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Pre-bonding technology based on excimer laser surface treatment

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Abstract

The application of ArF excimer laser for surface pre-treatment of polycarbonate, polyetherimide, polyaryl ether–ether–ketone (PEEK) composite, fiberglass, aluminum, copper and fused silica was investigated. Various substrates were tested with excimer laser irradiation using various parameters, such as: intensity, repetition rate, and number of pulses. The optimal laser treatment parameters were found for each material needed for achieving maximum adhesional strength of the corresponding bonded joints. Experimental results indicated that UV laser surface treatment improved significantly the adhesion strength compared to conventional treated substrates for all the materials tested. The improved adhesion was correlated with the roughening of the irradiated surface, chemical modification and removal of contamination. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Application of a proper surface treatment to the adherend is among the decisive factors with respect to the final quality and durability of an adhesive joint. Many treatments have been devised for preparing materials surfaces for adhesive bonding. The general purpose of these procedures is to modify the original surface of the adherend material: (a) to promote development of interfacial bonds with adhesives and (b) to enhance the environmental resistance to moisture and humidity effects. Various materials such as metals, plastics, composites and ceramics require different surface treatments, some examples of which are detailed below.

The present processes for prebond surface preparation of thermoplastics, composite thermoplastics, and ceramic adherends involve the use of abrasive, welding, chemicals and plasma treatments, These are to a certain extent destructive, poorly controlled and introduce undesirable changes in the morphology and composition of the surface such as cracks, uncontrolled pitting and contamination. The prebond surface treatments, which are commonly used for metals such as aluminum, are chromic acid anodization [1] with or without sealing. The treatment for copper is chemical etching or sand blasting. The treatment for thermoplastic polymers and composites is sand blasting or etching with oxidizing acids.

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Surface treatment for metal/ceramic bonds involves alumina blasting or brazing. All these treatments involve the use of ‘‘sand powders’’, acids (sulfuric, nitric, and hydrochloric), strong bases or hexavalent chromium compounds.

New Occupational Safety and Health Administration (OSHA) and Environmental Protection Agency (EPA) regulations ban such chemicals in industrial operations, hence, non-chemical new methods are needed such as UV laser treatments. An outstanding feature of UV laser radiation is its ability to break chemical bonds or cause chemical reactions on the radiated surface due to photochemical effects in addition to a thermal heating effect. Based on these effects, laser irradiation may provide a new method for surface preadhesion treatment for a wide range of materials.

Recently, excimer lasers were used for preadhesion surface treatment of metals [2], thermoplastics [3,4] and ceramics [5,6]. All treatments with those excimer lasers produced desirable effects on the treated surfaces providing a better adhesion to the adherend.

Laser treatment provides a clean and rather simple method of surface preparation and reduces the extent of damage to the treated surfaces. In our present and previous papers, the application of ArF excimer laser (UV range at 193 nm) for surface treatment of thermoplastic [7,11], carbon fiber reinforced, polyaryl ether–ether–ketone (PEEK), composite [8], aluminum [9], sealed anodic aluminum coating [10], copper, invar and fused silica is demonstrated.

2. Experimental

2.1. Laser treatment

The laser in this investigation was an ArF excimer laser model EMG 201 MSC (Lambda Physik, Germany). The laser parameters ranges were: repetition rate 5–30 Hz, energy density 0.9–4 J/pulse cm^2 and variable number of pulses 1–5000. All experiments were conducted at ambient temperature and in air. The samples were irradiated by scanning the surface with the laser beam using an X–Y computerized table for moving the sample.

2.2. Materials

Table 1 lists the adherends and adhesives investigated in this work.

2.3. Testing

The various substrates were treated with an excimer UV laser. The optimal laser treatment for each material was defined while achieving the maximal shear strength of the corresponding bonded joint. Joint properties were determined using the single lap shear (SLS) test according to ASTM D-1002-72 [12]. The surface morphology following the laser treatment and shear fracture was analyzed by means of scanning electron microscopy (SEM) JOEL model JSM-840. Chemical changes were investigated by means of Fourier transform infrared spectroscopy (FTIR) using a Nicolet 5DX spectrophotometer. Surfaces of the laser-treated compared to untreated adherends were studies for chemical changes due to laser irradiation by X-ray photoelectron Spectroscopy (XPS). A model PHI 555 spectrometer was used, with an Al Kα X-ray source, at 10 kV, 40 mA and pressure of 3×10^{-8} Torr.

