Sonochemical Surface Modification
A route to Lean, Green and Clean Manufacturing?

Cobley A J, Mason T J, The Sonochemistry Centre at Coventry University, Coventry, UK
Robinson J, Prosonix Ltd, Oxford, UK

Traditional surface modification techniques utilize hazardous chemistry, operate at high temperatures and require copious rinsing.
Ultrasound has long been a 'bolt on' for such processes with little thought to optimizing its driving force; the process of acoustic cavitation. This paper demonstrates that, by understanding the factors affecting acoustic cavitation and the employment of suitable ultrasonic equipment, sonochemical surface modification can be achieved on a range of substrates in solutions as benign as **water**, therefore reducing

- process stages
- rinsing
- operating temperatures.

Sonochemical surface modification is therefore lean, green and clean and could potentially lead to more sustainable manufacturing.

For more information contact:
Dr Andy Cobley
Head of Sonochemical Materials Processing
The Sonochemistry Centre at Coventry University
Faculty of Health and Life Sciences
Priory Street
Coventry
CV1 5FB
UK

Phone +44 (0) 24 7688 8624
Fax +44 (0) 24 7688 8173
Mobile +44 (0) 7706 955 901
a.cobley@coventry.ac.uk
www.coventry.ac.uk/sonochemistry

Introduction

To ensure the adhesion of a coating to its substrate it is essential to form a mixture 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 and metal finishing industries have always had a requirement for adhesion promotion on a vast array of dielectric substrates. The surface modification of polymers and plastics is important in the traditional manufacture of printed circuit boards (PCBs) (i.e. the desmear process[1]) and moulded interconnect devices[2] (MIDs), but will become even more so for polymer electronics, printed electronics, radio frequency identification (RFID) technology etc.

Traditional 'wet' surface modification techniques lend themselves most readily to high volume fabrication and an example of this is the desmear process used in PCB manufacturing. This is an essential part of the production sequence since, when the through holes of PCBs are drilled the drill bit becomes hot and may exceed the glass transition temperature of the epoxy material. Epoxy is thus transferred to the drill bit and then smeared onto the walls and inner layers of subsequently drilled holes. It is extremely important to remove this 'resin smear' before metallisation of the hole so that electrical connection can be made to the inner-layers. In addition the desmear process surface modifies the hole wall ensuring good coverage and adhesion of the plating. A typical desmear process is shown in Table 1.

Chemistry	Time (minutes)	Temperature (ºC)
Alkaline Permanganate	**5-15**	**65-85**
Rinse	3-5	
Rinse	3-5	
Solvent Swell	**5-15**	**65-85**
Rinse	3-5	
Rinse	3-5	
Neutraliser	**2-4**	**Ambient - 50**
Rinse	2-3	
Rinse	2-3	

Table 1 – Traditional desmear process used in PCB manufacturing

It can be seen that this desmear/surface modification process requires 3 stages and uses long dwell times which reduces production capability (although horizontal processing can cut these times dramatically). Heat (and therefore energy) is required to obtain the elevated solution temperatures and copious rinsing is necessary to prevent contamination of the subsequent processes (e.g. electroless copper). The chemistry employed is corrosive and oxidizing and will contaminate the rinse steps all of which will require waste treatment further adding to production costs. Similar problems are encountered in the metal finishing industry where chromic acid etching of plastic is utilized or hydrofluoric acid is used for the surface modification of glass and ceramics.

Although previous work[3,4,5] has indicated that sonochemical methods can be used to surface modify various substrates industry has largely ignored this and maintained its use of 'tried and tested' processes. However, increasing environmental and health and safety legislation coupled with concern about the industry's carbon footprint means that the use of 'lean, green and clean' methods for such processes need to be explored and one technology with great potential in this area is sonochemistry.

Sonochemical Surface Modification[6,7,8]

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 apart creating bubbles. These take in a small amount of vapour from the solution so that on compression they 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-spots[9] where, at a frequency of 20 kHz, it has been calculated that temperatures can reach 5000 K and pressures of 2000 atmospheres[10]. The generation and subsequent collapse of such bubbles is a process known as acoustic cavitation[11]. 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 water[12].

