The Nanomechanical Testing and Characterisation of Anti-viral Nano-structured Surface Coatings

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ABSTRACT

Nanoparticles of a number of inorganic compounds have been shown to possess anti-bacterial and anti-viral properties. The objective of the project was to produce an antiviral surface coating of these particles that could be used in applications such as air filtration and surfaces likely to act as vectors in the transmission of viral and bacterial infections. The main requirement for the coating was that the particles had to be completely exposed to the surrounding air. This raised the problem of bonding the particles to the surface without any encapsulation. The coatings were prepared by electrophoretic deposition and dipping from liquid suspensions of the nanoparticles. Several post coating treatments were applied to improve the bonding of the particles to the substrate. Nanoscratch testing has been used to measure the adhesion force between the coating and the substrate and SEM to characterise the coatings and scratch tracks.

Keywords**:** nanomechanical testing, nanoparticle surface coatings, anti-viral surface coatings.

1 INTRODUCTION

Nanoparticles of certain inorganic compounds and elements have been shown to deactivate bacteria and viruses. The objective of the project was to produce surface coatings of these particles that would possess anti-viral (AV) properties. It was assumed that the AV properties of the particles were directly related to the nature of their surface. This implied that the particles in the coating must be completely exposed to the atmosphere for the maximum AV effect. Initially, therefore, it was decided to prepare coatings from liquid suspensions of the particles in a medium that would evaporate to leave the dried particles deposited onto the surface. Coatings were produced by electrophoretic deposition (EPD) and by dipping from aqueous and solvent-based suspensions of the nanoparticles.

Having produced the coatings it was then necessary have a method by which measurements of the bonding force between the coating and the substrate could be made. The methods that are currently used for measuring the adhesion of surface coatings are a ‘pull-off’ test, a ‘bending’ test and a ‘peel-off’ test. These methods are typically applied to coherent coatings and were, therefore, not considered suitable for the anti-viral nanoparticle coatings. Nanomechanical testing is a relatively recent development and it has been effectively used to determine the mechanical properties of surface layers and coatings [1-3]. Nanoindentation, nanoimpact, nanofatigue and nanoscratch testing are the main methods currently available. The method that was most suited to the testing of the antiviral coatings was the nanoscratch test. This paper describes the methods of preparation of the nanoparticle coatings and the details of the nanoscratch test procedures that were adapted to measure the bonding force between the coating and the substrate.

For reasons of confidentiality the details of the nanoparticles presented in this paper have been withheld.

2 COATING METHODS

2.1 Electrophoretic Deposition

Electrophoretic deposition (EPD) is a method of laying down an even and reproducible particulate coating onto a surface [4]. The principle is that the object to be coated is immersed in a liquid suspension of the nanoparticles and it is connected as an electrode in a DC cell. A DC voltage is applied to the cell and the particles are attracted to the sample adhering to the surface. The quality and thickness of the coating will depend on the concentration of the suspension, the size distribution of the particles and the value and the time of application of the voltage. An important attribute of this process for the AV coatings is that it has the potential to evenly coat complex 3-dimensional parts.

The main requirement for the use of this technique is that the sample has to be electrically conductive. This is a limitation that had to be taken into consideration for the AV coatings.

2.2 Dip Coating

In the previous section it is stated that the sample had to be electrically conductive for coating by EPD. Some of the proposed artefacts that were studied in the project were polymer based and, therefore, were unsuitable for EPD. A simple dipping process was evaluated for these materials. The main factors involved with this process were the concentration of the suspension the particle size distribution and the nature of the suspension medium.

3 NANOSCRATCH TESTING

The four main nanomechanical testing methods are nanoindentation, nanoimpact, nanofatigue and nanoscratch. All four tests are carried out on the same nanotesting instrument and a schematic diagram of the working components is shown in figure 1a.