Two types of reference samples were used for each set of experiments. For the thermoplastics and thermoplastic composites, the reference substrates were untreated and abrasively treated with SiC (36 mesh). For the aluminum and sealed anodized aluminum adherends, the reference samples used were untreated aluminum and unsealed chromic acid anodized aluminum according to MIL-A-8625C [13], respectively. For copper, the references were samples with black conventional treatment formed by alkaline oxidation solution treatment (abonite) or sand blasting, for the glass epoxy fiberglass the reference was a sample with sand blasting and for the invar and alumina the references were samples abraded with aluminum blasting or silane primed.

3. Results and discussion

In Table 1, one can see the optimal laser treatment parameters for each of the materials tested. As can be seen from the results, different conditions are

Table 1
Optimal laser parameters, adhesive strengths[a] and failure modes[b] of the various bonded joints

Adherend/adhesive	Surface treatments		
	Untreated SLS[a] (failure mode)[b] (MPa)	Conventional SLS[a] (failure mode)[b] (MPa)	Laser treated SLS[a] (failure mode)[b] (MPa) Optimal parameters: *intensity* (J/pulse cm^2), **R.R.** (Hz), *pulse no.*
Polycarbonate/PU	3.5(A)[b]	5.0(M) SiC	7.5(C) *0.08*, **10**, *12*
Polyetherimide/PU	2.5(A)	5.0(M) SiC	5.5(C) *0.08*, **10**, *200*
Composite PEEK (APC2/AS4)/	6.1(A)	14.7(M) SiC	27.8(M) *0.19 or 1*, **5**, *100 or 10*
Structural Epoxy FM 3002 K	21.7(A)	34.0(M) SiC	45.4(C) *0.19 or 1*, **5**, *100 or 10*
Structural Epoxy AF 163-2		20.0(M) plasma	
Aluminum alloy/epoxy	2.0(A)	10.2(C) unsealed anodized	14.3(C) *0.19*, **30**, *2000*
Aluminum alloy/structural epoxy	12.8(C)	42.9(C) unsealed anodized	34.4(C) *0.19*, **30**, *2000*
Sealed anodized aluminum/epoxy	4.5(A)	10.2(C) unsealed anodized	11.0(C) *0.8–1.9*, **30**, *100–1000*
Copper/modified epoxy	6.1(A)	14.9(C) sand	14.3(C) *2.7*, **10**, *50*
Fiberglass epoxy/(rubber modified epoxy)/copper	–	31.7(C) sand	25.6(A/M) *0.18*, **30**, *100*; *2.1*, **30**, *50*
Fiberglass epoxy/(acrylic adhesive)/copper	–	8.5(C) sand	15.6(C) *0.18*, **30**, *100*; *2.1*, **30**, *50*
Copper/(acrylic adhesive)/polyimide	Peel tests (lb/in)	21.0(M) sand	25.0(A) *0.18*, **30**, *1000*; *0.18*, **30**, *100*
Invar/fused silica/(RTV)	–	3.6(A) alumina	5.6(C) *2.2*, **30**, *10*

[a] ±5% standard deviation (five samples for each test).
[b] A — interfacial, M — mixed, C — cohesive mode of failure.

required for different adherends tested. Pure polymers which are easy to activate require the least intensity for laser treatment (~ 0.1 J/pulse cm^2), composites which are more inert require higher energy (~ 0.2–1 J/pulse cm^2) and metals and ceramics which have strong chemical bonds require even higher energy (> 2 J/pulse cm^2).

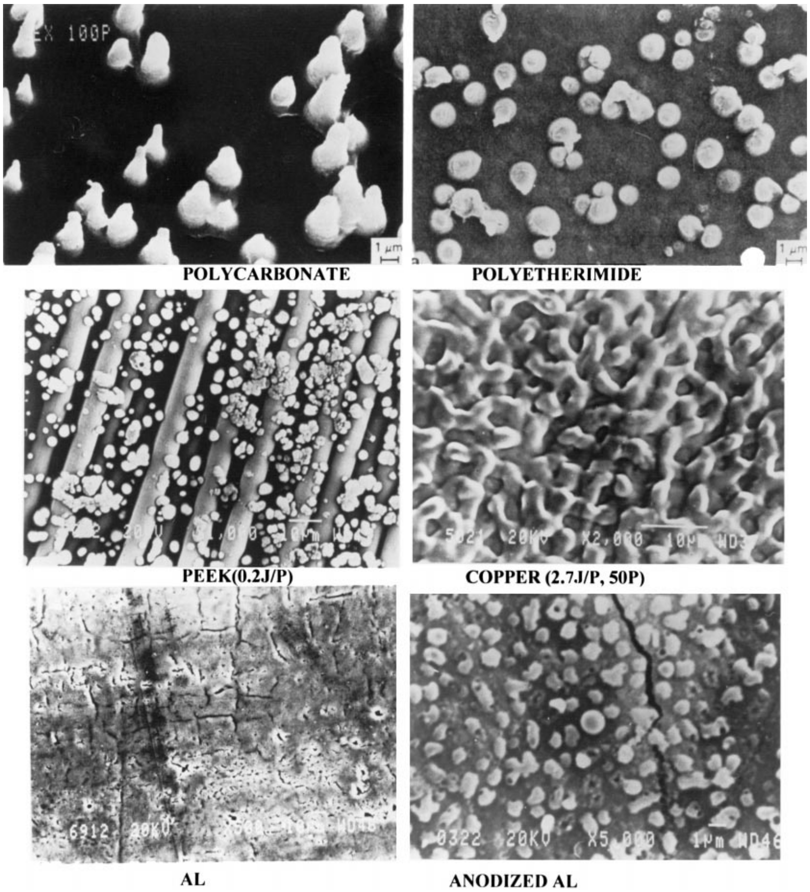
Table 1 gives also the maximal adhesive shear strength achieved for the various bonded adherends when applying these optimal laser parameters. The results indicate that ArF excimer laser treatment is effective for all the different treated and bonded adherends.