H_2O	$\rightarrow$	$H^o + OH^o$	OH^o (Hydroxyl radical)
$H^o + O_2$	$\rightarrow$	HO_2^o	HO_2^o (Perhydroxyl radical)
$HO_2^o + HO_2^o$	$\rightarrow$	$H_2O_2 + O_2$	
$OH^o + OH^o$	$\rightarrow$	H_2O_2	H_2O_2 (Hydrogen Peroxide)

In addition, if the bubble collapses close to or on a solid surface a phenomenon referred to as microjetting[13] or streaming takes place (see Figure 1). In this scenario asymmetric bubble collapse results producing a microjet of liquid directed towards the surface of the material at speeds of up to 200 m/sec.

Figure 1. Bubble Collapse at a Solid Surface – Prof. Crum, University of Seattle

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 may take place.

2. Microjetting

Microjetting causes mechanical or physical damage to the substrate, destroys boundary layers and improves heat and mass transfer ensuring that products are removed from, and reactants brought to, the surface of the material efficiently. In addition, any loosely adherent debris produced by the surface modification process is cleaned away producing a fresh surface on which reactions can take place.

However, the remarkable thing about Sonochemistry is that once the ultrasonic energy is turned off this aggressive, turbulent environment will rapidly return to a benign state.

Although ultrasound has been used for many years in the metal finishing and electronics industries to enhance cleaning, etching and surface modification processes it is often simply ‘bolted on’ to an existing process with little thought being given to optimum operating conditions. However, it is clear from the description of sonochemistry that to take full advantage of these effects one must create an environment where cavitation is optimised. For example low frequency ultrasound (20 kHz) will enable bubbles to grow to a relatively large size thus maximizing the effects brought about by their collapse. High temperatures (greater than 40 ºC) should be avoided as this will not only reduce the viscosity of the solution but, as boiling points are approached, molecular movement will increase causing premature bubble collapse. Adding a surfactant may also enhance cavitation by reducing the surface tension of the solution.

This paper will show that by careful choice of ultrasonic equipment and solution conditions significant surface modification can be achieved on three laminates used in PCB manufacture.

Experimental

Three widely available PCB laminates were used in this study which can be briefly described as follows:

1. A standard FR4 glass filled epoxy (Tg 135-140 ºC)
2. A ‘modified’ FR4 glass filled epoxy (Tg 180 ºC)
3. A glass reinforced ceramic/hydrocarbon (Tg >280 ºC)

This choice gave a range of materials with differing glass transition temperatures (Tg). High Tg materials are becoming more prevalent in electronic manufacturing due to the higher solder temperatures required for lead-free soldering and their improved performance at high frequency. However, as a general rule, the higher the Tg the more chemically inert are the substrates and, therefore, the more difficult they are to surface modify.

Bare laminate samples of each of these materials were prepared and cut to dimensions of approximately 2.5 x 3.0 cm.

The ultrasonic equipment used throughout this study is shown in Figure 2 below.

Figure 2. Ultrasonic processing device

The device is patent protected[14] and consists of a hard chrome plated cyclindrical core to which are attached an array of 10 (low density (LD)) or 21 (high density (HD)) 20 kHz transducers. The transducers are offset and when the equipment is switched on acoustic cavitation is concentrated in the centre of the cyclinder.

To surface modify the materials the equipment was filled with approximately 5 litres of town water. Six test plaques were then placed in the centre of the cyclindrical core and processed according to the conditions shown in Table 2 below.

Run No	Transducer Configuration	Power (W)	Solution	Temperature (ºC)	Time (minutes)
1	Low density	150	Town water	18	5
2	High density	150	Town water	12-18	5
3	High density	150	Town water	12-20	10
4	High density	150	Town water	13-20	10

Table 2. Process conditions used for Sonochemical Surface Modification

After processing the plaques were rinsed in de-ionized (DI) water for 5 minutes and then dried.

