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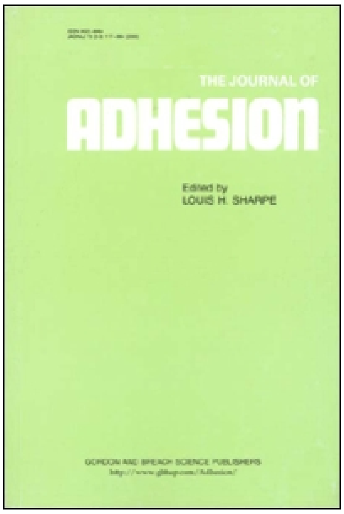

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Preadhesion Laser Surface Treatment of Carbon Fiber Reinforced PEEK Composite*

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An excimer UV laser (193 nm) was used for preadhesion surface treatment of PEEK (polyetheretherketone) composite. This method presented an alternative to other limited and polluting conventional surface treatment methods. Experimental results indicated that laser preadhesion treatment significantly improved the shear and tensile adhesion strength of structural epoxy FM 300 2K bonded PEEK composite adherends compared with untreated and SiC blasted substrates. Best results were obtained with laser energies of 0.18 or 1 J/P·cm.^{2} Shear strength of laser-treated joints was improved by 450% compared with that of untreated PEEK composite and by 200% compared with SiC-blasted pretreatment at ambient and at extreme temperatures. An order of magnitude of improvement was found in the tensile strength-of laser-treated PEEK composite in a sandwich structure compared with non-treated or abraded sandwich joints. The mode of failure changed from adhesive to cohesive as the number of pulses or laser energy increased during treatment. The latter phenomenon was correlated with surface cleaning as revealed by XPS, with morphology changes as revealed by scanning electron microscopy, and by chemical modification as indicated by FTIR and XPS. The bulk of the PEEK composite adherend was not damaged by the laser irradiation during treatment as indicated by the identical flexural strength before and after laser treatment. It can be concluded that the excimer laser has a potential as a precise, clean and simple preadhesion surface treatment for PEEK composite.

KEY WORDS Excimer laser; PEEK composite; surface treatment; FTIR; XPS; adhesion

INTRODUCTION

Fiber-reinforced thermoplastic composite materials are increasingly being considered for a wide variety of applications. Adhesives are often required for joining these materials for structural and other purposes. In order to achieve a strong and durable adhesive bond there is a need to establish an effective surface prebonding treatment and to develop a scientific understanding of the mechanism of surface modification and its effect on adhesion.

Thermoplastic composite materials such as carbon reinforced polyetheretherketone (PEEK) are used for engineering applications where toughness, fatigue, impact and

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* One of a Collection of papers honoring James P. Wightman, who received the 13th Adhesive and Sealant Council Award at the ASC's 1993 Fall Convention in St. Louis, Missouri, USA, in October 1993.

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abrasion resistance and thermal stability[1] are needed. In aerospace manufacture, especially for wing and tail components, in electrical and electronic automotive, bearing, medical,[2] nuclear, and chemical industries this composite is found. In all of these applications adhesive bonding is the preferred method of joining.

Surface energies of thermoplastic aromatic composites tend to be low, causing difficulty in wetting of the surface by an adhesive. Conventional surface treatments such as sand blasting, mechanical abrasion, chemical etching or swelling, as well as fusion or welding joining methods,[3] may cause delamination defects and damage the fibers and the bulk composite. These methods also present occupational health and safety and environmental risks.

Corona and plasma surface treatment do not damage the polymer but require special environments for the action. Thus, as each of these treatments have limitations, an alternative treatment should be provided.

UV lasers may offer an additional surface treatment for polymer composite adherends.[4] Lasers have been used for cleaning polymer surfaces, for microfabricating of polymers by ablation,[5] precise cutting, etc. Most organic materials adsorb UV radiation, creating photochemical reactions such as scissioning, branching and cross-linking on the surface of the polymer only several molecular layers deep (300–500 Å), without damaging the bulk polymer. The effect of laser irradiation on PEEK is especially interesting since PEEK is a model polymer without any aliphatic groups. Interaction of a laser beam with matter gives rise to multiphoton excitation of the polymeric bonds, which is then followed by thermal decomposition resulting in ablation. For ablation to take place there exists a threshold laser energy density beyond which irreversible damage of the sample surface occurs.[6] In the case of PEEK composite, no significant production of gaseous species occurs below 0.1 J/P. At higher fluences, above 0.2 J/P, fragmentation and volatile species were detected. Above 0.4 J/P, a complete conversion of the oxygen in the PEEK polymer to CO occurred, originating from the carbonyl and the ether linkages.

From variation of etch rate with fluence an effective threshold for the composite PEEK was determined which is 0.42 $\mathrm{J/P \cdot cm^2}$. Below this value removal of the matrix in the surface region occurs and over long exposure weak etching of fibers takes place. Once the matrix is removed, the bare fibers are immune to etching at low fluences. Near the threshold for ablation, cone-like structures appear. These structures probably result from the semicrystalline character of the polymer, since the crystallines have different UV absorptions and etch more slowly than the amorphous surrounding material.

Above the ablation threshold the composite fibers are observed to etch smoothly, and the crystallites also ablate with the bulk material and the etched region becomes smooth. Microparticles and debris redeposit onto the surface leaving a dust-like texture. When the ablation threshold was greatly exceeded, fibers were thinned and buckled.

The main effects caused by the laser irradiation, such as surface chemical modification (oxygen depletion), morphological alteration and formation of cone-like structures,[7, 8] were similar to those found in previous investigations on polyetherimide, polycarbonate,[9, 10] aluminium alloy[11] and aluminium oxide.[12] The UV laser etching was, thus, used as a preadhesion surface treatment[13] with the advantages of chemical and morphological modification and cleaning of the polymer surface with minimal fiber damage.

In the present investigation, the application of an excimer UV laser for preadhesion surface treatment of PEEK composite adherend has been studied. The objective of the research was to establish the effect of the excimer laser on the surface structure of the composite and to correlate the microstructure with the macrobehavior, as reflected in shear and tensile loading and failure location of bonded joints and sandwich structures bonded with a structural epoxy adhesive.

EXPERIMENTAL

Adherends and Adhesives

Composite plates 100 × 100 × 1.6 mm were prepared from commercial PEEK reinforced with unidirectional carbon fibers (APC-2/AS-4), a prepreg product of ICI Ltd., USA. The plates were produced from 14 prepreg layers in a unidirectional sequence $(0/0)_s$, laid up and consolidated under pressure of 110 Psi (0.76 MPa) at 385°C. Various degrees of crystallization were achieved by cooling the product at different rates (1, 7 and 33°C/min).

Bonding of treated and nontreated PEEK composite adherends was carried out with a structural epoxy adhesive FM 300 2 K, a product of American Cyanamid, USA. The adhesive was polymerized at 120°C under a pressure of 35 Psi (0.24 MPa) for 1.5 hrs. No primer was used.

Surface Treatment

All samples were wiped clean with acetone before treatment. Two references were used: a non-treated adherend and a SiC (36 mesh) abraded adherend for all the experiments conducted and described. Laser treatment was applied using a UV ArF (193 nm) excimer laser model 201 MSC, a product of Lambda Physik, Germany, with the following parameters: repetition rate of 5 Hz, intensity of 0.18–6.0 J/P·cm^2, number of pulses ranging between 1 to 500 P, and a beam area between 2 × 0.5 cm^2 and 0.3 × 0.1 cm^2 according to the fluence needed. The area of the beam was changed using a focusing lens. All experiments were conducted at ambient temperature and in air environment. The parameters tested are summarized in Table I. The specimens were moved under the beam by means of a controlled X-Y table.

