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Effect of GC METALPRIMER II on Bond Strength of Heat-Cured Acrylic Resin to Titanium Alloy (Ti-6Al-4V) with Two Different Surface Treatments

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Abstract - *This study investigated the bond strength of heat-polymerized acrylic resin to titanium alloy using a proprietary bonding agent (GC Metalprimer II). Two surface treatments (sandblasted or roughened with a tungsten carbide bur) were compared for their effect on bond strength with or without thermal cycling. Eighty specimens of heat-polymerized acrylic resin bonded to titanium alloy (Ti-6Al-4V) were prepared: 20 specimens (control) and 60 used a bonding agent. Four-point bend testing was used to record the load at failure. A chemical bond between heat-polymerized resin and alloy was achieved using GC Metalprimer II with both surface treatments. Reduced failure loads were recorded after thermal cycling. The predominant mode of failure was cohesive. GC Metalprimer II was effective in achieving a chemical bond with either the sandblasted or roughened surfaces.*

KEY WORDS: **Bond strength, Acrylic resin, Titanium, Bonding agent**

INTRODUCTION

Achieving high bond strength between acrylic resin and the base metal alloy is a requirement for success in the fabrication of removable or fixed partial dentures. An area of clinical concern and research has been to find the best combination of resin-based bonding agent and the metal surface treatment that would produce a good bond. Surface treatment of the alloy has included macro-mechanical, micro-mechanical and chemical bonding[1-4].

Titanium-based alloys have been introduced for use in prosthodontics, and are considered to be ideal materials due to their biocompatibility, corrosion resistance, and favourable strength to weight ratio[5,6]. A protective layer, which is primarily titanium oxide (2-5 nm in thickness), forms readily on scratching or abrading the surface of the metal[5]. It provides excellent corrosion resistance and environmental stability[7]. There are numerous commercial titanium alloy compositions available, supplied in a wide variety of forms such as annealed, wrought, or heat-treated bar, sheet, rod, wire plate, or powder forms[8]. The most common compositions for dental and medical purposes are commercially pure titanium, or titanium aluminium vanadium alloy (Ti-6Al-4V) where the composition is 90 wt% titanium, 6 wt% aluminium, and 4 wt% vanadium.

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The dental prosthesis should withstand mechanical, thermal, and chemical stresses found intra-orally. The adhesion of dental acrylic resin to unmodified metal surfaces is unreliable in the oral environment and a major factor is the difference in the coefficient of thermal expansion between PMMA resins[3]. Under repeated thermal cycling due to the imbibing of hot and cold foods, this would result in straining at the polymer/metal interface, possibly resulting in fatigue failure of the polymer at the interface or loss of adhesion between the PMMA and metal base.

Airborne-particle abrasion (sandblasting) is a method for achieving micromechanical retention. It increases the surface area and enhances wettability by increasing surface free energy. Many studies have investigated the effect of sandblasting and it has consistently been associated with improved joint strength [2,9-12].

Chemical bonding between the metal framework of a dental prostheses and the denture base resin is desirable to prevent leakage. There have been previous attempts to create a chemical bonding system to improve resin/metal adhesion [3,4,12,13]. One approach was to create a chemical bond between the metal framework and acrylic resin by incorporating 5% 4-META (4-methacryloxyethyl trimellitate anhydride), in the monomer of a conventional powder-liquid PMMA/MMA system [13]. 4-META is a monomer whose molecular structure contains both hydrophilic and hydrophobic groups. It occurs in nature as a white crystalline substance with a melting point of 95 to 96°C[13]. It improves the bonding of dental resins to certain metal alloys, thus reducing the problem of microleakage[14]. Silane coating is another chemical mode of retention to enhance the resin/metal bond, in which a silica layer is applied to the surface of the metal, to which silane coupling agents can

attach [10]. Systems available that use silane coating include the Silicoater and Kevloc Systems as well as Rocatec [3,10].

Several studies[3,12,14,15] have shown that the highest bond strengths were recorded between resin and metal alloys with the silane coating technique. Mudford *et al.*[3] stated that, using the silicoating process after sandblasting of the metal surface with 250µm aluminium oxide produced the most durable joint strength.

Many chemical agents have been introduced to produce higher shear bond strengths between acrylic resin and metal frameworks than other adhesives, one of which is GC Metalprimer II [16,17]. GC Metalprimer II contains a metal adhesive monomer, thiophosphoric acid methacrylate and has been reported to produce excellent bonding properties for all types of dental alloys [18].