The efficacy of sonochemical surface modification was determined by the following surface analysis techniques.

1. Weight loss

Before processing samples of the materials were baked in an oven at 120 ºC for 1 hour. They were then allowed to cool to room temperature in a dessicator and then weighed to 4 decimal places. The samples were then returned to the oven for a further

1 hour, allowed to cool and the reweighed. This procedure was continued until a constant weight (a difference of 0.002 g) was obtained.

This method was then repeated after the samples of the plaques had been processed through the sonochemical surface modification equipment.

The weight loss (mg/cm^2) was then calculated as follows:

(Initial Weight (mg) - Final Weight (mg)) / Surface area (cm^2)

Weight loss was determined for each of the 6 plaques produced per processing condition.

2. Contact angle

The contact angle of de-ionized water was measured using a Kruss D100 contact angle measuring system. Three readings were taken on each sample making a total of 18 per processing condition.

3. Roughness

Roughness was determined over a 1.3 cm length of the substrate using a Rank Taylor Hobson Form Talysurf 120L. This operates with a contact stylus and movements in the Z direction are measured using a laser interferometer. The software calculates roughness as a Ra value i.e. the arithmetic departure of the roughness profile from the mean line. Two measurements were made on each sample given a total of 12 per process condition.

4. Scanning Electron Microscopy (SEM)

A representative sample from each of the process conditions was taken and examined using a Jeol JSM-6060LV SEM.

Results and Discussion

The results from this study are shown in Table 3.

Table 3. Results from Sonochemical Surface Modification Process

Run No	Material	Weight loss (mg/dm^2)	Contact angle (θ)	Roughness Ra (µm)
As received	FR4	0.00	92.9	0.4985
1		13.25	101.0	0.4973
2		11.81	85.1	0.5139
3		13.97	86.9	0.5253
4		14.02	77.0	0.5383
As received	Modified FR4	0.00	86.2	0.3525
1		14.59	81.7	0.5135
2		16.07	89.1	0.5298
3		15.26	88.5	0.4931
4		17.41	74.5	0.5137
As received	Ceramic/Hydrocarbon	0.00	73.3	0.5986
1		16.31	96.6	1.1510
2		14.63	77.1	1.1186
3		12.29	77.3	0.9739
4		17.06	89.6	1.0097

The weight loss results for all three materials indicate that a significant amount of material has been removed for each of the three laminates under investigation using the sonochemical surface modification process. Figure 3 suggests that the process variations investigated did not have a consistent effect on weight loss for all three materials although in each case utilizing a dwell time of 10 minutes with the high density configuration and 1 % added surfactant produced the greatest weight loss values.

