

LASER SURFACE PREPARATION FOR ADHESIVE BONDING OF Ti-6Al-4V

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ABSTRACT

Adhesively bonded structures are potentially lighter in weight than mechanically fastened ones, but existing surface treatments are often considered unreliable. Two main problems in achieving reproducible and durable adhesive bonds are surface contamination and variability in standard surface preparation techniques. In this work three surface pretreatments were compared: laser etching with and without grit blasting and conventional Pasa-Jell[®] treatment. Ti-6Al-4V surfaces were characterized by contact angle goniometry, optical microscopy, and X-ray photoelectron spectroscopy (XPS). Laser-etching was found to produce clean surfaces with precisely controlled surface topographies and PETI-5 lap shear strengths and durabilities were equivalent to those produced with Pasa-Jell[®].

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1. INTRODUCTION

As the aerospace industry moves towards using more lightweight composite materials in aircraft structures, traditional methods of securing those structures – e.g. mechanical fasteners such as rivets and bolts – are becoming less desirable. Increasingly, composite materials will have to be bonded to metallic components and reliable methods to prepare both surfaces for bonding are needed. Typically the foremost reasons for bond compromise are surface contamination and preparation,^{1,2} while longer term effects on metal to composite bonds are generally due to corrosion caused by interfacial moisture ingress. To overcome these shortcomings the identification of novel surface preparation techniques for adhesive bonding is of significant interest.

State-of-the-art surface treatment techniques for adhesive bonding typically involve modification of surface chemistries and topographies in a low-fidelity fashion. (i.e., there can be dissimilarities across surfaces because of different operators, operator error, or other inconsistencies inherent with these techniques).³ Furthermore, standard surface treatment techniques can impact the treated surface in unintentional ways. It is generally accepted that increased surface roughness results in more durable bonds,⁴ which has been verified for grit-blasted steel and aluminum substrates.⁵ Recently, however, the size and chemical composition of the grit-blast media as well as the method of treatment were found to play a role in the surface properties of the treated substrate.^{6,7} These results suggest that specific interactions between the chemical functionalities on the grit-blast media and the impacted surface alter not only the topography, but also the surface energy of the material. Methods to deliberately impart changes

in the surface chemistry of substrates typically involve chemical or plasma surface treatment.⁸ For titanium alloys, these treatments provide a fresh titanium oxide layer. Pasa-Jell[®] or sol-gel processes used for this purpose are time consuming, highly variable, and use hazardous chemicals.⁹ It has been shown that techniques involving both chemical and topographical modification can reproducibly generate more reliable surfaces for adhesive bonding.^{10,11}

Laser irradiation provides an alternative to the usual low-fidelity techniques. In most reported applications, a laser is used to remove residual organics or other debris from a surface prior to bonding (i.e., the surface topography is not altered).¹² However, in some instances the surface energy has been unintentionally altered, as indicated by changes in the contact angle a solvent makes with the treated surface.¹³ Where surface topography has been altered for adhesion promotion, differences in ablation thresholds and rates were used to generate topographies.¹⁴⁻¹⁷ These techniques are fundamentally different than the laser ablation technique reported here, which specifically imparts well-defined patterning.

Titanium alloy (Ti-6Al-4V) substrates were laser-etched using a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser, which appears to be a promising way to both clean the surface prior to bonding as well as afford a very precise bond-promoting patterned surface without the inherent drawbacks from standard surface preparation methods (i.e., debris).

2. EXPERIMENTAL

2.1 Materials and Methods

Titanium alloy (Ti-6Al-4V, an alloy consisting of 90% titanium, 6% aluminum and 4% vanadium, 1.6 mm [0.063"] thick) was purchased from California Metal & Supply, Inc. and supplied in the configuration shown in Figure 1. This configuration, which is a slight modification of specimens called for in ASTM D1002-05, allowed for the use of existing bonding apparatus. Phenylethynyl terminated imide (PETI) high temperature adhesive PETI-5¹⁸ was chosen for this work to complement another study, which is also being presented at this conference.¹⁹ Optical micrographs were taken with an Olympus BH-2 optical microscope equipped with a Hitachi KP-D50 digital color camera. XPS spectra were collected on a ThermoFisher ESCAlab 250 X-ray photoelectron spectrometer.

