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

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

Keywords: *ultrasonic treatment, sonochemical surface treatment, green processing*

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 molded interconnect devices (MIDs).[2] Such processing will become even more essential for polymer electronics, printed electronics and radio frequency identification (RFID) technology, among other areas.

Traditional "wet" surface modification techniques lend themselves most readily to high volume fabrication. 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 metallization 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.

Table 1
Traditional desmear process used in PCB manufacturing

Process step	Time (min)	Temp. (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	
Neutralizer	2 - 4	Ambient - 50
Rinse	2 - 3	
Rinse	2 - 3	

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It can be seen that this desmear/surface modification process requires three 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 vapor 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 localized hot spots[9] where, at a frequency of 20 kHz, it has been calculated that temperatures can reach 5000 K (4730°C) 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]

$$H_2O \rightarrow H^{o} + OH^{o} \qquad OH^{o}\ \text{(Hydroxyl radical)} \tag{1}$$

$$H^{o} + O_2 \rightarrow HO_2^{o} \qquad HO_2^{o}\ \text{(Perhydroxyl radical)} \tag{2}$$

$$HO_2^{o} + HO_2^{o} \rightarrow H_2O_2 + O_2 \tag{3}$$

$$OH^{o} + OH^{o} \rightarrow H_2O_2 \qquad H_2O_2\ \text{(Hydrogen Peroxide)} \tag{4}$$

In addition, if the bubble collapses close to or on a solid surface, a phenomenon referred to as microjetting[13] or streaming takes place (Fig. 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.

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

Localized 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.

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 optimized. 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 40ºC) 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 (T_g = 135-140ºC)
2. A "modified" FR4 glass filled epoxy (T_g = 180ºC)
3. A glass reinforced ceramic/hydrocarbon (T_g > 280ºC)

This choice gave a range of materials with differing glass transition temperatures (T_g). High T_g 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 T_g the more chemically inert are the substrates and, therefore, the more difficult they are to surface modify.

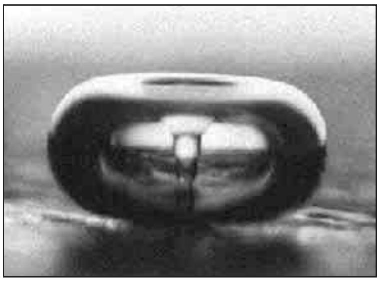

Figure 1—Bubble collapse at a solid surface (Photo by Prof. Crum, University of Seattle).

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

The ultrasonic equipment used throughout this study is shown in Fig. 2. The device is patent protected[14] and consists of a hard chromium-plated cylindrical 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 center of the cylinder.

To surface modify the materials, the equipment was filled with approximately 5 L of city water. Six test plaques were then placed in the center of the cylindrical core and processed according to the conditions shown in Table 2. After processing the plaques were rinsed in deionized (DI) water for 5 minutes and then dried.

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

Weight loss

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

$$[\text{Initial Weight (mg)} - \text{Final Weight (mg)}]/\text{Surface area (cm}^2) \quad (5)$$

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

Contact angle

The contact angle of deionized 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.

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 R_a 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.

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. 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 min with the high density configuration and 1% surfactant added produced the greatest weight loss values.

What was surprising was that in general, 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 Fig. 4.

It can be seen from this that the weight loss results obtained from the ultrasonic process for the three materials tested fall well within the types of values obtained conventionally 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 min, then this is an extremely encouraging result.

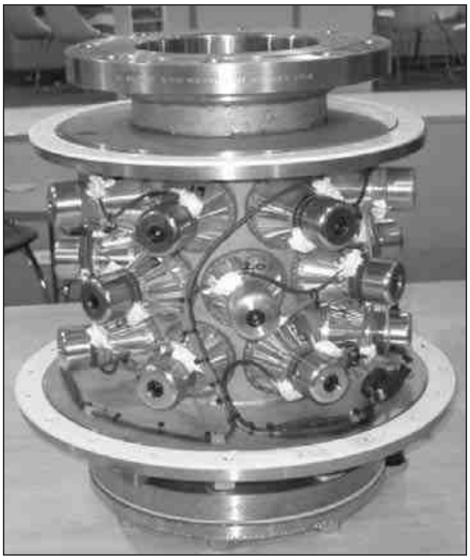

Figure 2—Ultrasonic processing device.