TABLE I
Laser parameters for APC2/AS4 reinforced PEEK composite samples

Laser energy J/P·cm^2	Repetition rate Hz	Pulse No.	Beam area cm^2
0.09	5	10, 52, 100	2 × 0.5
0.18	5	1, 5, 10 53, 106, 502	2 × 0.5
1.00	5	1, 10, 102	0.8 × 0.25
6.00	5	1, 10, 101	0.3 × 0.1

Testing

Optimal laser parameters were chosen using several techniques by which treated and untreated samples were compared:

a. The morphology of the surface after laser treatment was observed using a Scanning Electron Microscope (SEM) model JSM-840, Jeol, Japan.
b. The chemical changes in the surface were studied in an external specular reflection mode using a Fourier Transform Infra Red (FTIR) Nicolet 5DX spectrophotometer equipped with a horizontal stage in a near-to-normal incidence and a gold-coated mirror as a reference.
c. Chemical depth profile and surface composition were analysed using X-Ray Photoelectron Spectroscopy (XPS), with a model PHI555 spectrometer with an Al Kα X-ray source at 10 KV, 40 mA and 3×10^{-8} torr.
d. Adhesive joint properties were determined using single lap shear joints (SLS) according to ASTM D-1002-72. The SLS specimens were tested in an Instron machine, model 1185, at a rate of 2mm/min at -30°C, RT and 120°C to failure. The mode of failure was determined visually to be either adhesive (interfacial, 100% coverage of the adherends) or cohesive (200% coverage of the adherends, both adherends covered), or mixed.

The effect of laser treatment on the polymer matrix is mostly ablative photodecomposition.[11] As most organic materials exhibit very high absorption in the UV range, most of the energy is absorbed in a thin surface layer (0.1 – 0.5 μ) which is the only part of the material that is affected or changed.[14] In order to prove this assumption and to measure the effect of laser irradiation on the bulk properties of the laminate, flexural tests were conducted on treated and untreated samples.

In a flexural test, tension occurs on one side and compression on the other side of the sample. The tensional side is very sensitive to changes on the surface. A simple beam 2.2 × 21.7 × 100 mm (span 50 mm) was tested according to ASTM D-790 (3-point flexural test). The beam was loaded at a rate of 2 mm/min until failure. The side loaded by tension was laser treated at various conditions and compared with non-treated or SiC-abrasion-treated specimens. Stress, strain and flexural modulus were calculated and the mode of failure was determined visually.

PEEK is a partly-crystalline material with an equilibrium concentration of 48% crystalline phase. Thermal history of the PEEK processing affects its degree of crystallinity as well as its mechanical and morphological properties.[15] The efficiency of laser treatment may also be affected by this factor. In order to determine the optimal crystallinity for achieving the best effect of laser treatment, several PEEK composites with different crystalline concentrations were laser treated, bonded and tested.

Various crystalline concentrations were achieved by applying different cooling rates during laminate processing (1, 7 and 33°C/min). The various laminates were bonded (SLS joints) with FM 300 2K after laser or abrasion treatment and compared with non-treated ones. The level of crystallinity was determined by Philips Model PN-2000 X-ray apparatus equipped with a Cu lamp at the range of 15–35 degrees.

After optimal laser and crystalline conditions were determined and no damage was revealed to the composite adherends, a sandwich structure typical for aerospace applications was prepared. The structure contained two PEEK composite skins 37 × 37 × 2 mm and a Nomex® honeycomb. The skins were treated with the optimal laser conditions (compared with abraded and non-treated ones) and bonded to the honeycomb with FM 300 2K.

The whole structure was tensile loaded to failure in an Instron machine at a rate of 2 mm/min. The tensile strength was calculated and the mode of failure was visually assessed.

RESULTS AND DISCUSSION

Surface Morphology

SEM micrographs of the nontreated and SiC-abraded PEEK composite adherend are shown in Figure 1a and b. The surface of the abraded adherend is markedly damaged, cracked and the exposed fibers are broken.

SEM micrographs of the PEEK composite adherend after UV laser treatment at different conditions are presented in Figures 1c–f. At lower energies (less than the ablation threshold[6]–420 mJ/P·cm^2) and at a low number of pulses, etching of the surface is observed with shallow cracks. At a higher number of pulses, rounded granules are formed on the surface ~ 2μ in diameter. These granules grow in size (2–6 μ) as the number of pulses increases. The fibers close to the surface are being exposed but seem undamaged.

The phenomenon of the granules formed on the surface as a result of laser treatment is typical to various other materials.[7, 9, 12] At higher laser energies (above threshold) the phenomena at the surface are totally different. At a low number of pulses the etching of the surface is homogeneous without granules. At a higher number of pulses the fibers are exposed and fine powder collects on the surface, probably due to condensation of ablated material.[16]

At very high energy (6J/P·cm^2), deformed fibers are exposed and the matrix between them is ablated (Fig. 1f). It can also be seen that below threshold the effect of high energy with a low number of pulses is equivalent to low energy with a high number of pulses.

The formation of granules extending from the treated surface due to laser treatment significantly enlarges the surface area and contributes to better mechanical interlocking of the adhesive to the adherend.

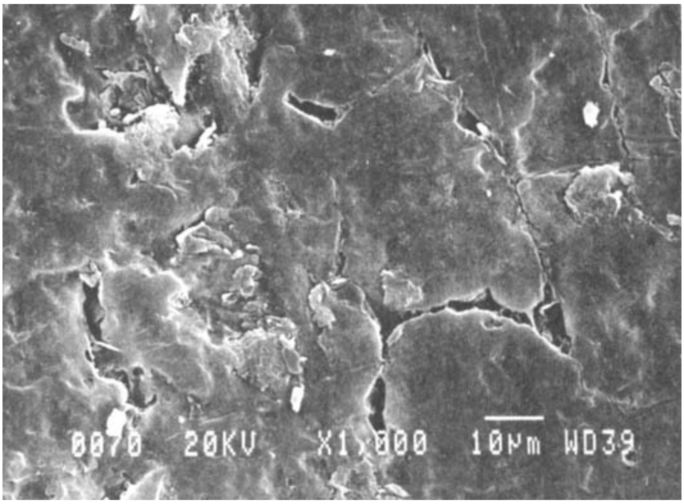
FTIR

Significant chemical changes in the PEEK composite surface were detected by FTIR after laser treatment. Typical FTIR spectra of the surface of laser-treated samples at the same energy (0.18 J/P cm^2) but at different number of pulses are presented in Figure 2.

The chemical mechanism at low laser energies is different from that at high energies. At low energies, C = 0 groups are formed (1653 and 1161 cm^{-1}), main chain bonds (C—O—C) break (1250 cm^{-1}), ϕ—CH end groups are formed (685 cm^{-1}) and new crosslinkings ($\phi - \phi$) appear at 951 and 1111 cm^{-1}. At higher energies, the chemical changes are less pronounced. No C = 0 groups are formed, only new ϕ – H groups and ϕ – ϕ crosslinking can be observed.

At 6 J/P·cm^2 a vast ablation, carbonization of the surface and a total decrease in all the absorptions of the organic groups occurs.

a



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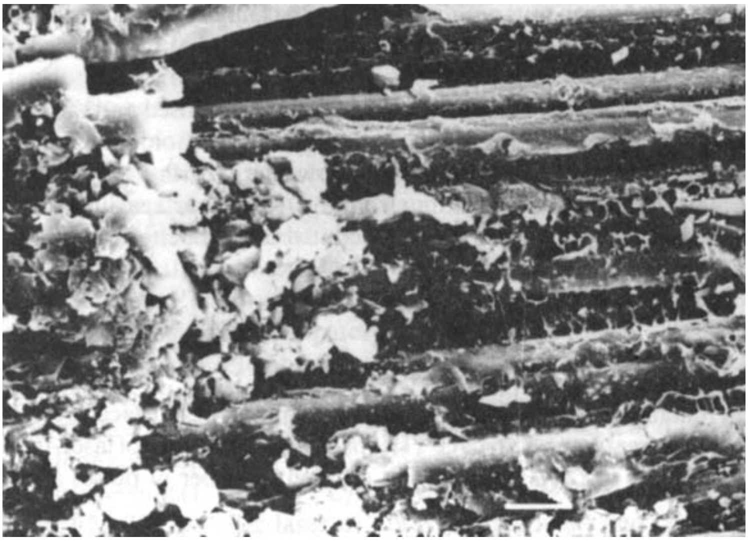

FIGURE 1 SEM micrographs of PEEK composite surface after treatment at various parameters. (a) non-treated, (b) SiC-abraded, (c) laser-treated: 0.18J/P·cm^2, 50 P, (d) 0.18J/P·cm^2, 100P, (e) 1J/P·cm^2, 10P, (f) 6J/P·cm^2, 10 P.

