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LASER ABLATION ASSISTED ADHESIVE BONDING OF AUTOMOTIVE STRUCTURAL COMPOSITES

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SUMMARY: Laser ablation has been evaluated as a surface pretreatment prior to adhesive bonding. In prior experimental work, it was observed that when adhesively bonded, composite, single lap shear samples fail, the fracture often occurs at either the adhesive/adherend interface or in the resin rich surface layer of the composite. These two areas represent the weakest portion of the joint. Laser ablation pretreatment generates areas where the resin on the composite surface is selectively removed leaving behind exposed reinforcing fibers which are the major load bearing members of the composite. In a subsequent adhesive bonding operation, this allows portions of the fibers to be encapsulated in the adhesive while other portions of the fiber remain in the composite resin. This type of pretreatment permits fibers to bridge and reinforce the interface between adhesive and adherend. A secondary benefit is the removal of surface contaminates by pyrolysis. Microscopic observation of laser ablated surfaces indicates a prominent, fiber rich area. Results of the mechanical evaluation indicated that the lap shear strength for laser ablated samples was significantly higher than specimens with no pretreatment or with solvent cleaning only, but were slightly lower than specimens that were mechanically roughened and cleaned with solvents prior to bonding.

KEY WORDS: Laser Ablation, Composite Bonding, Adhesive, Automotive Joining.

INTRODUCTION

In the past few years, Oak Ridge National Laboratory (ORNL) has been involved in a national initiative to conduct research aimed at promoting the use of lighter weight materials in automotive structures for the purpose of increasing fuel efficiency and reducing environmental pollutant emissions [1]. The commercial application of composites has an extensive history in the aerospace and industry and is achieving greater acceptance in the marine and construction industries but has evolved relatively slowly in the automotive industry during the past 20 years [2,3]. Composite use in automobiles has historically been limited to secondary structures such as appearance panels and dash boards. As the evolution of the automobile continues, however, fiber-reinforced polymers are being considered for weight reduction in future automotive load-bearing structures and components. [4] A key component of this initiative is the joining, specifically adhesive bonding, of composites. Unfortunately, the implementation of adhesives on the manufacturing plant floor suffers from a significant economical obstacle. Adherends joined with structural adhesives often require extensive surface preparation procedures to maximize joint integrity. These additional production steps result in increased assembly time and

costs. In order to make the use of adhesives for primary composite structures a reality in high production rate, consumer goods industries, technologies for rapid surface preparation of the adherends must be discovered, developed and deployed.

THEORY

The weakest portion of an adhesive joint is often the interface between the adhesive and adherend. The strength of the chemical bond and the contact area between the adhesive and adherend influence the strength of the joint. Since most composites have a highly resin rich zone on the surface, the chemical bond of greatest interest is the one that occurs between the adhesive and the resin. Strong chemical bonding at the interface can be inhibited by the presence of mold releases, grease, dust, dirt or other contaminants that are typically found in production plants. Laser ablation can quickly eliminate these contaminants by pyrolyzing them. Other solid particulates may be swept away by the pressure wave created during the rapid volummetric expansion created by the vaporization of surface chemicals.

Many composites contain a resin rich surface layer as a result of the molding process. Fibers lay adjacent to and parallel to this layer but they do not reinforce this layer because they do not protrude into it. Since the fibers are the load bearing portion of the composite and fibers are absent from this region, the resin rich, near surface layer has a lower strength and stiffness than the remainder of the composite. Failures that do not occur at the adhesive/adherend interface often occur through the resin rich surface layer of the composite resulting in a failure mode known as light cohesive transfer. Experience [3,5,6,7] has demonstrated that for many bonded composite materials used in industrial applications, failure systematically occurs in the fiber-free near surface region of the composite substrates. Laser ablation has the potential to remove this layer by photo-pyrolysis of the resin. This will result in fibers and resin being exposed on the composite surface to be bonded and a much stronger, reinforced interface which is more resistant to crack initiation and growth. Laser ablation will also leave a much rougher composite surface than the as-molded adherend. This increases the surface contact area and theoretically the mechanical strength of the resulting bond.