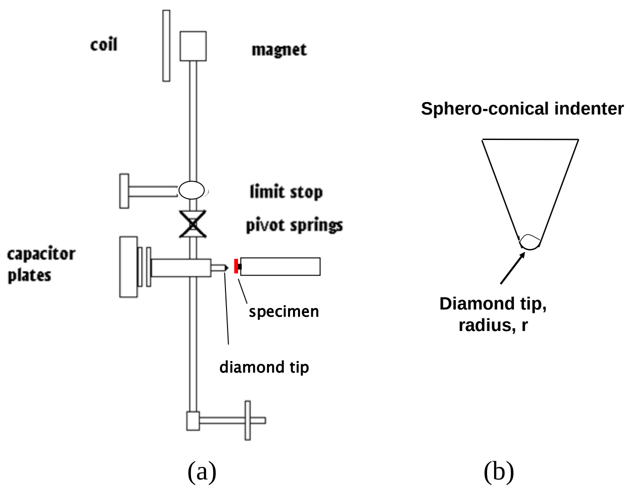


Figure 1: Schematic diagrams of the nanotesting instrument (a) and the scratch indenter (b).

The nano -indentation, -impact and –fatigue tests are all carried out using a Berkovitch diamond tip. The tip is driven into the surface of the specimen via the lever by the passage of an electric current through the coil. The depth penetration of the indenter into the surface of the sample is measured by the change in the separation of the capacitor plates.

The nanomechanical test method that is most suited to the AV coatings is the nanoscratch test. This test uses a sphero-conical indenter that has a diamond tip that has been polished to give a spherical tip surface. A schematic diagram of this is shown in figure 1b. There are three standard indenters available for the instrument used with a tip radius, r, of 25, 10 or 5µm.

In the scratch test the indenter is pressed onto the surface of the sample under a controlled loading programme while the sample stage is moved perpendicular to the indenter axis. The applied load programme, the velocity of the stage displacement and the length of the scratch track are the three conditions set in the test. The depth of penetration of the scratch, the friction force generated by the scratching process and the surface profile of the scratch track are the parameters that are recorded by the instrument.

A multi-scan test sequence that was used with the AV coatings was as follows;

- Scan (scratch) 1. The probe was moved along the surface of the sample under a constant low load (2mN) and the indenter height recorded. The result gave the initial surface topography of the scratch track. This would be used as the base line for the scratch test.
- Scan 2. The scan was repeated with the load profile applied. A schematic diagram of the conditions present in the loading scan is shown in figure 2. For the initial part of the test, the load used in scan 1 was applied. After a set distance the load was increased linearly to the maximum set value at a second set position. The maximum load was then maintained for the remainder of the scan. The penetration depth, (d), and the friction force, ($F_{||}$), were recorded throughout the scan.

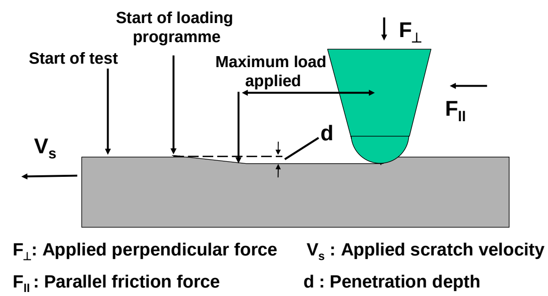


Figure 2: Schematic diagram of the nanoscratch test.

- Scan 3-N. The load scan used in scan 2 could be repeated a number of times if required.
- Scan (N+1). A second topography scan (same conditions as scan 1) is run to record the final track depth.

The objective of the scratch tests was to obtain quantitative data on the bonding force between the nanoparticles in the coating and the substrate. It was also essential that the scratch tracks were observed in a scanning electron microscope to enable the mechanical data to be effectively assessed.

4 SCANNING ELECTRON MICROSCOPY

A Zeiss Supra 35VP scanning electron microscope was used to examine the AV coatings after deposition and after the nanoscratch tests. Back scattered X-ray images were also used in the characterisation of the coatings.

5 RESULTS

5.1 Characterisation of the AV Coatings

Scanning electron microscopy (SEM) was used to examine the coatings for quality and composition. Figure 3 is a scanning electron (SE) micrograph of a nanoparticle coating produced by EPD onto an aluminium substrate. This illustrates a dense uniform coating of the substrate that is the requirement for an AV coating.

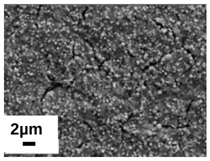
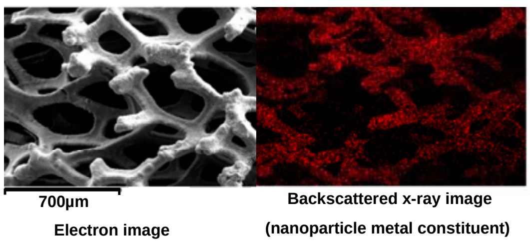


Figure 3: SE micrograph of a nanoparticle EPD coating

Figure 4a is an SE micrograph of a nickel sponge with an EPD coating of nanoparticles. Figure 4b is the backscattered X-ray image of the same area of the coated foam. The image was formed by the metal constituent of the nanoparticles and it illustrates the potential for EPD to evenly coat complex 3-D structures. This is important for applications such as AV coatings for air filtration elements.