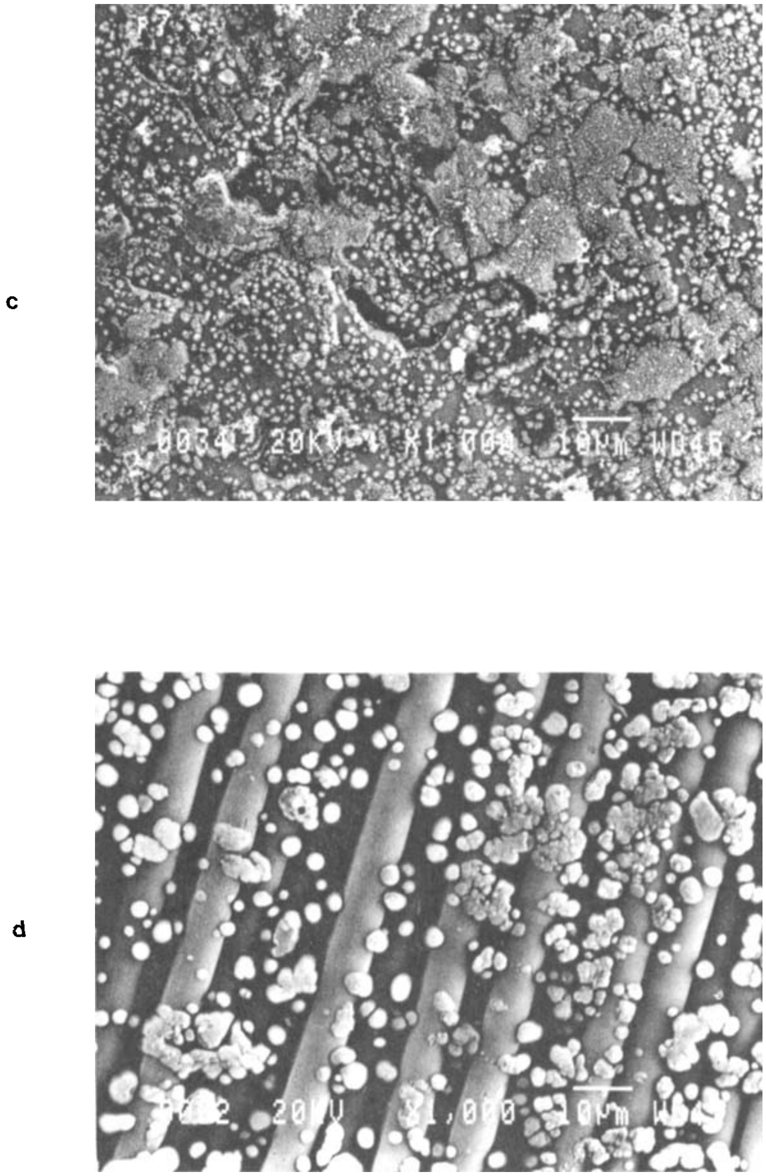

FIGURE 1 (*Continued*)

XPS

XPS surface spectra and surface atomic concentration of laser-treated and untreated composite PEEK specimens completed the information gained from SEM and FTIR results. The original C_{1s} spectrum of PEEK[17] is composed of a main peak of arylic C at

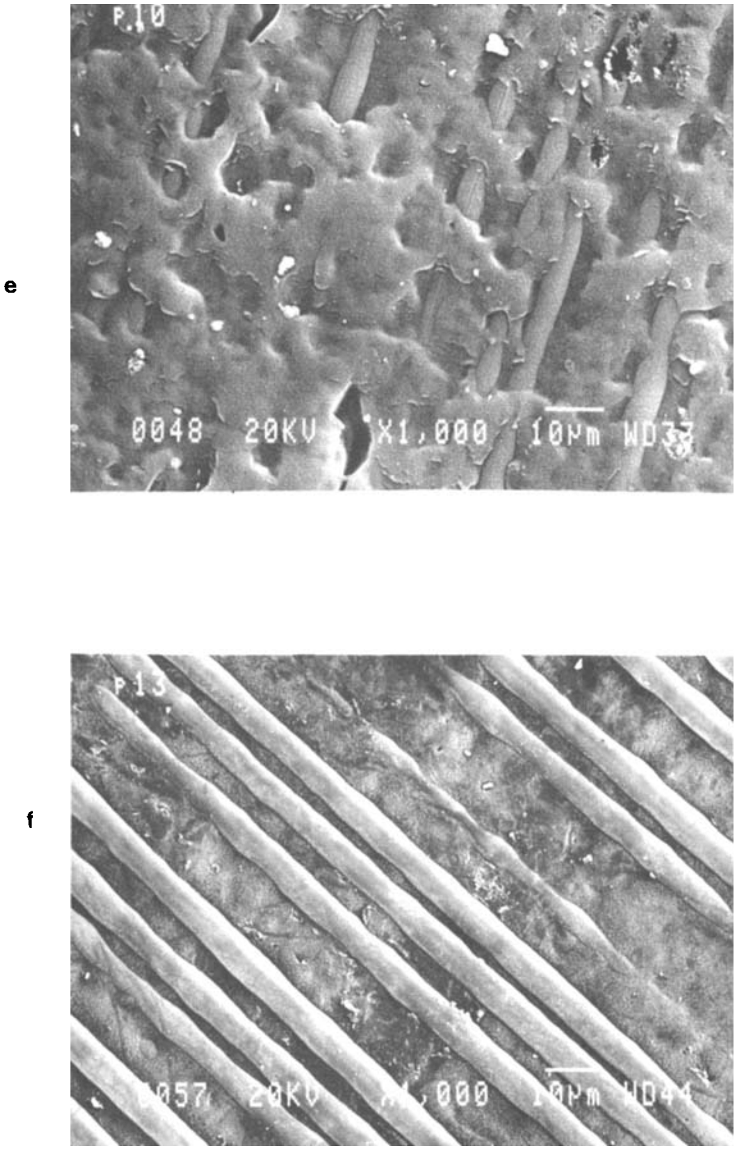

FIGURE 1 (*Continued*)

285.0 ev ($\underline{C}$ – H, $\underline{C}$ – C), and smaller C peaks at 286.5 ev ($\underline{C}$–O, etheric), 287.6ev ($\underline{C}$ = O, carbonyl) and 291.6 ev ($\underline{C = C}$, phenyl). The O_{1s} spectrum of PEEK is composed of 2 peaks at 533.6ev (C – $\underline{O}$) and 532.2ev (C = $\underline{O}$) and 532.7 (O – C = O)[18] appeared after extended oxidation.