We noted that the laser parameters for the surface treatment are more influencial on the nature of the adherend than on the kind of adhesive used for bonding. Improvements in adhesive shear strength by 200–600% were achieved for laser treated adherends compared to non-treated and similar or better as compared to conventional treatments.

Best results were achieved for the thermoplastic composite materials.

Laser treatment causes the mode of failure (Table 1) to change from interfacial in non-laser treated adherend to mainly cohesive at optimal laser operating conditions indicating that the interfacial adhesion was significantly improved.

SEM micrographs of laser treated adherends revealed morphological changes depending on the adherend material, laser energy and number of pulses.



POLYCARBONATE POLYETHERIMIDE

PEEK(0.2J/P) COPPER (2.7J/P, 50P)

AL ANODIZED AL

Fig. 1. SEM micrograph of polycarbonate (a), polyetherimide (b), composite PEEK, (c) copper, (d) Al 2024-T3, (e) sealed anodized aluminum (f) treated with excimer laser.

The thermoplastic adherends surfaces exhibited conic and rounded granules spread all over the surface (Fig. 1a and b). The reinforced PEEK composite exhibited similar granules accompanied by a partial exposure of the carbon fibers (Fig. 1c) at laser intensities of 0.1–0.2 J/pulse cm^2, while at higher laser intensities (above 1 J/pulse cm^2) the laser irradiated surface was smooth with randomly spreading cracks.

SEM micrographs of the Al adherend after laser treatment showed no morphological changes at low laser intensities (0.18–0.2 J/pulse cm^2). Increased laser intensity of 0.7 J/pulse cm^2 reveals a fine microstructure on the treated surface with cracks about 1 μm wide and small holes (Fig. 1e). Irradiation of the sealed anodized species at low laser intensities, 0.2 J/pulse cm^2, showed no change in surface morphology even after 1000 pulses. At 0.7 J/pulse cm^2, changes in the morphology included open bubbles resulting probably from evaporated water. Some spherical droplets of Al_2O_3 due to splashing caused by laser ablation of Al_2O_3 and cracks can be observed also (Fig. 1f). Irradiation of copper at low energy showed only color changes due to oxidation. At higher energies morphological changes were observed showing spheroids spread evenly on the entire surface (Fig. 1d). All these morphologies show the increased roughness of the surface, which enable mechanical interlocking of the adhesive. It should be noted that the roughness is relatively uniform, which presents an advantage over abrasive treatments.

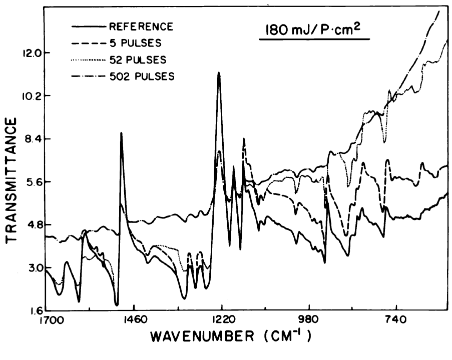


Fig. 2. FTIR spectra of carbon reinforced PEEK before and after laser treatment.

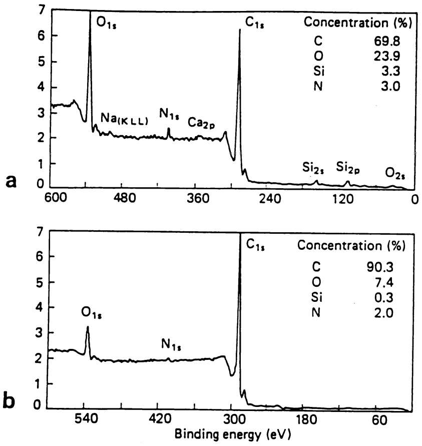


Fig. 3. XPS spectra of polyetherimide before (a) and after (b) laser treatment.