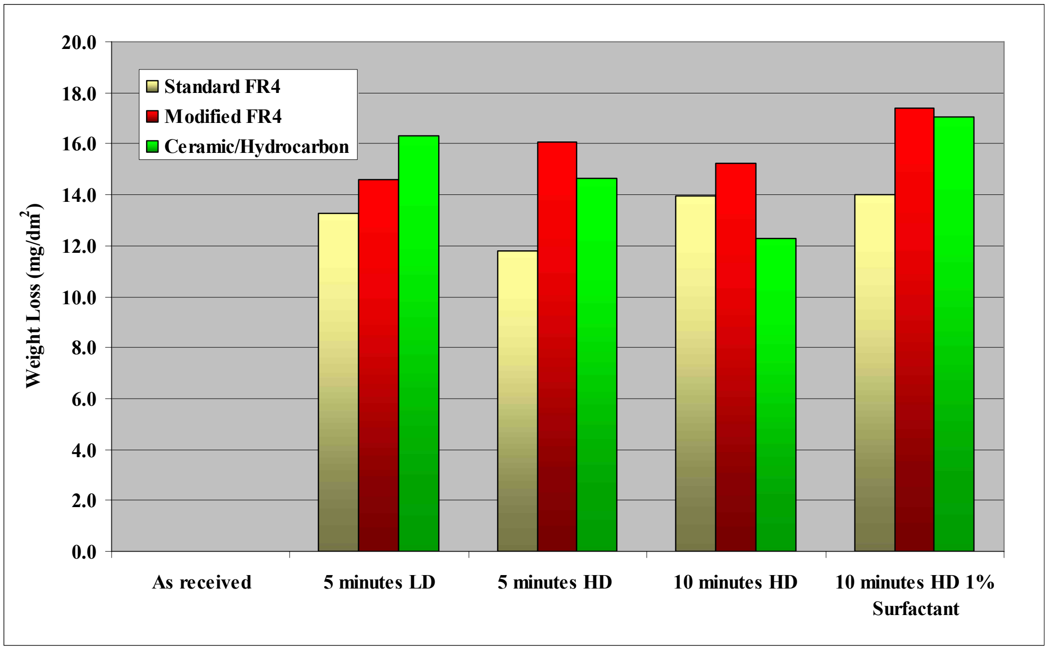


Figure 3. Effect of Sonochemical Surface Modification on Weight Loss

What was surprising was that the generally the standard FR4 material gave the lowest weight loss values although one might expect this material to be the least inert and most easily surface modified.

It is difficult to obtain a direct comparison of these results to a 'traditional' chemical desmear system as weight loss can vary according to the sweller used, permanganate concentrations, dwell times and temperatures as well as material and batch to batch variations. However recent work by Patton[15] studied the weight loss results for a number of PCB laminates using 'swell and etch' type systems. The results for this study are reproduced in Figure 4.

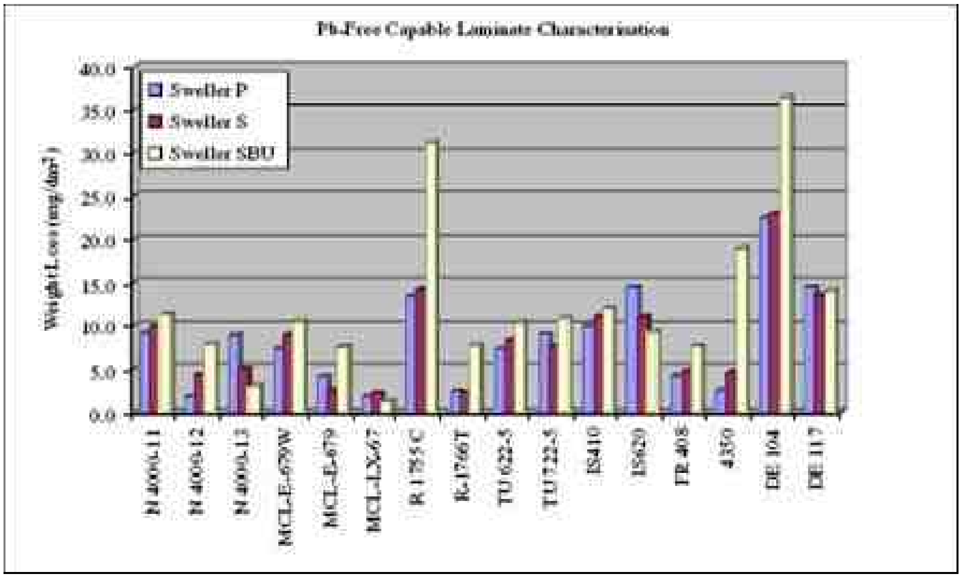


Figure 4. Typical weight loss results for PCB laminates using 'swell and etch' process after Patton[15]

It can be seen from this that the weight loss results obtained from the ultrasonic process for the 3 materials tested fall well within the types of values obtained by these workers and often exceed them. When one considers that this has been achieved by applying ultrasound through tap water (sometimes with a little added surfactant) for at most 10 minutes then this is an extremely encouraging result.

Consideration of the contact angle values (Figure 5) does not show any dramatic changes in this response from the as received material although it should be noted that for the FR4 and modified FR4 materials the most wettable surface was obtained when surfactant was added to the water.