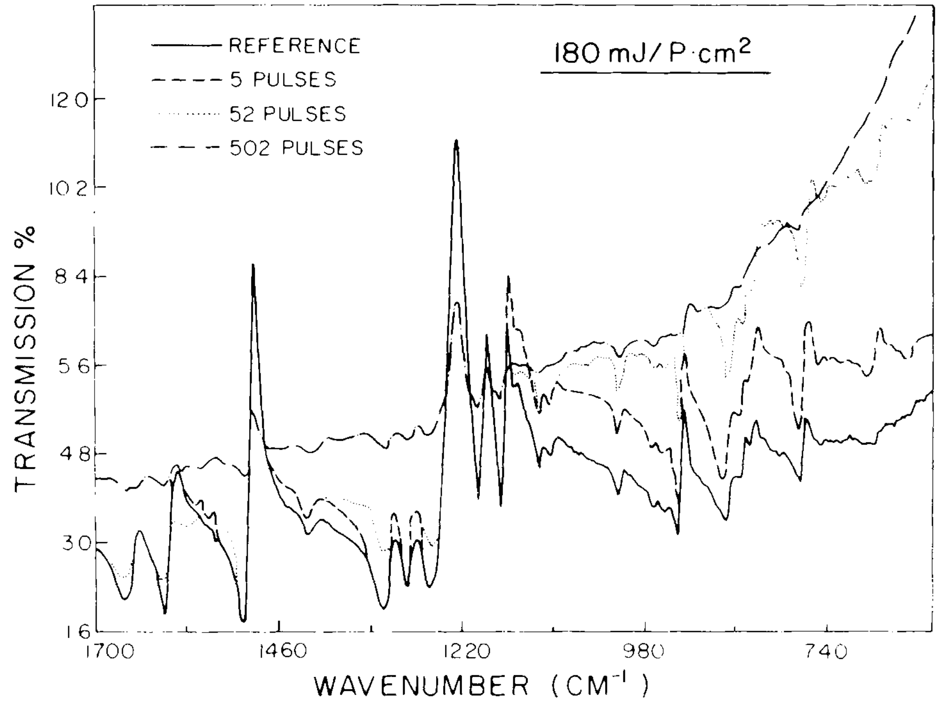

FIGURE 2 FTIR spectra of PEEK composite surface laser treated at 0.18 J/P at various no. of pulses.

The results of the laser-treated samples compared with the original PEEK spectrum are shown in Figures 3a and b and in Table II.

After laser treatment with low energy (0.18 J/100 P) the C_{1s} spectrum shows that the etheric peak (286.4 ev) decreased, the ketonic peak increased and new groups appeared ($O-\underset{\substack{\| \\ O}}{C}-C-CH_3$, 285.8 ev and $O-\underset{\substack{\| \\ O}}{C}-O$, 290.0 ev).[19] At higher energy only minor chemical changes were indicated (Fig. 3a).

The oxygen peaks after laser treatment show increase of the etheric peak and decrease of the carbonyl peak. The total intensity of the oxygen peaks was reduced by half (Fig. 3b).

The total ratio of O/C decreases, probably due to new crosslinking bonds ($\phi - \phi$) as indicated by FTIR. The same phenomenon (increase of C/O ratio) was also observed in References 7 and 8 due to bond breaking and evolution of CO derivatives. A similar mechanism of crosslinking was also observed as a result of PEEK bombardment with an electron beam.[20] Table II summarizes the XPS results.

The surface XPS spectra (Fig. 4) clearly show a cleaning process imposed by the laser irradiation. Various contaminants such as Mg and Si which were present at the non-treated APC-2/AS-4 surface are absent after treatment at 0.18 J/100 P. This phenomenon is typical of the laser treatments of all the materials tested.[9-12]

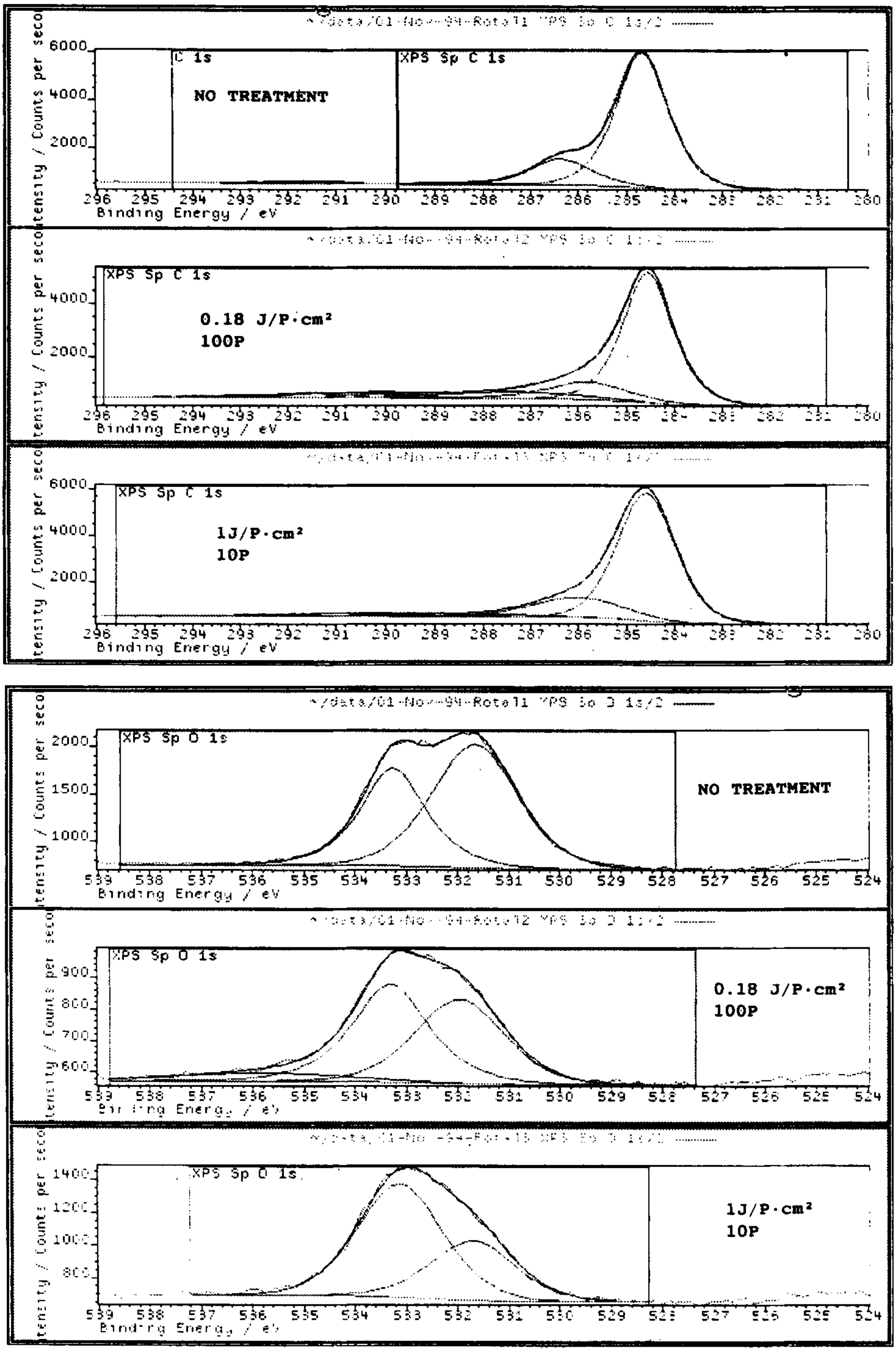

FIGURE 3 Comparison of XPS spectra of C_{1s} (a) and O_{1s} (b) of PEEK composite non-treated and laser-treated.