This study investigated the bond strength between Ti-6Al-4V and heat-polymerized acrylic resin, using a chemical bonding agent (GC Metalprimer II) at the resin/metal interface after 1 of 2 different alloy surface treatments. The different surface treatments chosen were sandblasting with 50µm alumina or surface roughening with a tungsten carbide bur. The effect of water and change of temperature on the bond strength of these systems was investigated by subjecting the specimens to thermal cycling.

MATERIAL AND METHODS

Cylinders 20 mm in length with 12 mm external diameter and 10 mm internal diameter were cut from a hollow acrylic-resin rod using a guided band saw. The ends of the cylinders were smoothed using glasspaper (60 grit) to allow close apposition of the testing surfaces. Eighty titanium alloy discs, 12 mm in diameter and 0.5 mm in thickness were machine punched from flat sheets of titanium alloy. The titanium discs were placed between 2 acrylic resin cylinders to provide a housing for the specimen of acrylic resin to be attached to the surfaces of the titanium alloy discs. A V-shaped block was used to align the cylinders to the discs. A thin layer of wax was applied at the junction of the disc and acrylic resin to keep the housing intact. Silicone putty was used to cover the housing specimens and provide support during investing. This facilitated removal of the titanium discs from the flasks during application of the surface treatment, allowing them to be repositioned prior to packing the acrylic resin dough. Silicone-housing specimen assemblies were positioned in a modified flask. The specimens were invested using dental plaster and boiled out. The acrylic-resin rods and titanium discs were removed from the silicone investment, cleaned with boiling water and detergent to remove all traces of wax.

Two surface treatments were performed on the titanium discs. Forty specimens were sandblasted with 50µm aluminum oxide, at an operating pressure of 5 bar, until a uniform colour was achieved. 40 discs were roughened using a tungsten carbide bur size 040, tungsten carbide bur at a speed of 27,000 rpm in a laboratory handpiece. Minimum pressure was used to produce a uniform appearance. All discs were cleaned of machining debris using compressed air. Surgical gloves were worn to prevent contamination of the discs.

GC Metalprimer II was applied immediately after treating the titanium alloy discs and allowed to dry. No primer was applied to 20 of the titanium alloy discs (10 of each surface treatment) and these specimens served as the control. The titanium alloy discs and the acrylic resin rods were repositioned in the flask. Heat-polymerized acrylic resin was mixed following the manufacturer's instructions and packed. The flask was closed under pressure of 100 kPa and processed using a wet heat procedure. A 5-hour stepped polymerization cycle was used with 3 hours at 70°C, and 2 hours at 95°C (manufacturer's recommended cycle). Eighty specimens were prepared, 40 of which were subject to thermal cycling prior to testing.

The thermal cycling was performed using a water bath at a temperature range of 5°C to 60°C in distilled water, for 744 1-hour cycles over a period of 31 days. Five specimens were removed from the water bath and tested from each group at 4 different stages; 24 hours, 7, 14, and 31 days to investigate the effect of thermal cycling on the bond strength over time. The specimens were tested using a 4-point flexure test, in a universal testing machine at a cross-head speed of 0.5mm/min. The 2 upper test-bearing edges were 8 mm apart and the 2 lower test-bearing edges were 24 mm apart. The load was increased slowly until a sudden decrease in load, indicative of failure in the bond, was observed. Bond strength is determined from the relationship [19].

$$:\sigma = M / W \qquad (1)$$

Where, M is the maximum bending strength, and W is the section modulus of the specimen.

For a circular rod,

$$W = \pi(2R)^3/32 \qquad (2)$$

Where R is the radius of the rod.

For 4-point bending

$$\sigma = F(L-l)/ 2W \qquad (3)$$

Thus, combining equations (2) and (3)

$$\sigma = 2F(L-l)/ \pi R^3 \quad (4)$$

where σ = bond strength (MPa); F = load at failure (N); L = distance between outer supports (mm) and was 24 mm; l = distance between inner supports (mm) and was 8 mm; R = radius of specimens (mm) and was 5 mm.

After testing, specimens were examined under an optical microscope (magnification ×8) and the percentage of acrylic resin retained on the titanium discs was measured using a computerized image analysis system. Failure mode was assessed as adhesive or cohesive.