The enhanced adhesion due to mechanical interlocking was revealed by observing the fractured surfaces for all UV laser treated adherends [7–10]. The cohesive mode of failure is indicated by an adhesive layer that can be found on each adherend showing a replica of the granules or bubbles formed during laser treatment.

At high laser intensity or large number of pulses, a weakening of the treated layer of the adherend is observed due to ablation. This can be a loosely connected granule at the thermoplastic surface or the deformed and exposed fibers of the composite.

Table 2
Contact angles of water on untreated and laser treated adherends and comparison to adhesive strengths (SLS)

Adherend	Surface treatment	Contact angle (deg)	SLS (MPa)
APC-2/AS-4	None	34	5.9
	Laser 0.18 J/ pulse cm^2, 100 pulse	110	27.2
	Laser 1 J/ pulse cm^2, 10 pulse	59	27.8
Al-2024	None	90	12.8
	Anodized	[a]	43.0
	Laser 0.18 J/ 2000 pulse cm^2	41	34.0

[a] Anodized species react with water.

Table 3
Lap shear strength of APC-2/AS-4 bonded with FM 300-2K with various surface treatments exposed to heat/wet environment
RH: relative humidity.

Time (days) at 60°C, 95% RH	Lap shear strength (MPa)[a] failure mode[b]		
	No treatment	Abrasive (SiC)	Laser treatment 0.18 J/pulse cm^2 100 pulse
0	6.1 ± 0.8(A)	14.7 ± 1.9(A)	27.2 ± 0.8(M)
10	2.6 ± 0.1(A)	16.6 ± 1.5(M)	38.6 ± 2.2(M)
30	3.9 ± 0.4(A)	13.2 ± 0.6(A)	32.9 ± 6.0(M)
60	4.5 ± 0.2(A)	12.8 ± 1.5(A)	29.2 ± 4.3(M)

[a] ± 5% standard deviation
[b] A — interfacial, M — mixed.

In addition to the pronounced morphological modification, chemical changes also take place following UV laser treatment of the adherends. These changes are based on FTIR and XPS (Figs. 2 and 3). FTIR analysis of the PEEK composite reveals formation of hydroxyls and aldehydic groups from the scissioned carbonate bonds (Fig. 2) [8]. It also reveals crosslinking of the outer surface layer. High laser intensities result in a total peak reduction due to degradation and ablation. Another important advantage of laser treatment is the cleaning of the adherend surface by evaporating the contaminants and the weak boundary layers from the adherend surface. For example, from polyetherimide surface (Fig. 3) Si was removed. In previous published work, FTIR and XPS results show scisson of carbonate bonds of the polycarbonate to form hydroxyls and carboxyls which resulted in an increase in surface polarity of the polycarbonate [7,11]. FTIR analysis of polyetherimide reveals smaller chemical changes, which occur mainly at the amide ring, to form polyamic acid, which improves the surface chemical activity [7,11].

Water contact angles on Al adherends and composite PEEK adherends, following laser treatment, monitoring the wetting properties of the treated surfaces, one given in Table 2. The Al adherend showed a decrease in contact angle and better wetting after laser treatment due to chemical modification of the surface. PEEK composites showed an increase in the contact angle due to increased crosslinking which lowers polarity and increases the hydrophobic character (a positive effect of rejecting humidity from the surface) (Table 2).

Durability tests were also conducted on Al 2024-T4 and on PEEK composites treated with UV laser at 60°C and 95% RH for up to 60 days. An example of durability results is given in Table 3. For both joints, no degradation was observed during this period.

4. Conclusions

The laser UV irradiation as a surface treatment proved to be effective and even better compared to other conventional treatments such as chemical etching, abrasive blasting and plasma treatments. The general phenomena observed due to UV laser treatment were: surface cleaning by removal of contamination and weak boundary layers through evaporation; modification of surface chemistry by imposing polar groups such as oxide derivatives and hydroxides and surface crosslinking as observed by XPS and FTIR spectroscopies; and change of surface morphology by introduction of uniform roughness as observed by SEM.

It can be concluded that all four important considerations effecting adhesion strength were met using UV laser treatment: cleanliness, mechanical interlocking, chemical attraction, and wetting. The potential of using UV laser for pre-adhesion surface treatment was confirmed for a wide variety of substrates, each requiring its optimal laser parameters for successful treatment. The process is effective in air and at room temperature, and is an effective, clean, environmentally friendly, precise, and safe process.

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