TABLE II
XPS results for laser treated and non-treated APC-2/AS-4 reinforced PEEK composite

Treatment	None	0.18J/100P	1J/10P
Peaks C_{1s}			
ϕ	+ + (284.7 ev)	+ + (284.5 ev)	+ + (284.6 ev)
C—O—C	+ (286.4 ev)	– (287.4 ev)	+ (286.1 ev)
C = O	+ (289.1 ev)	+ (290.0 ev)	+ (287.8 ev)
C = C (ϕ)	+ (291.3 ev)	+ (291.4 ev)	+ (291.0 ev)
O—CO—C	—	+ (285.8 ev)	—
Peaks O_{1s}			
C—O—C	+ + (535.3 ev)	+ (533.3 ev)	+ + (533.3 ev)
C = O	—	+ + (532.0 ev)	—
O—C = O	+ + (531.7 ev)	—	+ (531.7 ev)
Ratio O/C	0.197	0.05	0.091

+ + Strong peak
+ Weak peak
– Poor peak

Shear Strength and Failure Mode

Based on the SEM, FTIR and XPS results, laser parameters were chosen for treating the PEEK composite samples. A wide range of conditions was tested at RT and the optimal ones were tested at extreme temperatures. The results of SLS strength of APC-2/AS-4 joints bonded with FM300 2K at various laser parameters and tested at different temperatures are summarized in Table III, compared with those for untreated and abraded adherends.

It is evident that UV laser irradiation is effective as a preadhesion treatment on the APC-2/AS-4 reinforced PEEK adherends at all the chosen conditions tested. There are two optimal laser conditions for pretreatment (0.18 J/100 P and 1 J/10 P). At higher energies and greater number of pulses the effectiveness of the treatment is reduced, probably due to ablation and carbonization of the surface.

At the optimal laser treatment conditions, the single lap shear strength is increased by 250% compared with SiC abrasion treatment and by 450% compared with non-treated adherend.

Furthermore, SLS strengths of laser-treated adherends did not significantly deteriorate at lower test temperatures while a significant decrease was observed for non-treated (– 37%) and abraded (– 23%) joints at the same testing temperatures. At higher temperatures, this effect is less pronounced due to the thermal properties of the adhesive.

Visual inspections of the failure surfaces shows clearly that laser treatment caused a distinct improvement of failure mode from adhesive (interfacial) in non-laser treated adherend to mostly cohesive (mixed) following laser treatment at all temperatures tested. This indicates that the interfacial adhesion was significantly improved.

SEM micrographs of the fractured adhesive surfaces exhibit a smooth adhesive failure in the non-treated adherend (Fig. 5a) and a mixed failure in the SiC-abraded and

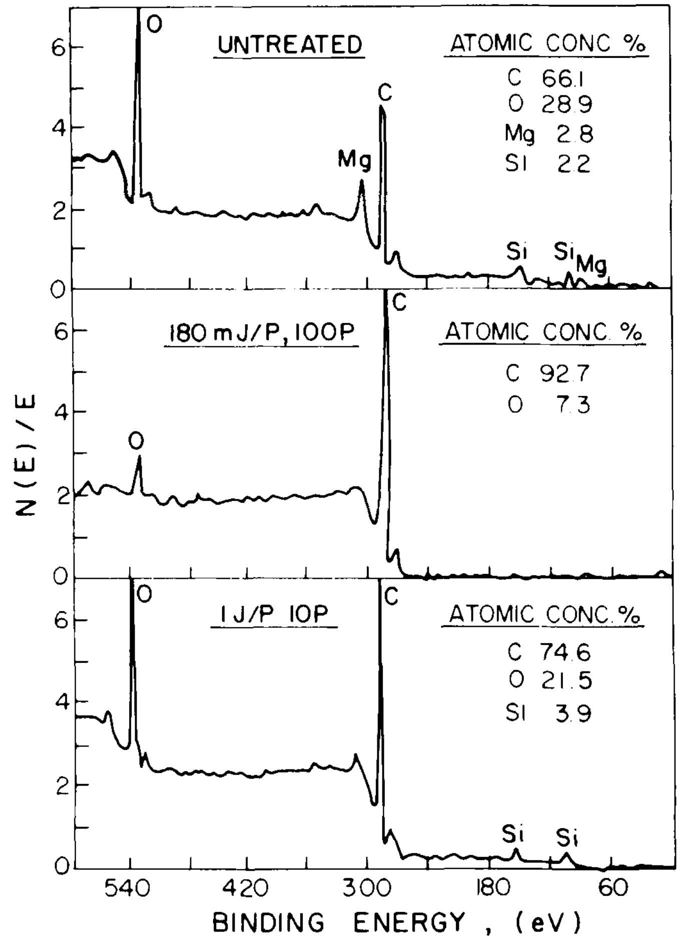

FIGURE 4 XPS spectra of surface atomic concentration of PEEK composite nontreated and laser-treated.

laser-treated adherends (Fig. 5b, c). At higher energy, the failure is mostly cohesive (Fig. 5d). Figure 5e and f reveal the effectiveness of the fine morphology formed on the adherend due to laser treatment which causes interlocking of the adhesive on the granules formed on the adherend. These granules are torn out during failure and are visible on both sides of the failed surfaces. They are not visible at higher laser energies.

Flexural Test

The flexural fracture strength (σ_b), fracture strain (ε_b), and modulus (E) data determined for PEEK composite samples subjected to different surface treatments are presented in Table IV.

No change in the mechanical properties of the adherend due to surface treatment is observed; the values are all within the tolerance of the reference (untreated) results.

TABLE III
The effect of laser pretreatment of APC-2/AS-4 reinforced PEEK composite adherends on SLS strength at various temperatures

Sample	Laser Treatment	Lap Shear Strength (MPa)		
		− 30°C	RT	+ 120°C
Untreated	-	3.8 ± 0.3 (a)*	6.0 ± 0.6 (a)	3.8 ± 0.4 (a)
SiC Abraded	-	11.3 ± 0.5 (a)	14.7 ± 1.3 (m)	12.3 ± 0.6 (a)
Laser treated	0.1 J/P·cm^2, 50P	-	26.6 ± 0.7 (m)	-
	0.1 J/P·cm^2, 100p	-	27.0 ± 0.6 (m)	-
	0.18 J/P·cm^2, 50 P	-	24.5 ± 3.6 (m)	-
	0.18 J/P·cm^2, 100 P	23.2 ± 1.1 (m)	27.2 ± 0.3 (m)	21.4 ± 1 (m)
	1 J/P·cm^2, 10 P	25.4 ± 0.5 (m)	27.8 ± 0.6 (m)	21.2 ± 1.8 (m)
	1 J/P·cm^2, 50 P	-	22.4 ± 4.3 (cc)	-

*a–adhesive failure
m–mixed failure (adhesive/cohesive in adhesive)
c–cohesive failure (in adhesive)
cc–cohesive failure (in adherend)

These results prove that microstructural changes resulting from laser treatment occur only in the thin outer layers (few molecular layers of the specimen)[21] and do not affect the entire bulk of the adherend. SEM micrographs of the fracture showed distinct structural differences between the tensile and the compression loaded sides of the specimen and the fracture was similar for treated and untreated specimens.

Effect of Crystallinity

The X-ray spectrum of PEEK composite is composed of three contributions: amorphous phase, Q_a, crystalline phase, Q_{cr}, and carbon fibers, Q_f.

$$Q_{\text{total}} = Q_a + Q_{cr} + Q_f$$

The crystalline phase has 4 main peaks at $2\theta = 18.9°, 20.9°, 23°, 29°$. The amorphous phase has a broad peak at $2\theta = 19$–$20°$ and the carbon fibers have a peak at $2\theta = 25°$.[22] Comparing the X-ray spectra of the PEEK composite consolidated at various cooling rates (Fig. 6a) shows that at slower rates (1°C/min) the area of the crystalline peaks was the largest when compared with the amorphous peak, meaning that the degree of crystallinity increases with reducing cooling rate. The degree of crystallinity was calculated and is presented in Table V.