Surface structure of the airborne particle abraded disks and the discs roughened with carbide bur were observed with a scanning electron microscope (×35, ×100, ×250). Specimens were mounted onto stubs using silver conductive paint sputter-coated with gold to a 15 nm thickness and viewed by scanning electron microscope. A laser profilometer with line scan density of 200 points per mm was used to determine the profile surface of 2 surface treatments.

The loads required to achieve bond failure were analyzed using statistical software. Statistics were performed on the failure loads (2-sample t-test with equal variance). The t-tests were performed on the 2 surface treatment groups

without any thermal cycling, and a 2-way ANOVA was performed on the data from the thermal cycled specimens. This was followed by an analysis of Contrasts and Sidak's method for multiple comparisons.

RESULTS

The control group of 20 specimens with no primer at the metal/resin interface did not bond and came apart during deflasking, so these specimens were not subjected to further testing. Descriptive statistics of failure loads in Newtons and in MPa are given in Table 1. No significant differences were found between the two surface treatment groups without thermal cycling (P=0.512) (Table 2), and the 95% CI for the difference of the means was -89.703 to 173.703.

ANOVA was performed on the results of thermal cycling on bond strength. A difference in the mean values among treatment groups, greater than would be expected by chance was shown (Bartlett's test for equal variances: χ^2=12.928 and p=0.074) (Table 3). However, the 95% CI's showed that where there was a difference, it was minimal. More importantly, there was a rapid reduction in the bond strength within 7 days of thermal cycling (Fig. 1).

SEM images of Ti alloy discs treated with either of the surface treatments (Fig. 2) showed irregularities created

Table 1. *Descriptive statistics of failure load in Newtons*

Column	*N*	*Mean*	*Std Dev*	*Range*	*Median*
G1 No TC	10	361 (29.4)	147	430	340
G2 No TC	10	319 (26.2)	133	420	245
G1 1day TC	5	342 (28)	113	290	310
G2 1day TC	5	332 (27.2)	155	380	320
G1 7daysTC	5	294 (24)	112	290	280
G2 7daysTC	5	262 (21.4)	47	130	270
G1 14daysTC	5	248 (20.2)	37	100	250
G2 14daysTC	5	188 (15.4)	63	140	170
G1 31daysTC	5	174 (14.2)	49	120	160
G2 31daysTC	5	143 (11.6)	67	170	145

G1= Bur treatment group
G2 =Airborne-particle abrasion treatment group
TC= Thermal Cycling

Table 2. *Two-sample t-test with equal variances for two surface treatment groups without thermal cycling*

	N	*Mean*	*Std. Err.*	*Std. Dev.*	*[95% Conf. Interval]*	
G1 No TC	10	361	46.48548	147	255.8425	466.1575
G2 No TC	10	319	42.05829	133	223.8575	414.1425
combined	20	340	30.88612	138.1269	275.3546	404.6454
diff		42	62.68812		-89.70285	173.7028

diff = mean(x) - mean(y) t = 0.6700
Ho: diff = 0 degrees of freedom = 18

Ha: diff < 0 Ha: diff != 0 Ha: diff > 0
Pr(T < t) = 0.7443 Pr(T > t) = 0.5114 Pr(T > t) = 0.2557

. sampsi 361 319, n(10) sd1(147) sd2(133

Estimated power for two-sample comparison of means

Test Ho: m1 = m2, where m1 is the mean in population 1
and m2 is the mean in population 2

Assumptions:
alpha = 0.0500 (two-sided)
m1 = 361
m2 = 319
sd1 = 147
sd2 = 133
sample size n1 = 10
n2 = 10
n2/n1 = 1.00

Estimated power:
power = 0.1028

NB. There is no significant effect of treatment (although the power is low)

Table 3. *Contrasts and Sidak's method for multiple comparisons*

Source	*SS*	*df*	*MS*	*F*	*Prob > F*
Between groups	202449.375	7	28921.3393	3.63	0.0054
Within groups	254808	32	7962.75		
Total	457257.375	39	11724.5481		