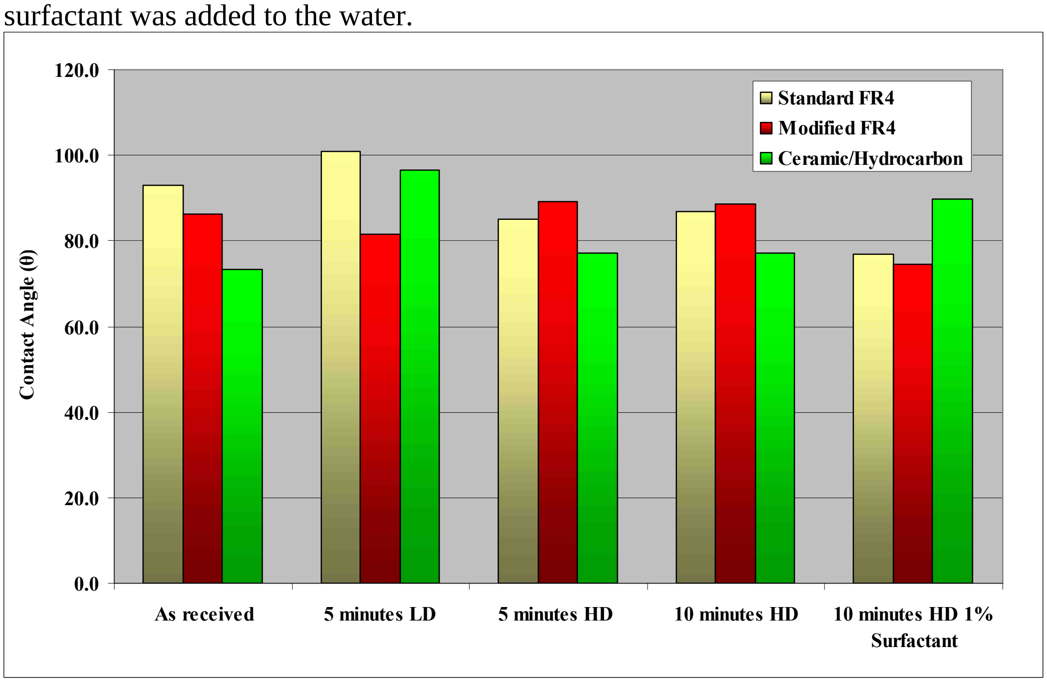


Figure 5. Effect of Sonochemical Surface Modification on Contact Angle

These findings suggest that the sonochemical surface modification process is a physical effect brought about through erosion of the surface by micro-jetting with little chemical change to the surface occurring.

The roughness data is illustrated in Figure 6 and it is very apparent that the ceramic/hydrocarbon substrate has been significantly roughened by the ultrasonic treatment. This effect seems to be reduced at higher dwell times and when using the high density configuration. This is probably due to extended process times producing a levelling effect as more material is removed. Roughness also significantly increased for the modified FR4 material and although the standard FR4 showed the least change in roughness it is notable that as the ultrasonic conditions were made more aggressive so roughness gradually increased.