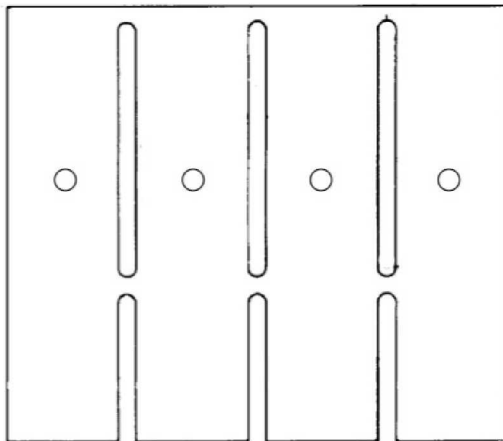


Figure 1. Modified adherend geometry.

2.2 Synthesis of PETI-5 Adhesive

A solution of PETI-5 in *N*-methylpyrrolidinone (NMP) was prepared at 2500 g/mol as shown in Figure 2. Using minimal NMP, 3,4'-oxydianiline (3,4'-ODA, 0.85 eq.) and 1,3-bis(3-aminophenoxy)benzene (APB, 0.15 eq.) were added to a dried 3-neck round bottomed flask fitted with a mechanical stirrer. Once the diamines were dissolved, the flask was immersed in an ice-water bath. To this was added a slurry of 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA, 0.91 eq.) and 4-phenylethynyl phthalic anhydride (PEPA, 0.18 eq.) in NMP. The content was adjusted to 30 wt. % solids with additional NMP. The reaction mixture was warmed to ambient conditions and stirred overnight under nitrogen. The PETI-5 amide acid solution was refrigerated until used.