The greatest increase in joint strength may be obtained if the ablation is allowed to progress further than just removing the contaminants and resin rich surface layer. The interface between adhesive and adherend in bonded joints is usually a relatively smooth plane of sharp contrast between two different materials with differing material properties. This is an ideal location for crack initiation and propagation. If ablation is used to remove the resin from around the fiber to a predetermined depth it will create a fiber rich layer. The fiber rich layer will be rough with layered fiber bundles protruding from the bulk of the composite. Upon application, an adhesive of low viscosity will be able to seep around the fibers and fiber bundles and into the rifts and valleys created by the absence of the composite resin. By doing this the reinforcing fibers protrude from the composite into the adhesive creating a fiber reinforced interfacial region. The result is a transition zone between the adhesive and adherend rather than a definitive interface typical of most bonded joints. Since fibers extend through the transition of one material into another, the interface is reinforced in much the same manner that the bulk of the composite is reinforced and thus should be more resistant to crack propagation.

Laser ablation may be conducted in the presence of oxygen which is especially attractive to high production rate manufacturing processes by avoiding the cost of an inert atmosphere. The presence of oxygen may result in the generation of free radicals on the resulting surfaces of the resin and fibers yielding a chemically active surface to which the adhesive in a subsequent bonding operation will readily react. The increased chemical affinity should result in greater adhesion and mechanical joint strength.

With laser ablation the rate of resin or contaminant removal is dependent upon the frequency, pulse repetition rate, pulse duration, laser energy density and amplitude of the laser pulse. It is also dependent on the spectrum of energy absorption for each material present which is an intrinsic material property. Since the fibers in glass reinforced composites are highly transparent to most laser operating wavelengths, it is expected that the resin will absorb much greater energy than the fibers and thus be ablated much more rapidly. Literature [8,9] indicates that argon excimer lasers and krypton excimer lasers are well suited for ablation of polymer composites since the absorption spectrum of most polymers is high near those wavelengths and the absorption spectrum of glass is very low at those wavelengths.

The expected benefits of using laser ablation for pre-bonding surface preparation include:

1. Removal of surface contaminates including mold release, grease and particulates.
2. Removal of the weak, resin rich surface layer of the composite.
3. Increased surface roughness for increased contact area and joint strength.
4. Fiber bridging from composite to adhesive for interface reinforcement.
5. Fiber and resin surface activation by the generation of free radicals.
6. Ablation of resin and not fiber by appropriate wavelength selection.

EXPERIMENTAL PROCEDURE

The composite used for this study was a SRIM polyisocyanurate resin system (DOW MM364) reinforced with 55 wt% OCF U750 E-glass random swirl, continuous strand mat. As previously noted by the authors [6,7], it was determined that a 48 hour, 101°C pre-drying treatment would remove more than 95% of the absorbed moisture resulting in good bonds. This composite pre-treatment was used for all samples following surface preparation and prior to bonding.

After drying, single lap shear samples were bonded using a urethane based adhesive, Ashland 3321. Lap shear specimens were made by bonding two 2.54 ± 0.13 cm by 10.16 ± 0.13 cm samples together with a 1.27 ± 0.13 cm overlap. The samples were nominally 0.32 cm thick and had a resulting overlap area of 1.27 x 2.54 cm. A consistent bondline thickness of 0.076 cm was maintained by placing four 0.076 inch glass beads in the bondline and clamping the specimens together with care taken to maintain proper alignment. The samples were then cured at 150°C for 60 minutes.

Prior to drying and bonding, laser ablation was carried out using a KrF excimer laser with a wavelength of 248 nm. A cylindrical lens was used to vertically compress the output beam, resulting in a line shape of 0.06 x 4.06 cm. Seventy percent of the beam intensity was in the 2.54 cm wide sample region, with 15% distributed on the 0.76 cm beam overhang of the sample on each side. Within the 70% region, the distribution of light intensity is near Gaussian. The laser was fixed and the samples were moved across the beam with a motorized translator set at a speed of 1.91 cm per minute. The fumes produced by vaporization of the resin were removed by a fume extractor. Ambient laboratory atmosphere was used with no other pretreatment of the samples. A pulse frequency of 10Hz was used with an average per pulse energy of 90 - 100 mJ and a pulse duration of twelve nanoseconds. The following five sets of samples were produced:

(1) 10 - 10K pulses, beam incident angle 0°;
(2) 10 - 15K pulses, beam incident angle 0°;
(3) 10 - 20K pulses, beam incident angle 0°;
(4) 8 - 10K pulses, beam incident angle 0° & 10K pulses, beam incident angle 45°;
(5) 8 - 10K pulses, beam incident angle +45° & 10K pulses, beam incident angle -45°.