Table 2
Process conditions used for sonochemical surface modification

Run No.	Transducer configuration	Power (W)	Solution	Temp. (ºC)	Time (min)
1	Low density	150	City water	18	5
2	High density	150	City water	12 - 18	5
3	High density	150	City water	12 - 20	10
4	High density	150	City water	13 - 20	10

Table 3
Results from the sonochemical surface modification process

Run No.	Material	Weight loss (mg/dm^2)	Contact angle (θ)	Roughness R_a (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

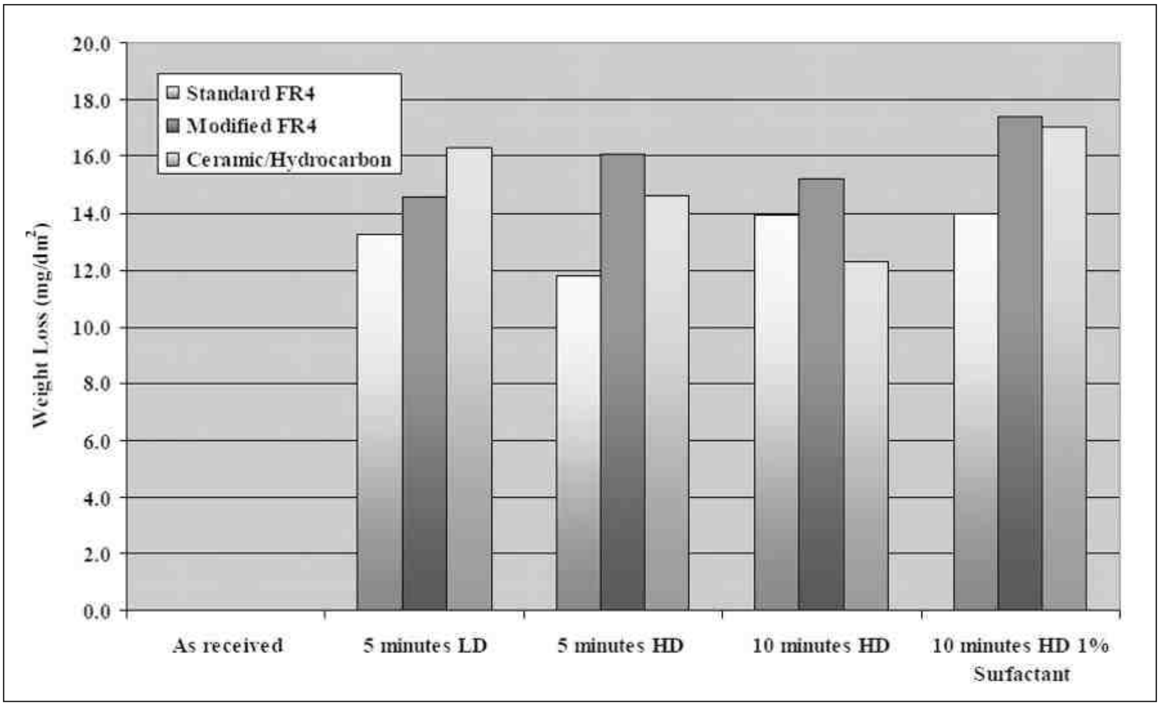

Figure 3—Effect of sonochemical surface modification on weight loss.