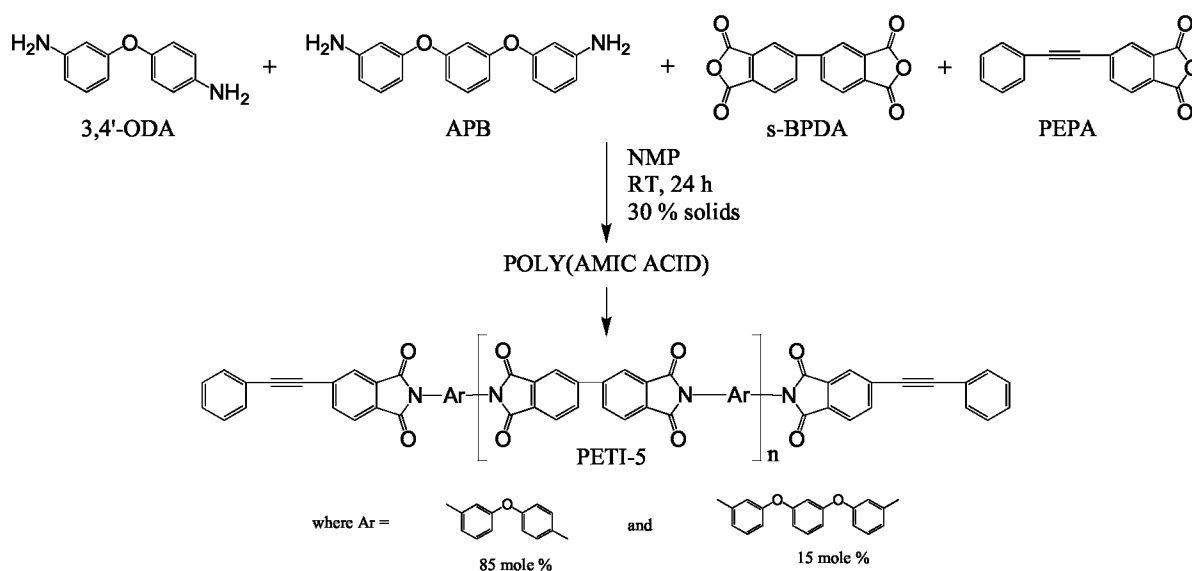


Figure 2. Synthesis of PETI-5 adhesive

2.3 Synthesis of Phenylethynyl Imide Silane Coupling Agents

PETI oligomers were modified using 1-amino-4-trimethoxysilylbenzene (TMSB)²⁰ as the end-cap and 3,5-diamino-4'-phenylethynylbenzophenone (DPBP) as the crosslinker according to Figure 3. Four solutions of phenylethynyl imide silane coupling agents were prepared. The first three had a fixed molecular weight of 2500 g/mol with 15, 25, and 50 mol % DPBP content. The fourth oligomer was prepared at 5000 g/mol with 25 % DPBP. A general procedure follows. Using minimal NMP, 3,4'-ODA, DPBP, and 1-amino-4-trimethoxysilylbenzene (TMSB) were added to a dried 3-neck round bottomed flask fitted with a mechanical stirrer. Once the amines dissolved, the flask was immersed in an ice-water bath. To this was added a slurry of s-BPDA in NMP. The content was adjusted to 35 wt. % solids with additional NMP. The reaction mixture was warmed to ambient conditions and stirred overnight under nitrogen. The resultant alkoxy terminated amide acid was subsequently refrigerated.