(a) (b)

Figure 4: SEM images of an EPD coated nickel foam.

5.2 Nanoscratch Tests

The instrument used was a Micromaterials Nano Test 600 fitted with a sphero-conical probe with a 25µm radius tip. The scratching velocity was kept constant for all of the tests reported below at 20µm/s. The two types of scratch tests carried out were the load/penetration (L/P) test and the load/friction force (L/F) test.

The load/penetration test comprised of three scans of the scratch track. Scan 1 was a topography trace as describe in section 3, scan 2 was a loaded pass in which the load was increased linearly from the start position up to the set maximum at the end of the track. Scan 3, the final pass, was a repeat of the scan 1 conditions to record the final topography of the scratch track. Figure 5 shows the results from a series of three L/P tests carried out on a coated aluminium substrate. The three tests were carried out next to each other and with the maximum loads of 25mN, 50mN and 100mN being the only difference in the test conditions between them. Figure 5 is an SEM image of the start of the three scratch tracks. It can be seen that as the loading profile is increased the distance along the scratch track at which the probe penetrates the coating decreases. Figure 6 shows the load/penetration depth traces for the three tests.

These traces show that the maximum depth recorded on all three traces was approximately 2600nm. The distance along the track where this was reached, however, decreased with an increase in the load profile. The reason that that all three of the traces showed the same maximum recorded penetration depth has been attributed to the probe making contact with the substrate after breaking through the coating. The hardness of the substrate resisted any further penetration by the probe under the conditions used. Consequently it could be concluded from these tests that the thickness of the coating was approximately 2600nm and that a load of approximately 18mn was required to break through the coating. The information derived from the L/P test was used to set the conditions for the L/F test.

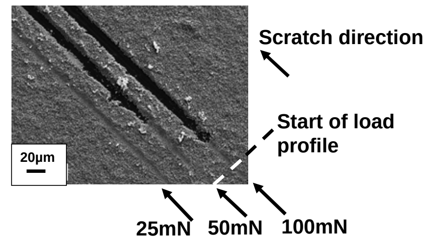


Figure 5: SEM image of the start of three L/P scratch tests.

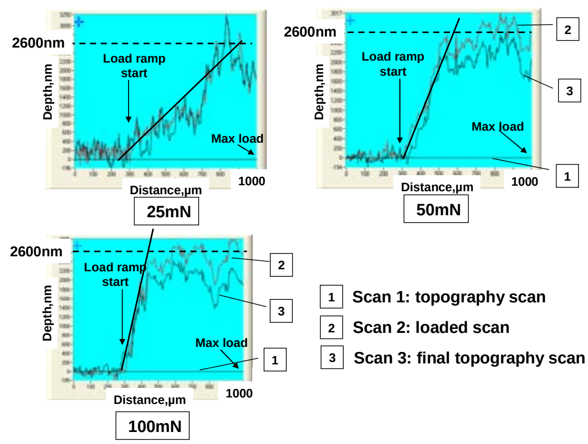


Figure 6: Penetration depth/distance traces for three L/P scratch tests. The initial topography trace has been subtracted from the other scans and is shown as a flat baseline. The rate of penetration of the coating by the three loading profiles can be seen by comparing the gradients of the traces after the start of the loading profile.

The objective of the L/F scratch test was to obtain quantitative data on the bonding force between the AV nanoparticle coating and the substrate. The ideal situation for this test is shown schematically in figure 7. The maximum perpendicular force, $F_{\perp}max$, would be just able to penetrate the coating and remove the coating as the scratch progresses. The measured parallel force, $F_{\parallel}$, would then be equal to the friction force of the probe on the substrate plus the force required to remove the coating from the substrate at the set scratch velocity. A repeat L/F scratch test on the uncoated substrate would provide the value of the friction force of the probe on the substrate under the same test conditions and hence the bonding force of the coating could be calculated.