Additionally, three control groups were used for comparison of results. The first control group consisted of lap shear samples that had been lightly sanded with 100 grit sandpaper and then ultrasonically cleaned in ethanol prior to drying and bonding. The second control group consisted of samples that were ultrasonically cleaned in ethanol prior to drying and bonding but on which no mechanical surface preparation was performed. The third control group consisted of samples on which no surface preparation was performed. These samples were bonded in the as-molded state after the 101°C, 48 hour drying treatment.

To aid in better alignment and to minimize bending during testing, 3.81 cm shoulders were bonded on each specimen. Lap shear tests were then conducted on all samples using a Model 1125 Instron tensile testing machine and a crosshead displacement rate of 0.13 cm/minute. Interpretation of the strength data from these tests is difficult. The raw data cannot be converted into a true stress - strain curve due to the specimen geometry and the resulting complex stress state present in the joint. As a result, only the load in kilograms of force is reported. Similarly, no attempt was made at defining strain values but instead the data is presented as total crosshead displacement. [10]

LASER ABLATION AND MECHANICAL TEST RESULTS

At ablation onset, the beam produced a bright yellow-orange flame at the composite surface extending beyond the width of the sample. After the initial 1800 pulses the flame rapidly decreased to two-thirds of its original size and then continued a slow decrease in size and intensity throughout the remainder of the ablation. As the flame begins to decrease in size a darkening of the composite begins. It is theorized, but by no means proven, that this effect is caused by the pyrolysis of the resin and/or mold release and that carbon is deposited on the surface as a by-product. It was noted that as the thickness of the carbon layer increased, the effectiveness of the laser in removing material decreased.

It was also noted that as time lapsed, ablation of the edges of the sample decreased and eventually stopped while ablation in the center of the sample continued. This may be due to the carbon film thickness increasing and correspondingly raising the energy deposition density required for the onset of ablation. Since the energy density across the beam is a Gaussian distribution, there may have been a sufficient density of energy penetrating the carbon film in the center of the sample to exceed the energy density threshold but not on the edges. The application of a mechanical profilometer was not possible to obtain as-ablated depths due to irregularities on the processed sample surfaces that were narrower than the diameter of the profilimeter point.

All lap shear samples were produced and tested as described above. The resulting single lap shear data is shown in Figure 1. It is apparent that the most effective surface preparation for this material combination was the mechanical abrasion and subsequent ethanol cleaning. The samples with no cleaning and the specimens with only ethanol cleaning demonstrated much lower ultimate strengths and correspondingly lower total elongations before failure. The laser ablated samples demonstrated strengths at failure that were consistently lower but within 15% of the strengths of the mechanically roughened, ethanol cleaned material. The stiffnesses of all samples were within the standard deviation of one another. The non-ablated, non-sanded samples appeared to have had a slightly lower stiffness than the other samples. This would be expected since these materials still have the softer, resin rich surface layer intact.

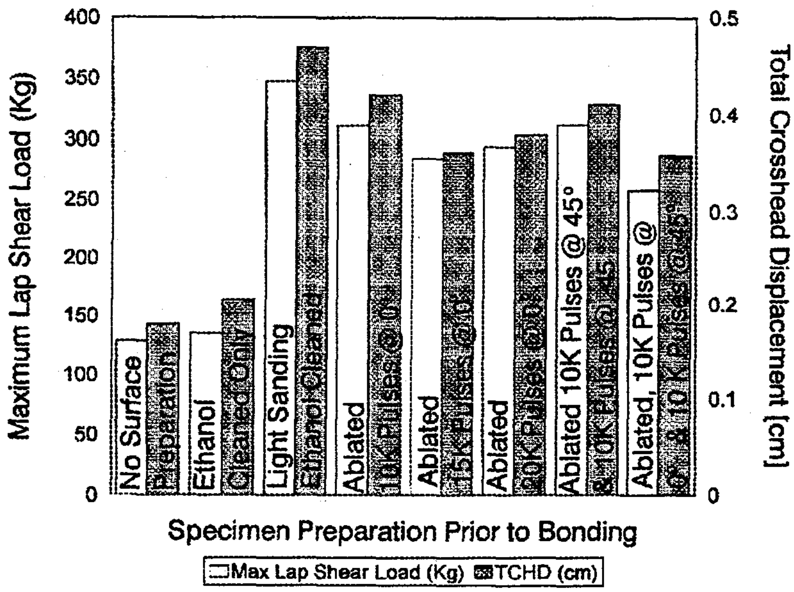


Figure 1. Ultimate load carried and total crosshead displacement vs surface pretreatment conditions for single lap shear samples.