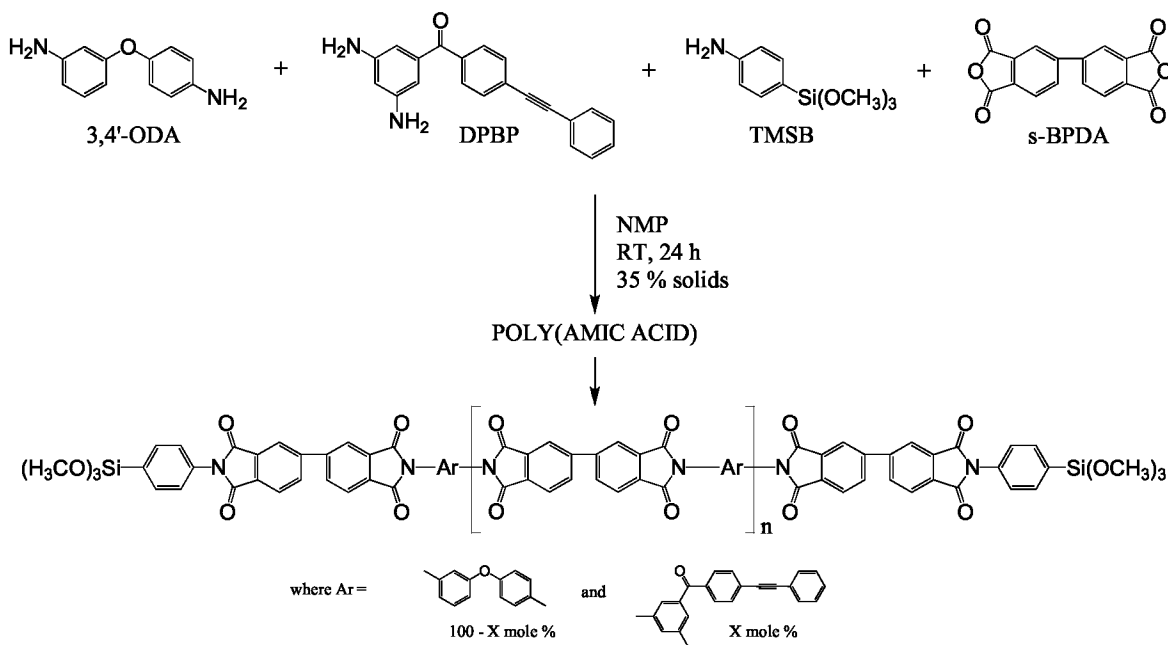


Figure 3. Synthesis of phenylethynyl imide silane coupling agents

2.4 Preparation of Adhesive Tape

PETI-5 adhesive tape was made for subsequent use in the preparation of bonded specimens. An E-glass scrim cloth (style 112, A-1100 finish, 2-ply twisted yarn in a 0°/90° plain weave, 0.09 mm thick) was stretched onto a 15" x 15" frame. The cloth was impregnated with adhesive by applying PETI-5 [poly(amic acid) solution in NMP] with a paintbrush. Application and drying procedures were optimized to afford adhesive tape with minimal bubbles and irregularities (visual inspection). The first few coats were applied at 2 wt. % with subsequent coats applied from a ~15 wt. % solution and the final few coats applied from a 30 wt. % solution. Multiple coats (approximately 15 to 25 depending on the procedure) were required to obtain the desired tape thickness of 0.15 mm (~6 mil). Adhesive tape was dried to a final temperature of 250 °C to reduce the volatile content of the tape to less than 2.5 %. Imidization of the PETI-5 amide acid is thought to occur partially during the adhesive tape preparation and is completed at the elevated temperature sustained in the bonding step.

2.5 Laser Etching

Laser etching of Ti-6Al-4V coupons was done using a PhotoMachining, Inc. laser ablation system with a Coherent Avia® frequency tripled Nd:YAG laser (7-watt output at 355 nm). Single lap shear specimens were laser-etched with a 0°/90° crosshatch only on the lap joint section according to Figure 4. Additional specimens were grit-blasted prior to laser etching. These specimens were prepared to generate surface topographies on different length scales – further increasing the surface roughness and available surface area for adhesive interactions. The following laser parameters could be adjusted: power, frequency, beam width, line spacing, scan speed, and number of passes. After determining laser parameters necessary to overcome the ablation threshold of the Ti-6Al-4V substrate, the following parameters were selected for this

work: 6.3 W laser power, frequency at 30 kHz, beam width was kept at the maximum resolution of the laser (25 μm [1 mil]), scan speed and number of passes were maintained at 25.4 cm/sec (10 in/sec) and 1, respectively, while line spacing was varied.

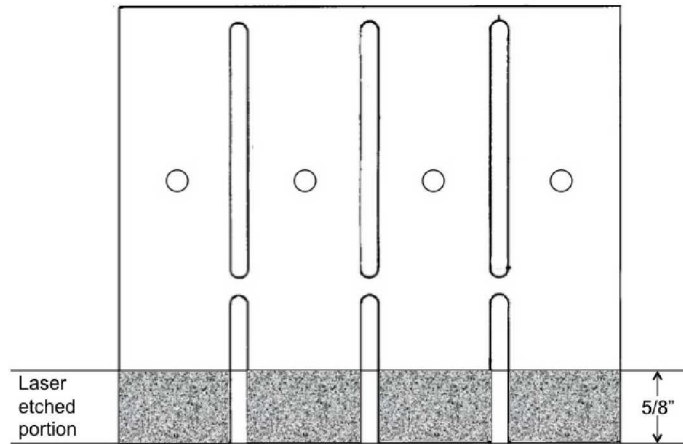


Figure 4. Adherend geometry indicating laser-etched portion.

2.6 Application of Coupling Agent and Bonding

After being laser-etched, Ti-6Al-4V coupons were primed with dilute (~3 wt. %) coupling agent solutions and then dried at 100, 150 and 225 $^{\circ}\text{C}$ with 1 h holds at each temperature. Imidization of the coupling agent amide acid was thought to be completed during the three step heating cycle. Other Ti-6Al-4V coupons were grit-blasted, treated with Pasa-Jell[®] 107-M[™] and subsequently treated with dilute coupling agent and thermally treated as above. Standard lap shear adhesive specimens (bond area was 2.54 cm wide with 1.27 cm overlap) were bonded in a Carver Press for 1 h at 371 $^{\circ}\text{C}$ and ~0.34 MPa. Bonding configurations were shimmed to maintain a 0.15 mm (6 mil) bondline thickness.