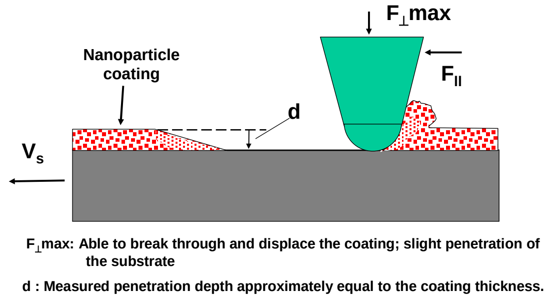


Figure 7: Ideal L/F scratch condition.

The situation that was observed, however, was more complicated than that shown in figure 7. Figure 8 illustrates the situation that can occur. The value of $F_{||}$ is now composed of the friction force of the probe that also includes the force required to deform the substrate and the force required to remove the coating. $F_{||}$ will also be influenced by the presence of any embedded nanoparticles. This situation had to be taken into consideration when the results of the tests were analysed. Some of the results obtained to date are presented in the following paragraphs.

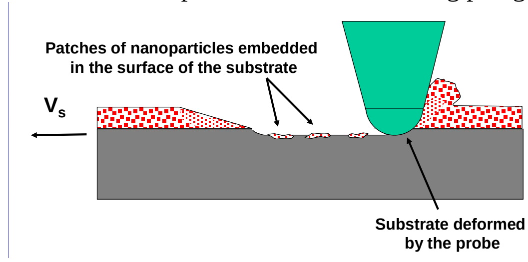


Figure 8: Conditions observed in the L/F scratch test.

The L/F tests carried out took the following form. An initial topography scan was made with a load of 0.1mN. As series of 10 loaded scans were made and the friction force/distance traces recorded. The load profile for the L/F scans was; 0.1mN from 0 to 200µm, 200 to 300µm the load increased linearly to the maximum set load, 300 to 500µm (the end) load maintained at the set maximum. The test was concluded with a final topography trace.

Figure 9 shows the traces taken from an uncoated polymer and the same substrate dip-coated with nanoparticles. The lower traces are the results from the topography traces. The load traces clearly show the effect of the coating on the value of $F_{||}$. Figure 10 shows SEM images of the scratch tracks on the coated polymer substrate. Patches of embedded nanoparticles can be seen in the bed of the track in the image on the left. Displaced particles can be seen at the end of the tracks shown in the right hand image.

Other scratch tests have been carried out on coated polymer substrates that have been heat treated and on coatings that have been made with treated nanoparticles. The value of $F_{||}$ for the heat treated sample was 15% higher than the untreated sample. $F_{||}$ for the coating of the treated particles was approximately 40% higher than the untreated coating.

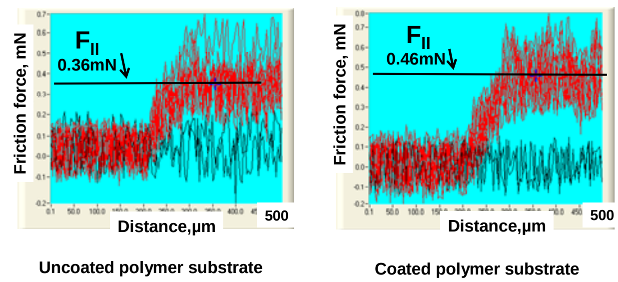


Figure 9: Traces from L/F tests on a coated and uncoated polymer substrate. $F_{\perp}$max was 2mN for both tests.

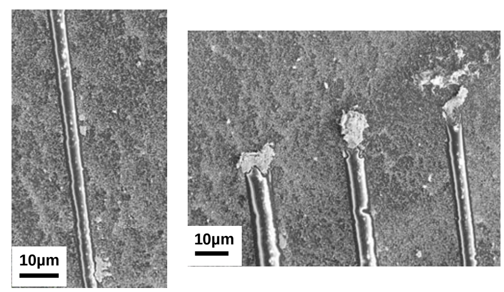


Figure 10: SEM images of scratch tracks on a coated polymer surface.

6 SUMMARY

The methods used for the preparation, characterisation and testing of AV nanoparticle coatings have been described. EPD and dip coating have both been shown to be effective methods for coating complex shapes with AV nanoparticles. Nanoscratch testing combined with SEM has been used to compare the bonding of AV coatings to metallic and polymeric substrates. Coatings made with treated nanoparticles gave the best performance in the mechanical tests. It has yet to be established whether the treated particles will retain their anti-viral properties.

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