have been shown to cause damage in strong polymers such as Novolak (metacresol), polystyrene (PS) and chloromethylstyrene (CMS) [6]. Both coating procedures resulted in the TMPTA behaving in a similar fashion and it was evident that during the coating process the foam underwent some form/series of 'contraction events'. This could possibly be due to ion bombardment leading to thermal process, chain scission [7]; other factors may well be involved in conjunction with thermal process such as chemical reactions between the remaining stericly hindered unreacted double bonds on or near the surface.

5. Conclusions

Comparing the ESED images to the coated images, it is apparent that the original foam structure is affected by Au coating. The ESED images show that the pore size is an order of magnitude smaller than was previously thought. When looking at uncoated sample in Fig. 4a and b, the scale bar indicates that the pore size is in the order of 0.1 μm when compared with modified coating results.

It has been shown here that the 'effective' pore size of TMPTA undergoes changes during the Au sputtering process, even at very low sputtering times. Characterisation of low density TMPTA using conventional gold sputtering process is not a reliable technique for pore size determination. The advantage of using the ESED as opposed to Au sputtering is that ESED is a more reliable method of surface characterisation of low density TMPTA since the foam is seen in its unmodified state.

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