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The Evaluation of Sonochemical Techniques for Sustainable Surface Modification in Electronic Manufacturing

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Abstract

Traditional ‘wet’ surface modification techniques used in electronic manufacture are characterized by the use of hazardous chemistry, high process temperatures, copious rinsing and long dwell times. A three year study at the Sonochemistry Centre at Coventry University funded by the Innovative electronic Manufacturing Centre (IeMRC) addresses these issues by evaluating sonochemical surface modification techniques with the objective of producing a process that utilizes benign chemistry at lower temperatures with less rinsing.

This article describes some of the results from this study and suggests that sonochemical surface modification has the potential to provide a more sustainable manufacturing process.

Introduction

To ensure the adhesion of a coating to its substrate it is essential to have a combination of physical (or mechanical) and chemical bonds between them. To achieve this, the substrate is often roughened or textured in a process frequently referred to as surface modification (or adhesion promotion) of the substrate.

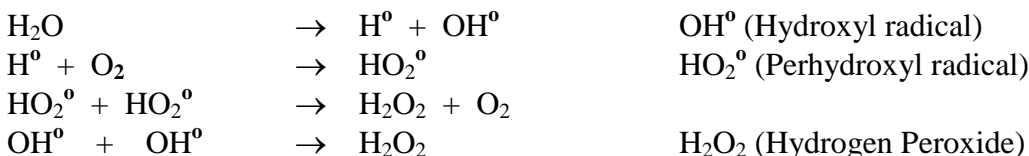
The electronics industry has always had a requirement for adhesion promotion on a vast array of dielectric substrates and with the emergence of printed electronics the choice of substrate will increase still further as, theoretically, anything that can be printed could become an electronic device. The surface modification of polymers and plastics is important in the traditional manufacture of printed circuit boards (PCBs) (i.e. the desmear process¹) and moulded interconnect devices² (MIDs), but will become even more so for polymer electronics, printed electronics, Radio frequency identification (RFID) technology etc. In addition, the metallization of glass and ceramics is becoming of interest in the production of electronic displays and optical circuits.

Traditional ‘wet’ manufacturing techniques for surface modification lend themselves most readily to high volume manufacturing but are often characterized by the use of hazardous chemistry (Table 1), operate at high temperatures and require copious rinsing³ (see for example the ‘desmear’ process shown in Table 2).

Increasing environmental and health and safety legislation coupled with concern about the industry's carbon footprint means that the use of 'clean and green' technologies for such processes needs to be re-evaluated⁴, one strong candidate for this is sonochemistry.

Sonochemical Surface Modification^{5,6,7}

When ultrasound is applied to a solution a series of rarefaction, compression cycles occur as the sound wave passes through it. This is a mechanical process and during the rarefaction phase the molecules of the solution are literally pulled creating cavities. These take in a small amount of vapour from the solution to form a bubble which, during the compression phase, do not collapse but instead continue to grow in size in successive cycles of the sound wave. Eventually these bubbles grow to an unstable size and then undergo violent collapse creating localised hot-spots⁸ where, at a frequency of 20 kHz, it has been calculated that temperatures can reach 5000 K and pressures of 2000 atmospheres⁹. The generation and subsequent collapse of such bubbles is known as acoustic cavitation¹⁰. Under such extreme conditions on collapse it is perhaps not surprising that some quite extraordinary chemistry can take place for example the sonochemical decomposition of water¹¹.



In addition, if the bubble collapses close to or on a solid surface a phenomenon referred to as microjetting¹² or streaming takes place (see Figure 1). In this scenario asymmetric bubble collapse occurs leading to a microjet of liquid being directed towards the surface of the material at speeds of up to 200 m/sec.

Therefore, even in a benign aqueous solution acoustic cavitation can cause a number of effects that are useful for surface modification.

1. Localised high temperatures and pressures

These generate radical and other oxidizing species which can attack the surface of the substrate. Also, under these extreme conditions, bonds (both chemical and physical) can be broken on the surface of the material (e.g. polymer scission) and other chemical reactions can take place.

2. Microjetting

Microjetting can erode/abrade the surface causing mechanical or physical surface modification, destroying boundary layers whilst enhancing heat and mass transfer ensuring that products are removed from, and reactants brought to, the surface of the material efficiently. However, once the ultrasonic energy is turned off this aggressive oxidizing environment will rapidly return to its original benign state.

Previous work on Sonochemical Surface Modification

Ultrasound has been used in surface engineering for many years to assist in the cleaning of articles and/or for degreasing. Indeed Niemcelski^{13,14} has published extremely informative papers in this field concerning the optimization of solutions/solvents and conditions for ultrasonic cleaning. However it is important to make a clear distinction between this type of work, which is directed towards cleaning a surface, and sonochemical surface modification which attempts to change the physical and chemical properties of the surface of a material (although cleaning may occur as well).