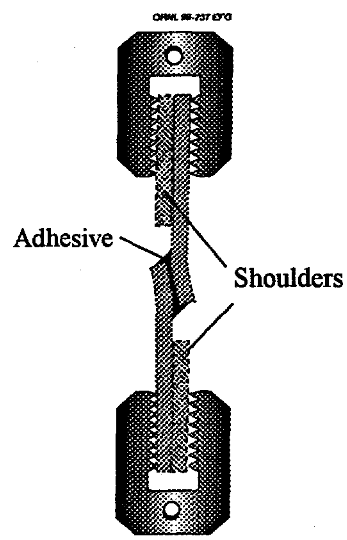
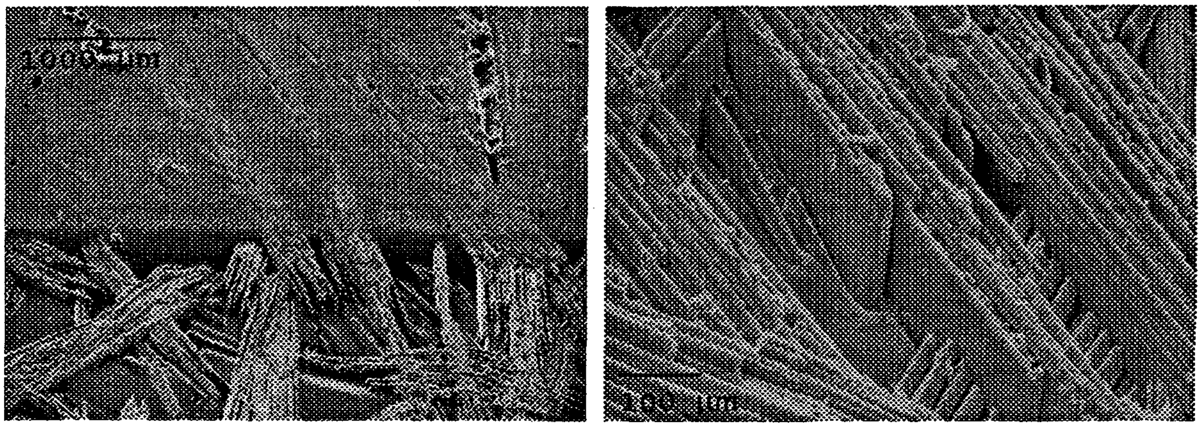


Figure 2. Experimental Set-up for Mechanical Testing

The tests began with a period of low load introduction as the machine grips dug into the softer resin. The tests then continued with uniform stressing of the system. After sufficient load was acquired crack growth began accompanied by significant fiber bridging across the interface. As the test progressed, fiber breakage became prevalent resulting in "jumps" in the data plot. This was followed by the attainment of the ultimate load as the resin failed and shortly afterward by the failure of the last of the fibers. The resulting failure surface was cohesively through the composite matrix (not at the interface or through the adhesive). Extensive fiber tear with only light adhesive transfer was the predominant failure mode for the cleaned and sanded samples and all laser ablated samples. The samples that underwent no surface preparation failed at the adhesive composite interface with only a light transfer of the resin rich composite layer to the adhesive. The samples that underwent only ethanol cleaning failed cohesively through the resin rich near surface region of the composite.