2.7 Contact Angle Goniometry

Contact angle goniometry was performed using a FTA 1000B system (First Ten Angstroms). Sessile drop contact angles were measured for each sample using 3 μL drops of water, 3 μL drops of ethylene glycol, or 2 μL drops of diiodomethane. Interfacial tension of a suspended drop of each liquid was measured prior to analysis to verify the purity of the liquid and precision of the focused image. Contact angles were determined by drop shape analysis and standard deviations were calculated by comparison of the contact angles observed for each frame of a 40 frame movie collected after drop deposition on the sample surface. Each sample was measured twice.

2.8 Mechanical Testing

Single lap shear specimens were tested according to ASTM D1002-05 using an MTI-Phoenix Universal Test Stand with an Instron 2511-303 Reversible Load Cell [44.5 kN (10,000 lb) limit]

and tension pin fixtures. This test was used as a measure of joint bond quality and to determine comparative shear strengths of joints made with a singular adhesive but different surface preparation techniques (minimum of four specimens per set of conditions). Prior to mechanical testing, additional lap shear specimens were subjected to a 72 h water boil according to ASTM D1151-00. Specimens were tested at room temperature both as prepared and after a 72 h water boil. Apparent shear strength values corresponding to water boiled samples were compared to the same for neat samples. Failure modes were determined by visual inspection of the post-tested lap shear specimens.

3. RESULTS AND DISCUSSION

3.1 Laser Etching

Surface preparation via laser etching resulted in highly reproducible and precise topographical modification of the Ti-6Al-4V surface, as shown in Figure 5. Patterns with closer line spacings affected a greater fraction of the total surface area. Crosshatch patterns with 1, 2, and 4 mil line spacing yielded essentially similar contact angles so only the 4 mil crosshatch was considered for further use since such a pattern would use fewer resources while providing similar results.

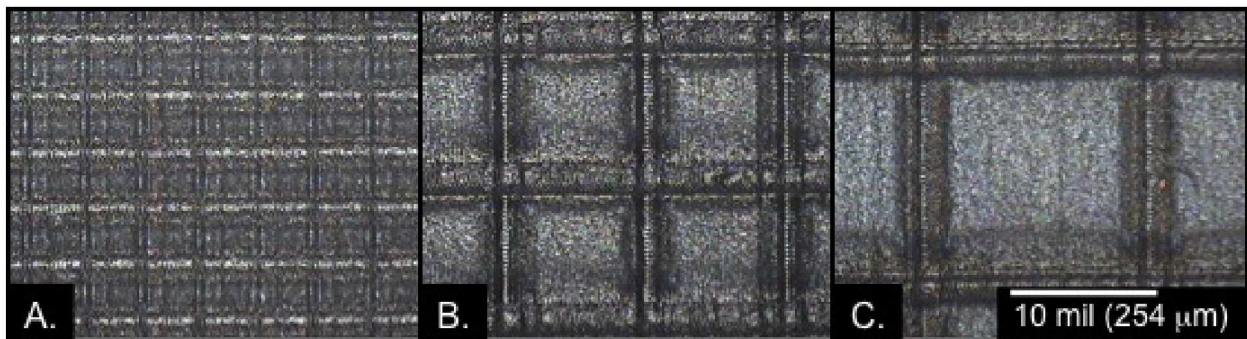


Figure 5. Laser-etched Ti-6Al-4V surfaces: A. 4 mil, B. 10 mil, and C. 16 mil crosshatches.

As shown in Figure 6, the Ti-6Al-4V surface that was grit-blasted before being laser-etched had considerably greater surface roughness and irregular topographies in addition to the highly precise and regular topographies provided by laser ablation.