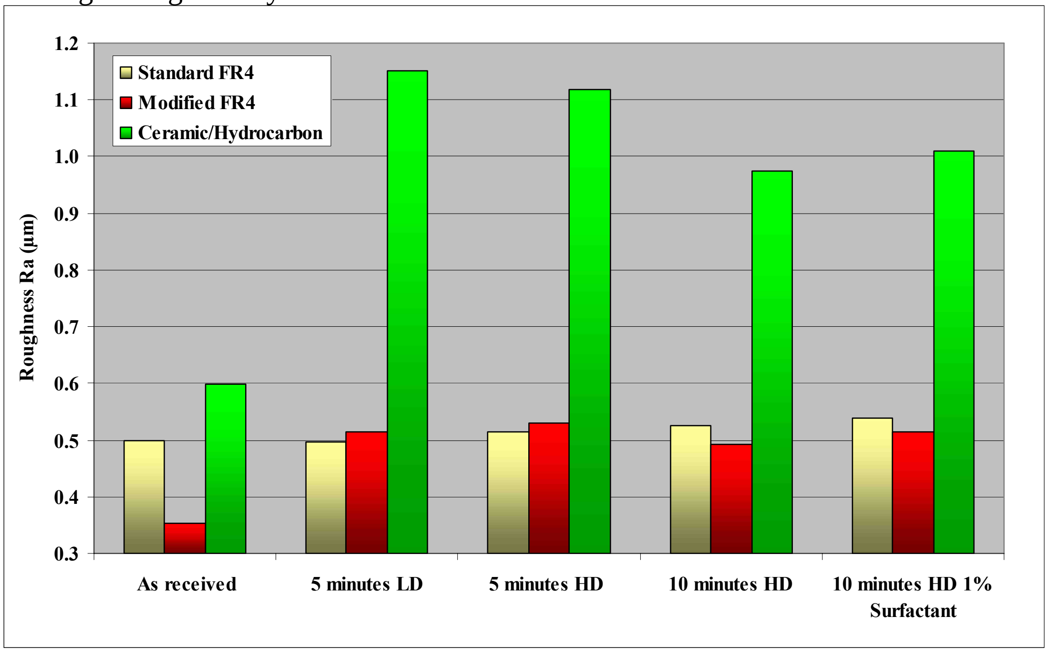
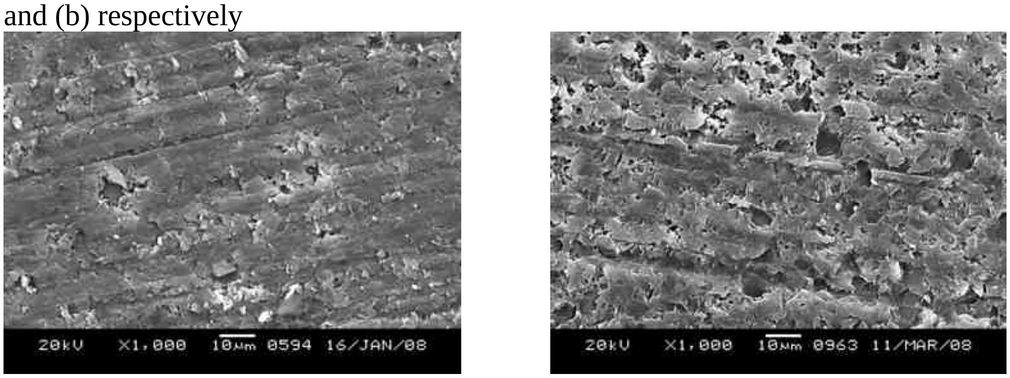


Figure 6. Effect of Sonochemical Surface Modification on Roughness

The SEM photographs for the FR4 laminate in the as received state and after 10 minutes in the HD ultrasonic process (plus 1% surfactant) are shown in Figure 7 (a) and (b) respectively

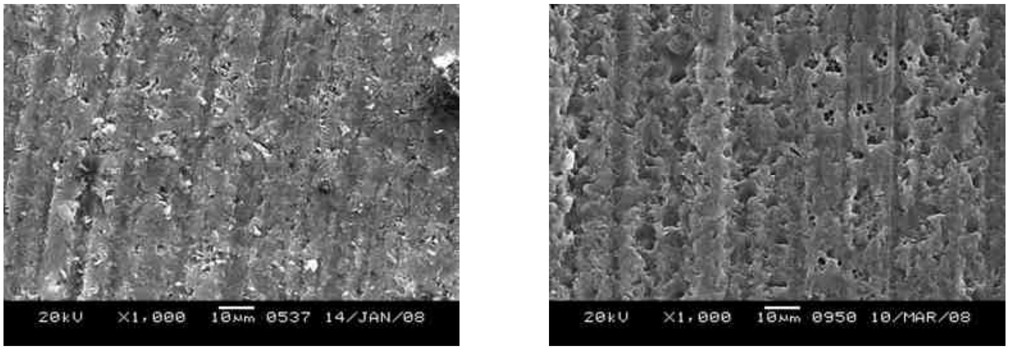


(a) *(b)*

Figure 7. FR4 (a) as received and (b) after 10 minutes ultrasonic treatment (HD) using town water plus 1% surfactant

The surface of the FR4 has obviously been significantly altered by the ultrasonic treatment, the generally planar 'as received' surface being replaced with a cleaner somewhat textured morphology.