SURFACE/CROSS-SECTION OBSERVATIONS

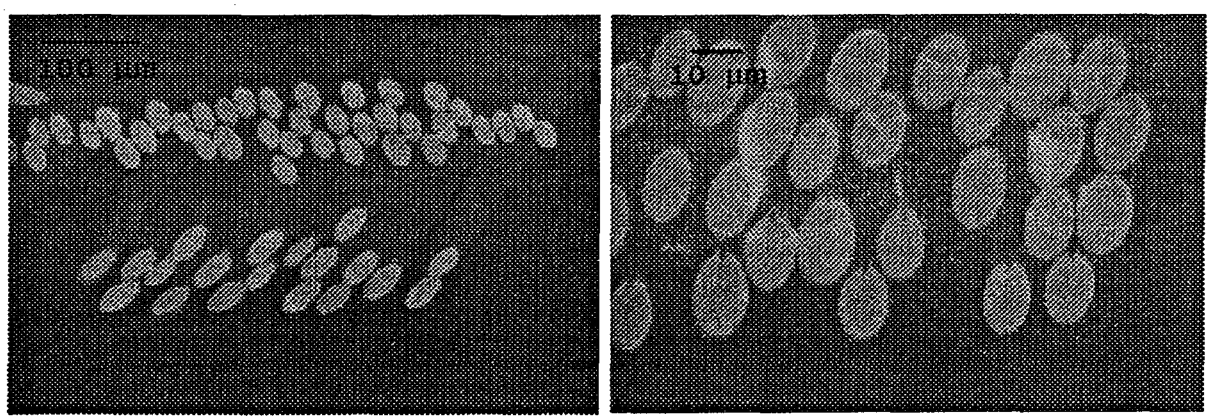
To examine the surface effects of ablation, ablated and unablated samples were examined by scanning electron microscopy. A good comparison between ablated and unablated areas can be found in Figure 3A which shows the ablation edge. Obvious is the removal of the near surface resin rich layer and the exposure of numerous fiber bundles. A closer view, Figure 3B, shows that the fibers produced a shadowing of the laser energy resulting in resin being removed above, and beside the fibers but not from underneath the fibers.



(A) (B)

Figure 3. A contrasting view between ablated and unablated areas. (A) Resin removed from around fiber bundles. (B) Shadowing effect leaves resin under the fiber unablated.

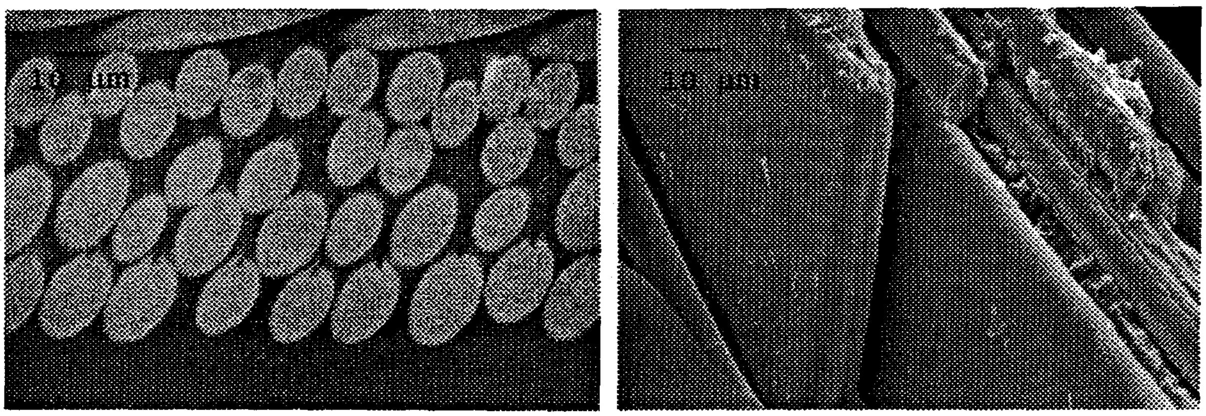
Scanning electron micrographs were also made of cross-sectioned, ablated samples that had been bonded but had not been mechanically tested. Figures 4A and B show cross-sections of the bonded, ablated samples and fibers that protrude into the adhesive. Notable on the micrographs of ablated samples was a small crack in each of the surface fibers. The crack was consistently on the fibers that had been directly exposed to laser light and on the side of the fiber directly opposite of the direction from which the laser energy came. This was noted not only in cross-sectioned samples but also on the mechanically tested ablated samples.



(A) (B)

Figures 4A-B. Adhesive has partly surrounded many of the surface fibers and crept into deeper voids. Note cracks in surface fibers.

It is theorized that, after the resin was ablated to expose the glass fibers, the fibers acted as a cylindrical lens. Light incident on the front surface of the fiber was refracted such that it was concentrated on the axis of incidence and near the rear surface of the fiber. Consequently, extreme heat gradients were generated there causing rapid, localized thermal expansions. This localized expansion resulted in severe stress gradients that lead to fracture of the fiber. The extreme energy intensity created by the focusing of this light energy may have been responsible for cracking of the fibers.