Bartlett's test for equal variances: $\chi 2 = 12.9279$ $p(\chi 2) = 0.074$

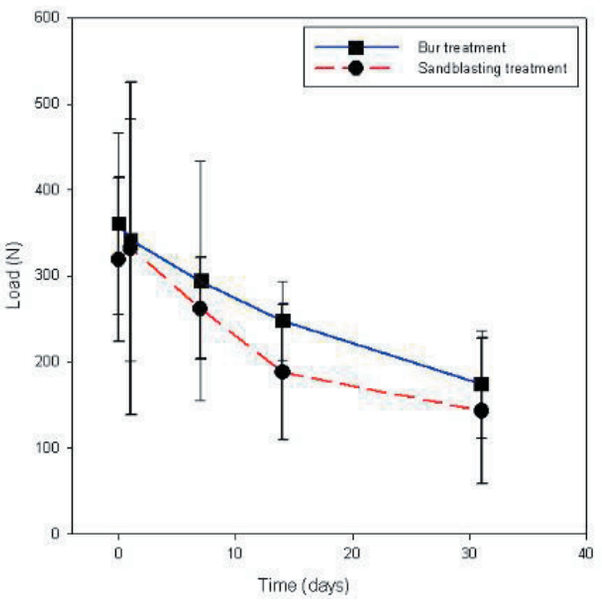


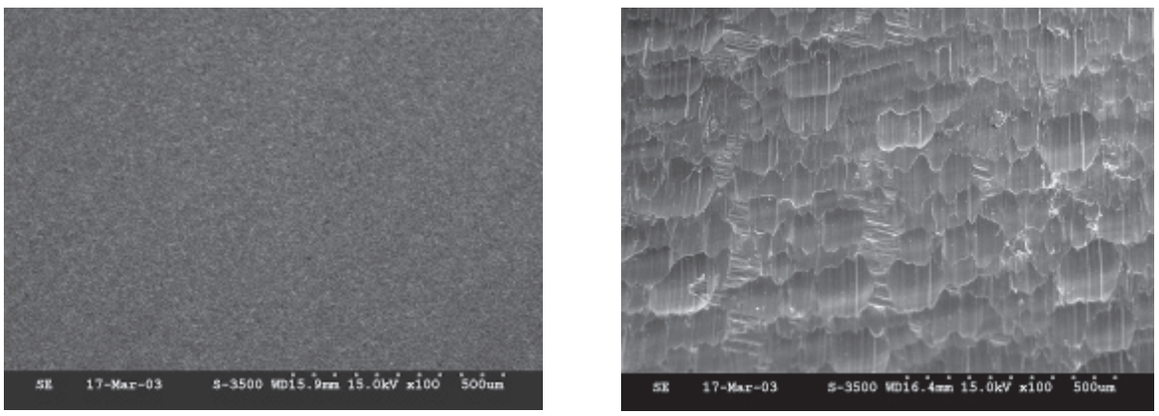
Figure. 1. *Mean and 95% confidence interval for bond-failure load of acrylic to Ti-6Al-4V prepared by 2 different methods.*

on the surface. Scanning the prepared discs for surface roughness using a laser profilometer showed that treating Ti alloy discs with a tungsten carbide bur created twice the mean surface-roughness (R_a=18µm) compared with airborne-particle abrasion (R_a=9µm). A cohesive mode of bond failure in the PMMA was predominantly detected in SEM images of tested specimens, as there was retained acrylic resin on the Ti alloy discs (Fig. 3). The surface area of the Ti alloy disc covered by acrylic resin after testing was determined with the previously described imaging system attached to an optical microscope. The amount of acrylic resin retained on the Ti alloy discs decreased as the number of thermal cycles increased. The retained acrylic covered a maximum area of approximately 30% at day one dropping to approximately 15% at day 31.