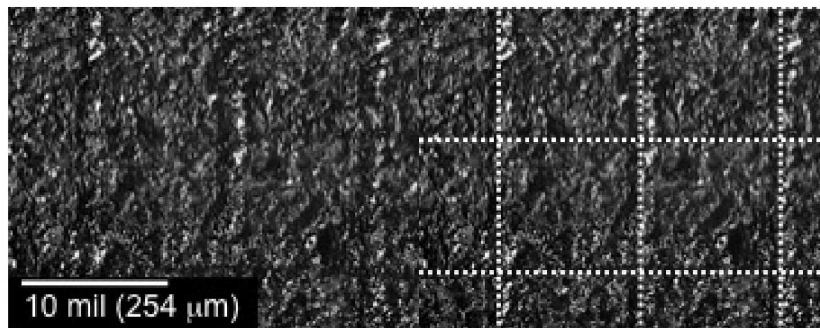


Figure 6. Grit-blasted and laser-etched Ti-6Al-4V surface (dashed lines included to aid in pattern visualization).

3.2 Contact Angle Analysis

Ti-6Al-4V coupons that were laser-etched showed higher surface energies when compared to pristine Ti-6Al-4V surfaces (see Table 1). Although the interactions between solvents and treated surfaces are often used as a predictive tool for determination of adhesive interactions, contact angle data could not be used here as a discriminator for selection of laser etching parameters. The variance among surface energies determined on laser-etched surfaces was not significant enough to identify optimal conditions. One point of significance, however, is that the Ti-6Al-4V substrate laser-etched with 16 mil line spacing did exhibit a measurable ethylene glycol contact angle. This is likely the result of the large surface area that was unmodified during laser etching with these pattern dimensions.

Table 1. Contact angles for various surface treatments on Ti-6Al-4V substrates. [Angles reported as $<5^\circ$ were essentially unmeasurable, almost immediately wetting the surface.]

Surface Preparation Method	Solvent			Surface Energy (mJ m^{-2})
	Water (within 1 day)	Methylene Iodide (within 4 days)	Ethylene Glycol (within 5 days)	
None	74	56	55	33.8
Grit-blasted	91	<5	11	54.0
Laser-etched, 4 mil	<5	<5	<5	54.4
Laser-etched, 10 mil	9	<5	<5	54.0
Laser-etched, 16 mil	8	<5	9	54.9
Grit-blasted, laser-etched	<5	<5	<5	54.4

3.3 XPS Analysis

XPS spectral data were collected on laser-etched Ti-6Al-4V and Ti-6Al-4V that was grit-blasted and treated with Pasa-Jell[®]. The relative atomic percentages of carbon and oxygen varied depending upon the surface treatment (Figure 7). The titanium surface concentration was not greatly affected. Laser-etched Ti-6Al-4V surfaces demonstrated a much larger carbon surface concentration compared to the Pasa-Jell[®] treated surfaces, 50% and 24%, respectively. Oxygen concentrations also varied, with the Pasa-Jell[®] treated surface having higher oxygen content. Interestingly, these data show that laser etching, when compared to chemical techniques, modifies the Ti-6Al-4V surface chemistry differently. High-resolution XPS data provided even greater insight into the effects surface treatment had on the resultant adherend surface chemistry.

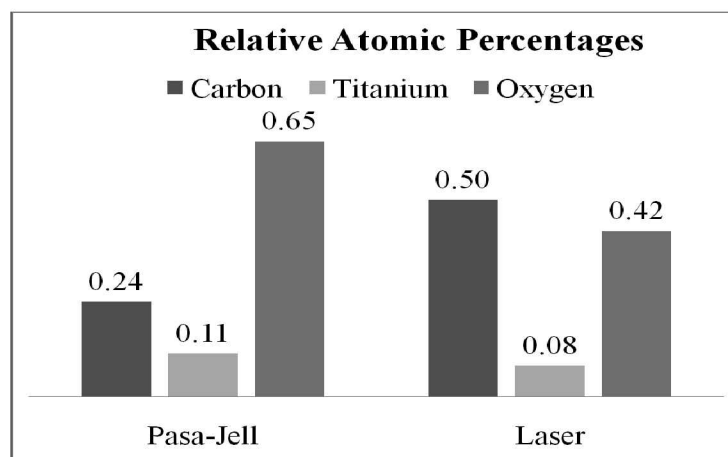


Figure 7. Relative atomic percentages of C, Ti, and O found in Ti-6Al-4V coupons.