Laser treatment causes shifting of the crystalline peaks to lower 2θ, probably due to a change in the crystalline structure caused by the laser irradiation (Fig. 6b). Comparing the lower energy laser treatment (0.18J/100P) with the higher energy laser treatment (1J/10P) on the X-ray spectra indicates that at higher energies the crystalline peaks are sharper and larger than the carbon fiber peaks (although more fibers were exposed at this energy). Increasing laser energy causes crystallization at higher temperatures leading to more perfect crystals.[15] This is another proof that at high energies the laser effect is mostly thermal.

The effect of degree of crystallization of the adherend on the effectiveness of the laser treatment was tested mechanically by SLS joints with FM 300 2K structural adhesive (Table V).

The results show that for all the degrees of crystallinity laser treatment markedly improves the lapshear strength compared with untreated or abrasion-treated

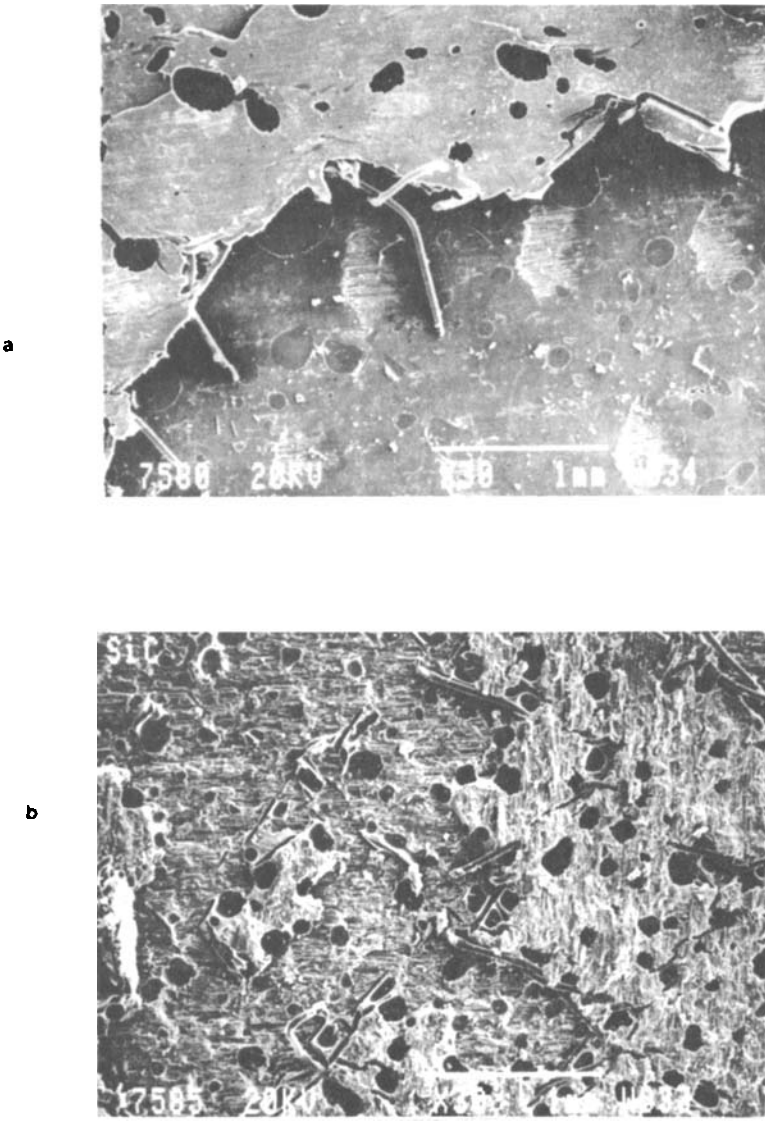

FIGURE 5 SEM fractographs of joint surfaces of PEEK composite bonded with FM 300 2K at various treatments: (a) non-treated, (b) SiC-abraded, (c, e, f) laser-treated 0.18 J/P·cm^2, 100P, (d) laser-treated 1 J/P·cm^2, 10 P.

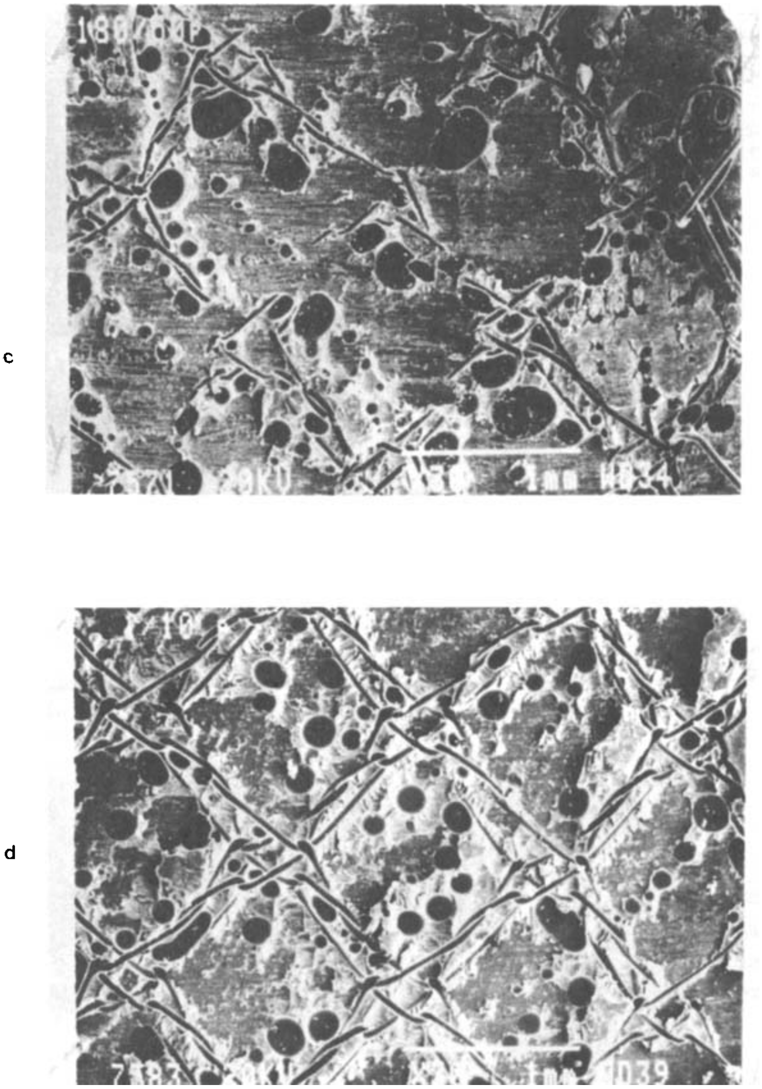

FIGURE 5 *(Continued)*

adherends. The degree of crystallization has no effect on the SiC-abraded adherend as the adhesion mechanism for this treatment consists of mechanical interlocking, which is not affected by crystallization.