DISCUSSION

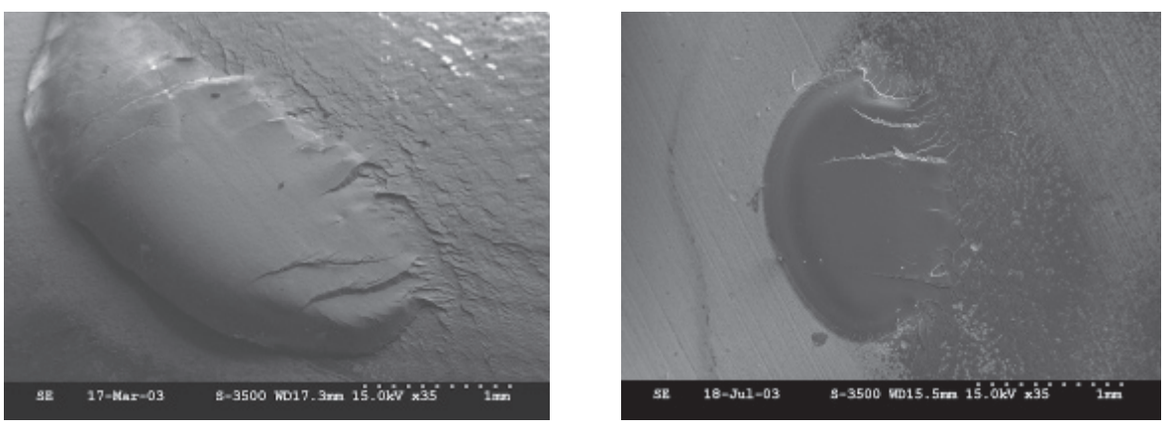
Within the limitations of this study, the null hypothesis that bond strength would not be enhanced with a chemical bonding agent or a rougher surface was rejected. The Ti-6Al-4V alloy is characterized by its high corrosion resistance and reduced allergenic potential when compared to other base metal alloys [5]. When the Ti-6Al-4V discs bonded to acrylic resin with metal adhesive using 2 different metal surface treatments were subjected to flexure load until failure occurred, bond strengths up to 48 MPa were recorded. Previous studies have reported that Metalprimer II showed superior bonding to metals compared to other adhesive primers [4,16,17]. This study showed that the use of Metalprimer II was effective in achieving a bond between acrylic resin and Ti alloy compared to the control specimens which demonstrated a lack of bonding. The relatively high values of standard deviations for the failure loads are likely to be attributed to several factors, including difficulties in aligning the load-train of the testing apparatus and variations in surface treatment from specimen to specimen prior to application of the bonding agent. Furthermore, local variations in polymerization of the acrylic at the interface could also contribute to the large scatter in the standard deviation.

Taira *et al.*[4] tested the shear bond strength of 3 primers and 4 luting agents, including MPII. These authors reported bond strengths ranging from 35.5 to 45.1 MPa before thermal cycling, and values varied from 13.8 to 50.7 MPa after 100,000 thermal cycles. The difference in bond strength achieved in the current study and previous studies could be related to the method of producing specimens, differences in equipment and other factors during testing such as the alignment of specimens in the universal machine (4 point flexure). Previous studies have investigated GC Metalprimer II bonding [4,18,22]. MPII molecules are thought to be directly adsorbed to Au, Ag and Cu surfaces and the sulphur-containing functional monomer was reported to be advantageous for coupling noble-metal alloys with polymeric materials [22]. Titanium is a base-metal, the surface of which is covered with a passive oxide layer having hydrophilic groups in the atmospheric environment [5]. The metal primer contains sulphur molecules that form a primarily cohesive adsorption layer on the metal surface, and dimethacrylate species form a direct chemical bond with the metal oxide [22]. Manufacturer's directions for GC Metalprimer II recommend sandblasting the metal surface with aluminium oxide as a pre-treatment. Although the particle size is not specified by the manufacturer, many previous studies investigating the effect of metal adhesives used 50µm alumina [4,11,16]. The rationale is to increase the surface area and the wetability of the metal surface. The current SEM investigation showed a number of alumina particles attached to the metal surface after sandblasting (Fig. 2A), which possibly affected the bond strength. In this study, an alternative surface treatment was investigated which was considered to be more practical, as it does not require additional expensive equipment and will increase the surface area of the titanium alloy by creating a uniformly roughened surface. The tungsten carbide bur treatment created surfaces with a higher R_a than by sandblasting. While this treatment appeared to result in higher bond strengths (mean failure load = 361 N) compared with



A B

Figure 2A. *Ti-6Al-4V disc treated with airborne-particle abrasion at ×100 magnification, field width 1.27 mm.*
Figure 2B. *Ti-6Al-4V disc treated with tungsten-carbide bur at ×100 magnification, field width 1.27 mm.*



A B

Both images show acrylic resin retained on Ti discs after testing and fracture occurred in acrylic resin (cohesive failure).

Figure 3A. *Tested specimens in bur treatment group before thermal cycling showing Ti-6Al-4V disc part of specimen at ×35 magnification, field width 3.75 mm.*
Figure 3B. *Tested specimens in airborne-particle abrasion treatment group after 31 days thermal cycling showing titanium alloy portion of specimen at ×35 magnification, field width 3.75 mm.*

the sandblasted group (mean failure load = 319 N), there was no significant difference.