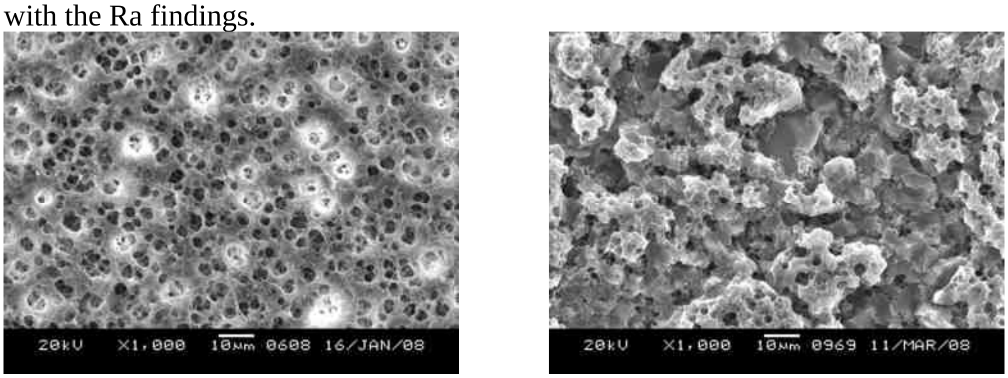
A similar effect is seen with the modified FR4 SEMs shown in Figures 8 (a) and (b). Once again the sonochemical process has clearly changed the microscopic appearance of the substrate and produced a more 3 dimensional, debris free structure.



(a) *(b)*

Figure 8. Modified FR4 (a) as received and (b) after 10 minutes ultrasonic treatment (HD) using town water plus 1% surfactant

The ceramic/hydrocarbon laminate shows the most dramatic change in morphology as is illustrated in Figures 9(a) and (b). After treatment using ultrasound the surface is completely transformed from the as received state. It appears that a significant amount of material has been removed and a much rougher surface is produced correlating well with the Ra findings.



(a) *(b)*

Figure 9. Ceramic/Hydrocarbon (a) as received and (b) after 10 minutes ultrasonic treatment (HD) using town water plus 1% surfactant

Conclusions

1. Taking the weight loss and roughness data into consideration it can seen that sonochemical surface modification of the three laminates tested is possible in water.

2. Changing from the low to high density transducer configuration did not cause any dramatic alteration in the surface analysis results but adding a small amount of surfactant tended to increase weight loss and roughness and also produced lower contact angles.

3. Overall it seems that the ceramic/hydrocarbon material has been most affected by the sonochemical surface modification process. This is surprising as it has the highest Tg and its chemical composition would lead one to expect it to be the most inert of the three materials. In contrast the standard FR4 laminate was the least affected by the ultrasonic treatment although this substrate has the lowest Tg. This seems to suggest that surface modification is occurring by physical erosion of the harder, less resilient surface through microjetting surface due to microjetting rather than chemical attack of the surface and explains why little change in contact angle also occurred.

4. Comparing these results with those obtained by Patton[15] indicates that weight loss values are comparable to 'swell and etch' processes. In terms of developing a more sustainable surface modification process the fact that this has been achieved simply by using ultrasound through water at room temperature is very promising. Clearly it is

necessary to perform more work to see if these findings can be reproduced in PCB through holes but, on the basis of the work carried out so far, sonochemistry promises to reduce process times and rinsing as well as eliminating the need for hazardous chemistry.

Acknowledgments

The authors would like to thank the Innovative Electronic Research Centre (IeMRC) for funding this work and our research collaborators Prosonix Ltd, Chestech Ltd and Moulded Circuits Ltd. In addition they would also like to thank Isola Werke UK Ltd and the Rogers Corporation for supplying samples of their laminates.

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