It has been reported that ultrasound can surface modify materials such as ABS¹⁵, PVC¹⁶, polyethylene^{17, 18} as well as piezoelectrics such as lead zirconium titanate¹⁹. Zhao et al³⁸ used an ultrasonic horn in water and found that the adhesion of electroplated copper to ABS was always better compared to equivalent chromic acid etching times whilst weight loss and roughness were higher when treatment times of more than 30 minutes were used. XPS measurements also indicated a chemical change to the surface and these workers found similar results with PVC³⁹. However, ultrasound can also be used in conjunction with wet chemical treatments e.g. persulphates⁴⁰ and other mild oxidizing agents⁴¹ where it has been shown that under sonication polyethylene materials can be surface modified and become more hydrophilic as determined by contact angle. More aggressive formulations were employed (e.g. tetrafluoroboric acid / nitric acid) to etch lead zirconium titanate⁴² and the application of ultrasound produced a linear increase in weight loss.

Kathirgamanathan²⁰ demonstrated that no chemical pre-treatment was required if ultrasound was applied during the electroless plating of polyethylene microporous membranes, adequate adhesion apparently being obtained.

The PCB industry has used ultrasonics to enhance the desmear process for many years and it is particularly useful in horizontal equipment²¹ where it has been shown to improve the topography, debris removal and the adhesion of subsequent metallisation in through holes.

The Sonochemical Surface Modification Research Programme

The IeMRC funded research study at the Sonochemistry Centre at Coventry University was instigated to investigate sonochemical surface modification techniques. For the reasons given above it was thought that these methods could have the flexibility to process a diverse range of substrates, employ fewer process stages, require less rinsing, utilize non-hazardous, benign aqueous solutions and be operated at lower temperatures.

The research programme began²² by screening a number of surface modification formulations that had been selected from various literature sources. Four materials were surface modified in each of these solutions either under silent conditions or by applying ultrasound using a 20 kHz ultrasonic probe. In each case the treatment time was 60 minutes at 40 °C. Figure 1 shows the weight loss results for a dielectric ceramic material

(by its very nature one of the most inert substrates tested). For most of the formulations tested higher weight loss was found in the presence of ultrasound. However the most remarkable result was that if water was utilized as the liquid medium through which ultrasound was applied some of the highest weight losses were recorded and these effects were confirmed by SEM analysis (see Figures 3 and 4).

These very promising early results led to a more intensive study of the factors affecting the process in water. One parameter with significant effect was found to be the distance between the tip of the ultrasonic probe and the substrate surface²³. Comparison of Figures 5 and 6 clearly show that when a short probe to samples distance is utilized (5 mm) a more dramatic change in surface morphology is observed on a polyphenylene/polyester substrate (Noryl HM4025) than when the probe is further away (25 mm).

Other process enhancements have also been investigated based upon the experience of the Sonochemistry Centre. Thus by adding a surfactant to lower the surface tension of the solution it is possible to reduce the energy required to induce acoustic cavitation. Another approach is to employ solution temperatures close to zero as this will decrease the solvent vapour pressure so that less vapour enters the cavitation bubble resulting in more violent and energetic collapse. This fundamental understanding of sonochemistry was translated into more effective surface modification on an high Tg epoxy laminate²⁴ used in PCB manufacture (Isola 370HR). A sonication time of 15 minutes was used and comparing the SEM photographs of the 'standard' sonochemical process at 40 °C (Figure 8) to when either surfactant was added (Figure 9) or the temperature was reduced (Figure 10) indicates that more effective surface modification can be achieved under either of these two conditions.

Clearly therefore it is very important to understand the factors affecting acoustic cavitation as ultrasound is often simply 'bolted on' to an existing cleaning or surface modification process with very little thought being given to optimising the sonochemical conditions to get the very best performance.

The evaluation of sonochemical surface modification at the Sonochemistry Centre has produced a technology platform from which potential commercial applications are beginning to appear. A good example of this is research that was carried out in conjunction with Loughborough University and a Norwegian company (Conpart AS) which has shown that ultrasound can be used to surface modify polymeric microspheres in aqueous solution which subsequently leads to improved adhesion when the spheres are electroless plated. In addition, equipment that might allow scale-up of these surface processing methods has also been evaluated²⁵.

Sonochemical surface modification has been shown to reduce process times operates effectively at low temperatures and can be used in solutions as benign as water. It therefore has the potential to be 'lean, green and clean' and provide a route to more sustainable manufacturing.

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