The high resolution XPS signals for C, O, and Ti were fitted using a minimalist approach – a minimal number of Gaussian curves were employed to fit the collected data – as an effort to prevent fitting the data to a predetermined surface chemistry (Table 2). Once the data was fitted, the peaks were identified via assignments from previous studies^{21,22} and the online NIST XPS database.²³ For carbon, fits using three peaks with binding energies from 282 to 285 eV accurately reproduced the experimental data for both Pasa-Jell[®] and laser-etched surfaces. The peaks correspond to Ti-C, residual organic material, and C-C bonds. The peak assigned to Ti-C was 266% greater for the laser-etched surface compared to the Pasa-Jell[®] treated adherend. Exposure to laser irradiation could have provided enough energy (both electronic and thermal) to overcome activation barriers for titanium carbide formation. This added energy was necessarily absent in the Pasa-Jell[®] treatment. In fact, the carbon signal from the Pasa-Jell[®] treated surface exhibited a similar line-shape to data collected on an untreated Ti-6Al-4V surface (data not shown). It may be that chemical treatment removed the residual organic layer temporarily whereas exposure to laser irradiation changed the surface chemistry in a more permanent fashion, perhaps preventing the re-accumulation of an organic over layer.

The oxygen data also indicated that the surface chemical composition was dramatically different as a result of surface treatment. The Pasa-Jell[®] treated surface required fitting with four Gaussian peaks while the laser-etched surface required only three. Thus different oxygen-containing surface chemical functionalities result from chemical exposure. For the three peaks present in both spectra, the relative percentages again differed depending upon surface treatment. Interpretation of the Pasa-Jell[®] treated spectrum is difficult due to the possible introduction of contaminants from both the chemical treatment and the grit-blast media. The oxygen spectrum collected for the laser-etched surface had a distinctly different line-shape compared to an untreated Ti-6Al-4V surface, which indicated that, in agreement with the carbon spectrum, the surface chemistry was significantly altered. The relative percentage of the oxygen signal assigned to a sub-oxide of titanium (Ti_2O_3 and TiO , 530 eV) was 195% greater for the laser-etched surface compared to the Pasa-Jell[®] treated adherend. This sub-oxide has been shown to be important for promoting highly favorable adhesive interactions between the titanium adherend and the adhesive material.²⁴

The final piece of evidence from XPS experiments indicating dramatic differences in surface chemistry was found in the high resolution titanium spectrum. First, there was a signal that can be attributed to Ti-C bonds (453 eV) observed for the laser-etched adherend. This signal was not observed on the Pasa-Jell[®] treated surface. This correlated well with the analysis of the carbon XPS spectrum described previously. The presence of both TiO₂ and sub-oxides of TiO₂ were detected on both surfaces. For TiO₂, peaks were observed at 457 eV (2p_{3/2}) and 464 eV (2p_{1/2}), while the sub-oxide peaks were observed at 456 eV (2p_{3/2}) and 462 eV (2p_{1/2}). As indicated above, the presence of the sub-oxide has been considered significant for promotion of adhesive interactions compared to TiO₂; therefore, calculation of the relative concentrations of these two titanium species may be of utility for discussion of adhesion promotion due to surface treatment technique. For the Pasa-Jell[®] treated surface, it was determined that the sub-oxide surface concentration was 39%, while the laser-etched surface was calculated to have a sub-oxide surface concentration of 44%.

Table 2. Deconvolution results for high-resolution XPS spectra.