The lower-energy laser treatment imposes a photochemical mechanism which chemically modifies the adherend's surface and is, thus, affected by the degree of crystallinity. The lowest cooling rate shows the highest lap shear strength.[23] The high-energy laser treatment, the effect of which is mostly thermal, vastly affects the

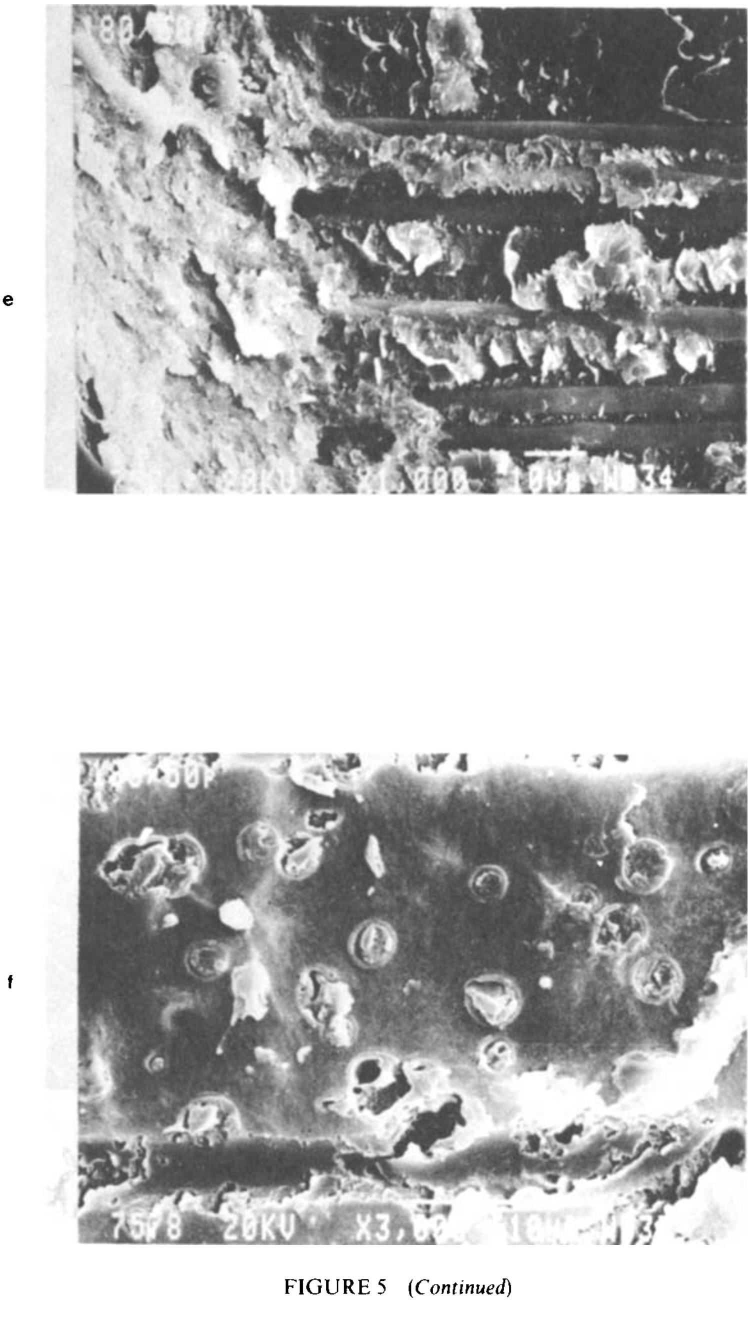

FIGURE 5 (*Continued*)

matrix crystallinity, compared with the low-energy treatment, possibly increasing the degree of crystallinity due to annealing which results in higher lapshear strength than for the low-energy laser treatment. In both cases, the lowest cooling rate shows the highest strength as indicated in Table V. These results support the FTIR, XPS, SEM

TABLE IV
Effect of surface treatment on flexural properties of APC-2/AS-4 reinforced PEEK composite

Treatment	ε_b(%)	σ_b(MPa)	E(GPa)
None	1.55 ± 0.04	1.94 ± 0.03	121.4 ± 4.2
SiC	1.52 ± 0.05	1.88 ± 0.08	120.3 ± 3.0
0.1 J/50 P	1.48 ± 0.06	2.05 ± 0.14	133.8 + 4.7
0.18 J/50 P	1.40 ± 0.1	1.91 ± 0.1	130.9 ± 0.5
0.18 J/100 P	1.52 ± 0.06	1.97 ± 0.2	130.0 ± 2.2
1.0 J/10 P	1.55 ± 0.02	2.07 ± 0.06	130.2 ± 2.6
1.0 J/50 P	1.54 ± 0.04	2.06 ± 0.07	130.6 ± 3.9

TABLE V
Single lap shear strength (MPa) of joints bonded with FM 300 2K adhesive using APC-2/AS4 reinforced PEEK composite adherends with different degrees of crystallinity

Cooling rate °C/min (Crystallinity) (%)	Laser treatment		SiC	No treatment
	0.18 J/P·cm^2, 100 P	1J/P·cm^2, 10 P		
1 (32.7)	29.5 ± 1.3 (m)*	35.5 ± 0.5 (m)	14.3 ± 1.2 (m)	4.6 ± 1.5 (a)
7 (30.8)	27.2 ± 0.8 (m)	27.8 ± 0.7 (m)	14.7 ± 2.0 (m)	6.1 ± 0.8 (a)
33 (21.2)	26.4 ± 4.0 (m)	30.3 ± 1.6 (m)	14.8 ± 0.5 (m)	5.3 ± 0.1 (a)

*a–adhesive failure
m–mixed failure

and mechanical behavior results, indicating two different mechanisms: below the ablation critical point where the mechanism is mostly chemical ablation, and above the critical point where the mechanism is a combination of chemical and thermal ablation. SEM fractographs (Fig. 7) of laser-treated adherends after SLS failure indicate that the interfacial part of the mixed failure was actually partly cohesive in the adherend, and that the PEEK matrix was torn out from between the carbon fibers, indicating excellent adherence.

SANDWICH STRUCTURE

The skins of the structure were treated using two optimal laser parameters (1J/P/10P and 0.18 J/100P) and compared with non-treated and abrasive SiC-treated skins. The tensile results of the skins bonded to Nomex® honeycomb with FM 300 2K adhesive are summarized in Table VI.

The results show that laser treatment is preferable for the composite sandwich structure. The tensile strength is one order of magnitude higher for the treated compared with the non-treated adherend. The failure shifts from adhesive in the non-treated PEEK, to divided adhesive for the SiC-abraded, and to cohesive in the honeycomb and in the adhesive in the laser-treated ones (Fig. 8).

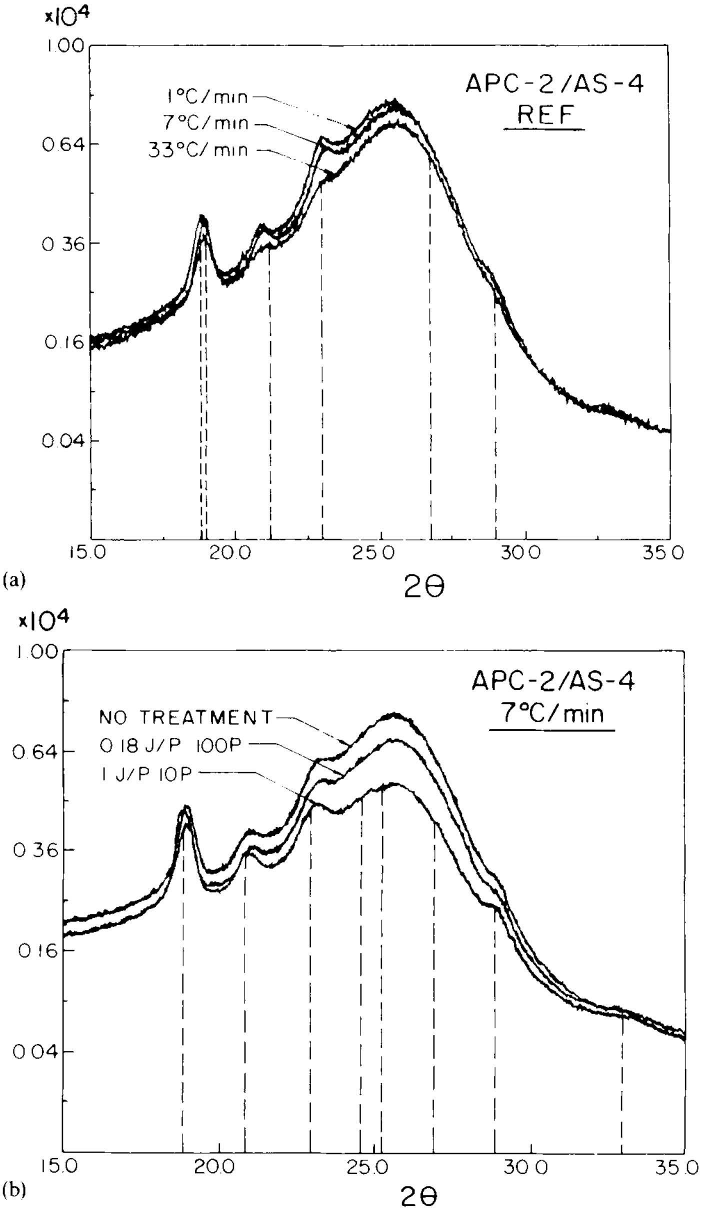

FIGURE 6 X-ray diffraction of PEEK composite. (a) non-treated PEEK composite at various cooling rates during consolidation; (b) the effect of laser treatment at cooling rate of 7°C/min.