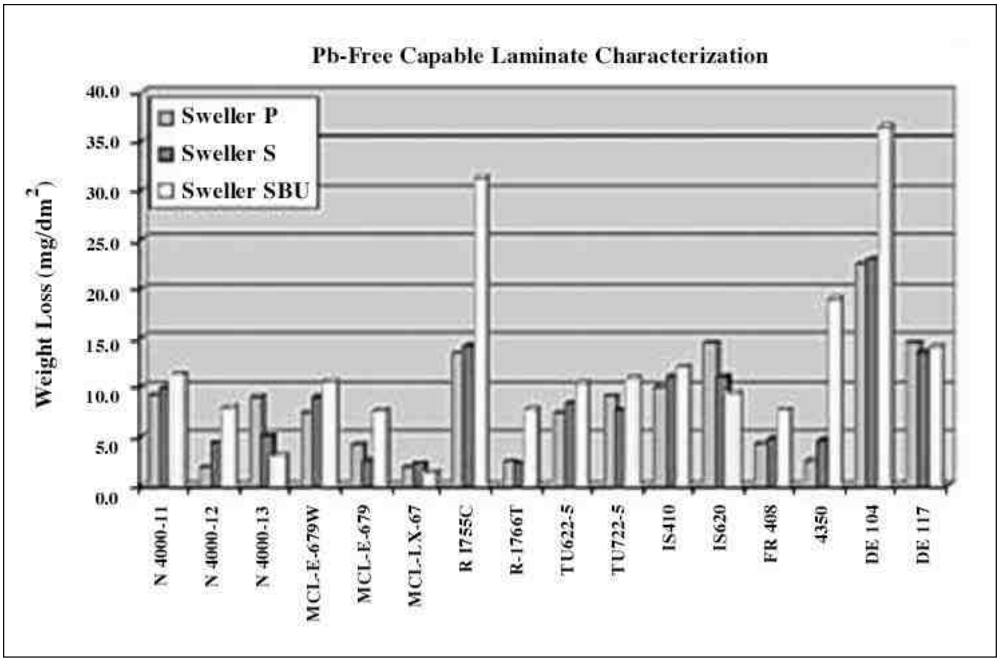

Figure 4—Typical weight loss results for PCB laminates using the "swell and etch" process after Patton.[15]

Consideration of the contact angle values (Fig. 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.

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 Fig. 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 leveling effect as more material is removed. Roughness was 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, roughness was gradually increased.

The SEM photographs for the FR4 laminate in the as-received state and after 10 min in the HD ultrasonic process (plus 1% surfactant) are shown in Figs. 7a and b respectively. 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 SEMs of the modified FR4 shown in Figs. 8a and b. Once again the sonochemical process has clearly changed the microscopic appearance of the substrate and produced a more three-dimensional, debris-free structure.

The ceramic/hydrocarbon laminate shows the most dramatic change in morphology, as is illustrated in Figs. 9a 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 R_a findings.

Conclusions

1. Taking the weight loss and roughness data into consideration, it can be 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 was most affected by the sonochemical surface modification process. This is surprising as it has the highest T_g and its chemical composition would lead one to expect it to be the most inert of the three materials. By contrast, the standard FR4 laminate was the least affected by the ultrasonic treatment, although this substrate has the lowest T_g. This seems to suggest that surface modification is occurring by physical erosion of the harder, less resilient 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 eliminate the need for hazardous chemistry.