Sample	Binding Energy, eV (Relative Percentages)			
	C 1s	O 1s	Ti 2p _{3/2}	Ti 2p _{1/2}
Grit-blasted, Pasa-Jell [®]	282 (9%)	528 (39%)	456 (22%)	462 (15%)
	283 (85%)	529 (21%)	457 (46%)	464 (13%)
	285 (2%)	530 (22%) 531 (17%)		
Laser-etched (10 mil crosshatch)	282 (24%)	528 (8%)	453 (1%)	462 (19%)
	283 (54%)	529 (49%)	456 (23%)	464 (11%)
	285 (14%)	530 (43%)	457 (41%)	

3.4 Mechanical Testing Data

Apparent shear strength data, bondline thicknesses, and failure modes for single lap shear specimens of Ti-6Al-4V with various surface treatments are summarized in Table 3. Strength values and failure modes corresponding to three surface treatments (first, second, and fifth table entries) were similar and considered to be good, while the other two surface treatments were similar but poor in both strength and failure mode. Samples with high apparent shear strength had a mixed failure mode, mainly cohesive, while those with low values exhibited adhesive failure. There were no apparent trends due to variation of the coupling agent formulation (data not shown for clarity). Surface treatment methods that afforded high shear strengths at room temperature (first, second, and fifth entries from Table 3) were reproduced on additional specimens for the 72 h water boil exposure and subsequently mechanically tested (see Table 4). In all three cases, retention of strength was identical within experimental uncertainty, roughly 75 %, and failure modes were again similar.

Table 3. Averaged data for Ti-6Al-4V coupons bonded after different surface treatments.

Surface Treatment	Bondline Thickness, μm (mil)	Apparent Shear Strength, MPa (psi)	Failure Mode
Grit-blasted, Pasa-Jell [®]	114 (4.5)	29.3 \pm 0.9 (4247 \pm 133)	Mixed
Laser-etched, 4 mil	142 (5.6)	30.2 \pm 1.8 (4386 \pm 265)	Mixed
Laser-etched, 10 mil	130 (5.1)	17.9 \pm 1.8 (2595 \pm 254)	Adhesive
Laser-etched, 16 mil	132 (5.2)	16.1 \pm 1.7 (2339 \pm 257)	Adhesive
Grit-blasted, laser-etched	127 (5.0)	28.9 \pm 1.7 (4188 \pm 253)	Mixed

Table 4. Retention of apparent shear strength after 72 h water boil.

Surface Treatment	Apparent Shear Strength, MPa (psi)	Retention	Failure Mode
Grit-blasted, Pasa-Jell [®]	22.4 \pm 1.3 (3246 \pm 190)	76 %	Mixed
Laser-etched, 4 mil	22.6 \pm 0.8 (3274 \pm 122)	74 %	Mixed
Grit-blasted, laser-etched	22.8 \pm 0.8 (3300 \pm 113)	79 %	Mixed

4. SUMMARY

A Nd:YAG laser was used to etch patterns conducive to adhesive bonding onto Ti-6Al-4V surfaces. After being grit-blasted, laser-etched according to three different pattern sizes, or grit-blasted and subsequently laser-etched, Ti-6Al-4V coupons were subjected to contact angle measurements with multiple solvents. Surface energies were determined to be essentially the same for all surface treatments, which were significantly higher than that for the untreated substrate. XPS analysis of the laser-etched surfaces indicated the formation of Ti-C functionalities and the presence of a greater TiO₂ sub-oxide concentration relative to a Pasa-Jell[®] treated surface. Ti-6Al-4V adherends were bonded after receiving one of several surface treatments involving laser etching, grit blasting, Pasa-Jell[®] treatment and several combinations thereof. Mechanical testing was done according to ASTM D1002-05. Ti-6Al-4V that was grit-blasted and then treated with Pasa-Jell[®], as well as that laser-etched with the 4 mil crosshatch, and that which was grit-blasted and subsequently laser-etched (10 mil crosshatch) all had similar apparent shear strengths both before and after a 72 h water boil. In addition to the reproducibility, high precision, and rapid processing time afforded through the use of laser etching as a surface treatment, laser ablation is also a more “green” procedure compared to Pasa-Jell[®] treatments, which use toxic chemicals.

5. ACKNOWLEDGEMENTS

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