TABLE VI
Tensile strength of composite sandwich structure

Treatment	σ_b (MPa)	Fracture mode
None	4.9 ± 0	Adhesive from skin
SiC	49.5 ± 0.2	Adhesively divided from honeycomb and skin
1J/10 P	55.6 ± 6.4	cohesive in adhesive and in honeycomb
0.18 J/100 P	60.7 ± 5.5	

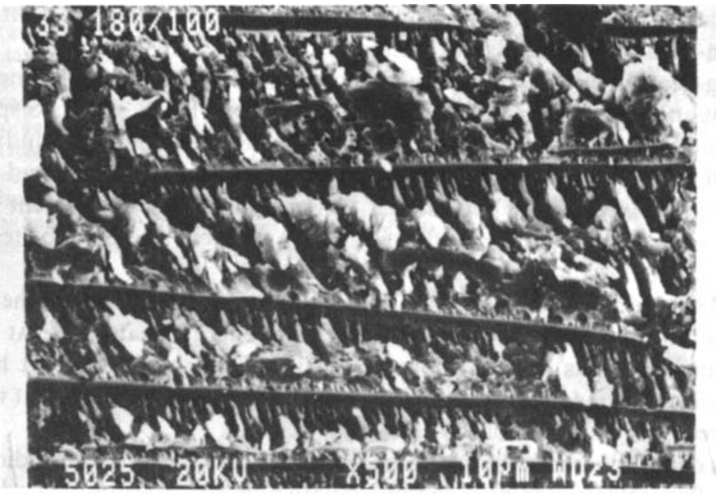

FIGURE 7 SEM fractograph of PEEK composite bonded with FM 300 2K (21.2% crystallinity)-cohesive failure.

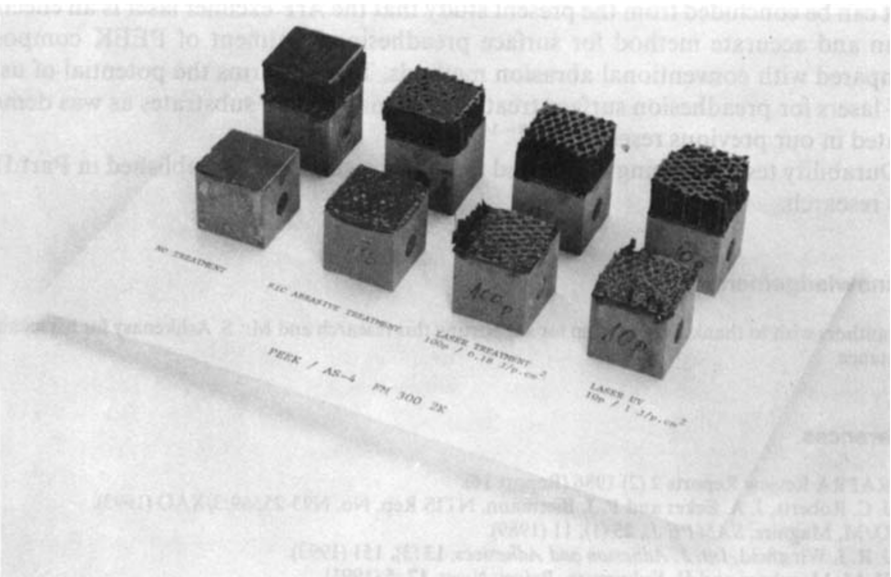

FIGURE 8 Failure mode after tensile loading of a sandwich structure for various treatments of the PEEK composite skin. See Color Plate I.

CONCLUSIONS

The use of an ArF excimer laser as a preadhesion surface treatment for a composite thermoplastic substrate (PEEK matrix reinforced with AS-4 carbon fibers) has been investigated. Structural epoxy bonded single lap joints with laser-treated adherends had significantly higher lap shear strength (450% and 250%) than joints with untreated or abrasion- treated adherends (respectively).

Scanning electron microscopy revealed morphological changes including increase in surface roughness and partial exposure of carbon fibers. FTIR and XPS spectroscopy indicated chemical changes of the surface following laser treatment, including increase in carbonyl groups as well as formation of new crosslinking bonds and removal of contamination (Si, Mg) from the surface. Using optimal laser treatment parameters resulted in a cohesive or mixed mode of failure in ambient and extreme test temperatures.

SEM, FTIR and XPS analysis as well as a crystallinity effect indicated the presence of two different mechanisms at higher or lower laser energy treatments. At low energy (0.18 J/P) the effect was mostly photochemical and morphological. At high energy (1 J/P) the effect was mostly thermal. Thus, only the high energy treatment was affected by the degree of crystallinity of the adherend.

The bulk of the adherend was not damaged by the laser treatment as indicated by the short beam flexural test of treated compared with non- or abrasion- treated specimens.

The combination of increased surface roughness, surface cleaning and chemical modification by the laser treatment of PEEK composite adherends is responsible for the high strength of these joints, best illustrated in the structural sandwich joint.

It can be concluded from the present study that the ArF excimer laser is an effective, clean and accurate method for surface preadhesion treatment of PEEK composite compared with conventional abrasion methods. This confirms the potential of using UV lasers for preadhesion surface treatment of many other substrates as was demonstrated in our previous researchers.[9-12]

Durability tests are being conducted and their results will be published in Part II of this research.

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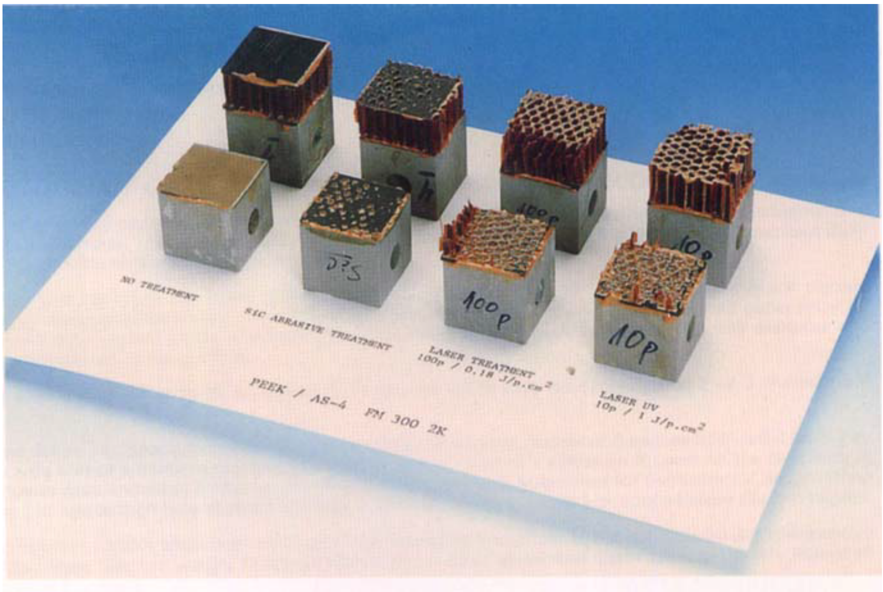

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COLOR PLATE I. See M. Rotel *et al.*, Figure 8.