Thermal cycling by temperature controlled water-bath subjected the specimens to a combination of factors in an attempt to simulate changes in conditions that would be found clinically. This can only be used as a guide as in the clinical situation saliva would be substituted for water and the temperature range would also include low temperature conditions. Matsumara *et al.*[22] stated that thermal cycling in water (accelerated water aging) is a useful method to observe how bond strength of the specimens is decreased within a short time period. In this study, the specimens were maintained in water throughout the thermal cycling procedure and this was deemed to be a greater challenge for the bonding of the interfaces, rather than an attempt to simulate the clinical situation.

There was a significant and rapid reduction in bond strength on the specimens subjected to thermal cycling. This was associated with the stress induced at the interface by the different coefficients of thermal expansion between acrylic resin and Ti alloy. These results were different from those obtained by Ohkubo *et al.*[16] who showed that the bond strength of MPII did not significantly decrease after thermal cycling. Any decrease in bond strength was most likely associated with the stresses induced at the interface by the difference in coefficient of thermal expansion between acrylic resin ($81x10^{-6}$/°C), and Ti-6Al-4V ($8x10^{-6}$/°C) [3]. It follows that the greater time in water as used in this study, could have contributed to the greater reduction in bond strength observed, compared to data of Ohkubo *et al.*[16].

Specimens viewed with an optical microscope and a SEM showed a mixed mode of failure, with cohesive failure being predominant. The specimens that were not subjected to thermal cycling underwent cohesive failure. Fracture occurred in the acrylic resin, leaving most of the Ti alloy disc covered by acrylic resin (Fig. 3A, B). After 31 days thermal cycling, a mixed mode of failure was observed, cohesive and adhesive, as there was less acrylic retained on the Ti alloy disc (Fig. 3B). This concurs with the previous study by Ohkubo *et al.*[16], who observed mixed failure within the denture-base resin in specimens primed with Opaque Primer and Metal Primer materials. Further stud-

ies are needed to investigate the effect of roughening the base metal surface with carbide burs as pre-treatment for other metals and other metal adhesive primers. This study was limited by the use of just 2 surface treatments and one commercially available adhesive metal primer.

CONCLUSIONS

Within the limitations of this study, the following conclusions were drawn:

1. There was no significant difference between airborne-particle abrasion of Ti-6Al-4V discs with 50µm alumina, and roughening the surface with a tungsten carbide bur as pre-treatments for application of Metalprimer II.
2. There was a significant decrease in bond strength of heat polymerized acrylic resin to titanium alloy within 7 days in the specimens subjected to thermal cycling (P=.074).
3. Cohesive failure resulted when Metalprimer II was used.

MANUFACTURERS' DETAILS

- Silane coating Silicoater and Kevloc Systems (Heraeus Kulzer GMBh, Hanau, Germany).
- Rocatec (3M ESPE Dental Products, Loughborough, UK).
- GC Metalprimer II (GC Europe N.V., Leuven, Belgium).
- Acrylic-resin rod (ICI Chemical and Polymers Ltd, Middlesborough, UK).
- Titanium alloy (Ti-6Al-4V; Grade 5, Timet UK Ltd, Birmingham, UK).
- Silicone putty (Zetalabor, Zhermack, Rovigo, Italy).
- Flask (Teledyne Hanau, Buffalo, NY USA).
- Tungsten carbide bur (Gebr. Brassler GmbH and Co. KG, Lemgo, Germany).
- Heat cured acrylic resin (Trevalon, De Trey, Dentsply UK Ltd, Weymouth UK).
- Water bath (Julabo MH/F10 Jencons Scientific Ltd., Leighton Buzzard, UK).
- Universal testing machine (Model 1193 Instron: Instron Corp, Canton, Mass. USA).
- Optical microscope, Emz-2 Stereo Zoom Microscope Meiji Techno Ltd, Tokyo, Japan).
- Image analysis system (Global Lab Image Version 3, Data Transformation Ltd, Basingstoke, UK).
- Silver conductive paint (Agar Scientific Ltd, Stanstead, UK).
- Sputter-coater (Emscope SC 5000 sputter coater, Emitech, Ashford, UK).
- SEM Hitachi S-3500N Scanning Electron Microscope, (S3500 SEM, Hitachi High-Technologies Corp Wokingham, UK).
- Laser profilometer (Realscan USB, Model No.100, Serial No. 1113, 3D Digital Corp, Bedford Hills, NY, USA).
- Statistical software (Stata Release 9.2, StataCorp LP, Texas, USA).

ADDRESS FOR CORRESPONDENCE

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