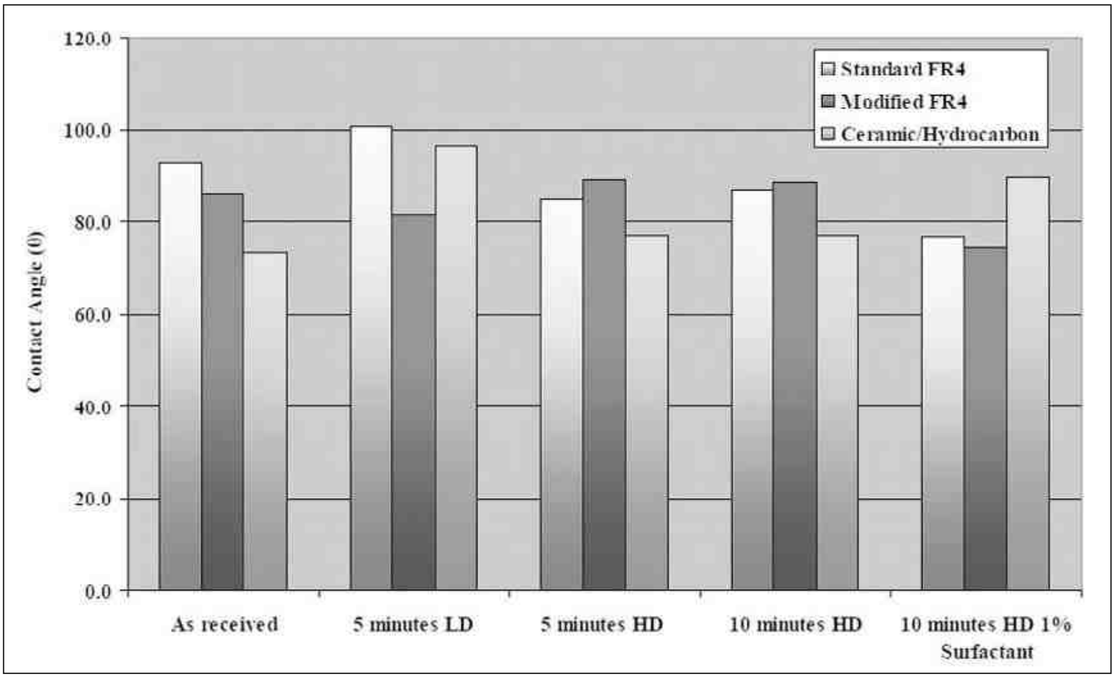

Figure 5—Effect of sonochemical surface modification on contact angle.

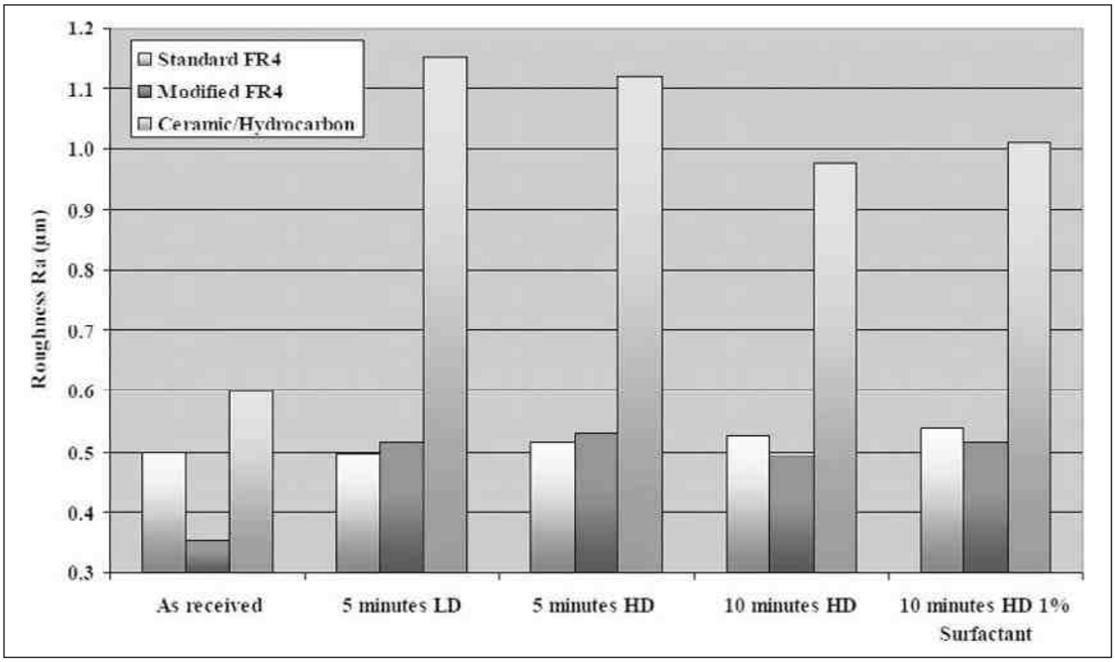

Figure 6—Effect of sonochemical surface modification on roughness.

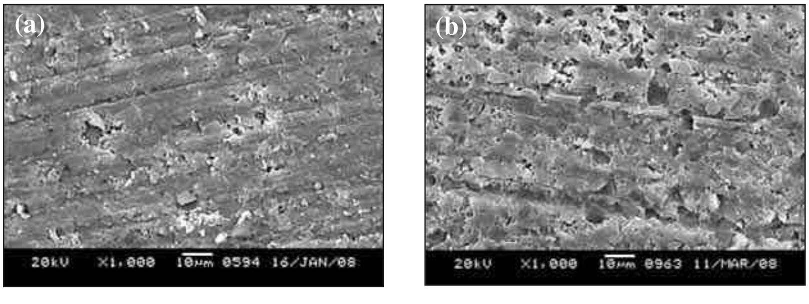

Figure 7—FR4: (a) As received and (b) after 10 min of ultrasonic treatment (HD) using city water plus 1% surfactant.

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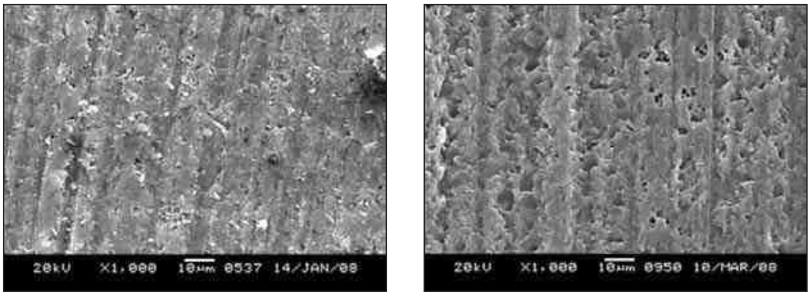

Figure 8—Modified FR4: (a) As received and (b) after 10 min of ultrasonic treatment (HD) using city water plus 1% surfactant.

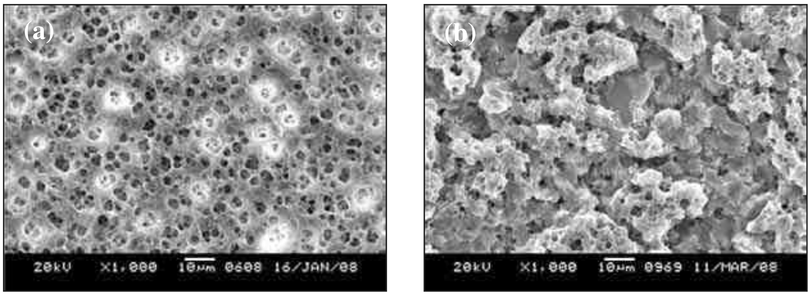

Figure 9—Ceramic/Hydrocarbon: (a) As received and (b) after 10 min of ultrasonic treatment (HD) using city water plus 1% surfactant.

About the authors

Dr Andy Cobley is Senior Research Fellow and Team Leader Materials at the Sonochemistry Centre at Coventry University. Andy graduated from Portsmouth Polytechnic in 1986 and, after a brief spell at the International Tin Research Institute, he joined British Aerospace, working as a Process Chemist in their Metal Finishing and PCB facilities. In 1989, he moved to Shipley Europe (now Rohm and Haas) where he developed electroless and electroplating processes, publishing several papers and patents along the way. In 2002, Andy completed a Ph.D. at Loughborough University and, in 2006, joined the Coventry University Sonochemistry Centre where he now heads the Materials Group. Dr. Cobley is a Chartered Chemist, a Member of the Royal Society of Chemistry and a Member and Councilor for both the Institute of Metal Finishing and the Institute of Circuit Technology.

Timothy J. Mason is Director of the Sonochemistry Centre at Coventry University. He attended Southampton University, graduated in Chemistry and received his Ph.D. in Organic Chemistry in 1970. After two years as a NATO Fellow at Amherst College (USA) he returned to the UK and eventually moved to Coventry University in 1975, was appointed Professor of Chemistry in 1989 and awarded a D.Sc. for this research into sonochemistry in 1996. He was the first president if the European Society of Sonochemistry and is Editor in Chief of the journal Ultrasonics Sonochemistry. As Director of the Sonochemistry Centre in Coventry, his interests are in a range of applications of power ultrasound technologies including environmental protection, materials processing, food processing, electrochemistry and therapeutic ultrasound. He has over 300 publications and 15 books on sonochemistry.

Dr. James Robinson is a senior scientist with Prosonix Ltd. He did an HND in Chemistry with Computing at Portsmouth Polytechnic, UK, and gained his first degree in Applied Chemical Sciences from University of the West of England, Bristol, UK. In later years he earned a Ph.D. in Theoretical Organic Chemistry with Prof. I.H. Williams, at the University of Bath, Bath, UK. He has over ten years of experience as a Process Chemist. He has also worked as a Molecular Modeler and a Computational Chemist. Before joining Prosonix Ltd., he worked for Evotec OAI, Bath University, Sigma Aldrich and MTM John Ross Chemicals.