(A) (B)

Figure 5A-B. Cracking and splitting of the cracks as they grew down the fiber. Shielding of the resin underneath the fiber but the presence of a highly disturbed region laying directly underneath the crack in the backside of the fiber.

Referring to Figure 5A and B, it can be seen that the fiber was cracked directly opposite of where the laser energy entered the glass fiber. A secondary crack was also seen on the top of some of the fibers which may be the result of reflected energy since the glass fiber was against a mostly opaque background of resin. Shadowing can be seen where the light did not exit except at the focal point thus yielding a slightly pyramidal shaped area of unablated resin. Since most of the energy was focused along a line running directly underneath the glass fiber a dynamic event would be expected in the resin along this line. Figure 5B depicts this clearly with a highly disturbed region running out from directly under the fiber and a darkened line being present in the neighboring fiber which appears to split the pyramidal shadowed region in two. Even though positive benefits were gained by laser ablation by being able to mechanically interlock the fiber with the adhesive, the benefits were more than offset by the negative benefits of weakening the fiber due to intense focusing of the energy by the glass fibers. This explains why the ablated samples had slightly lower strengths. Carbon fiber may not allow the energy to be refracted and focused and will also have better heat transfer properties than glass fibers.

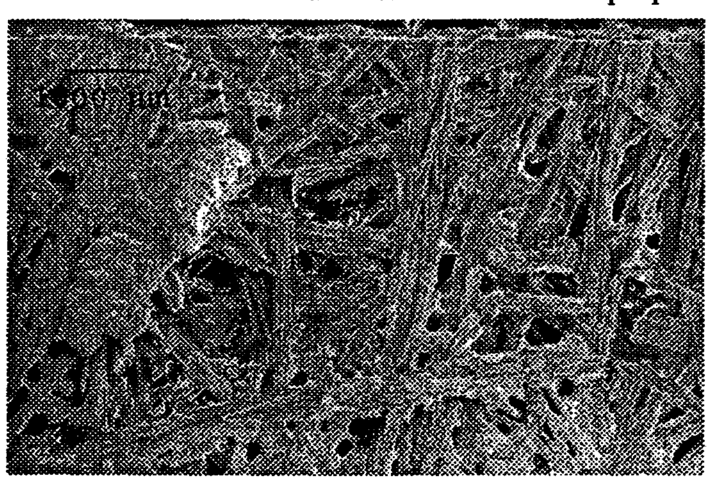
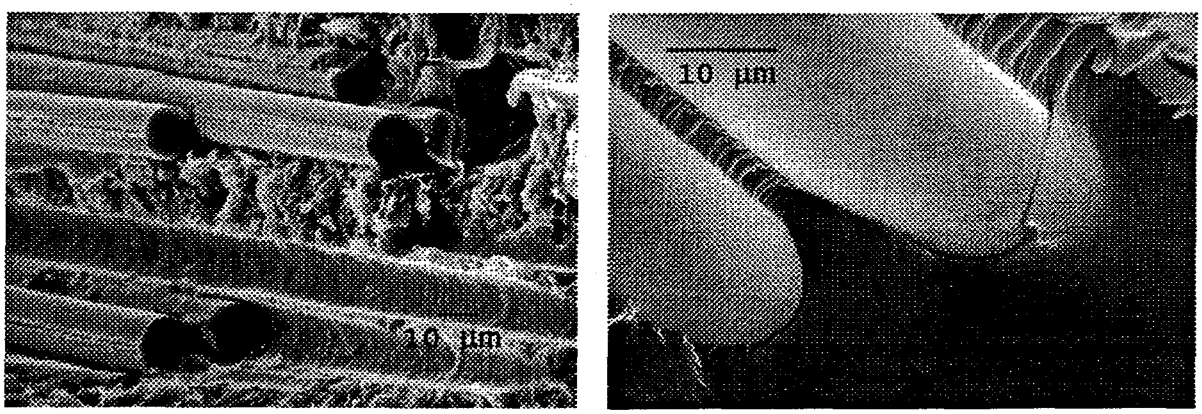


Figure 6. Failure scar of ablated composite surface. Surface roughness is increased. Extensive adhesive transfer is apparent due to mechanical interlocking around fibers.

The test group that underwent no surface preparation failed directly at the interface between the adhesive and composite. The specimens that underwent only ethanol cleaning failed cohesively through the resin rich surface layer of the composite. The observed interfacial and near surface failure is the reason for the much lower mechanical strengths of these joints.

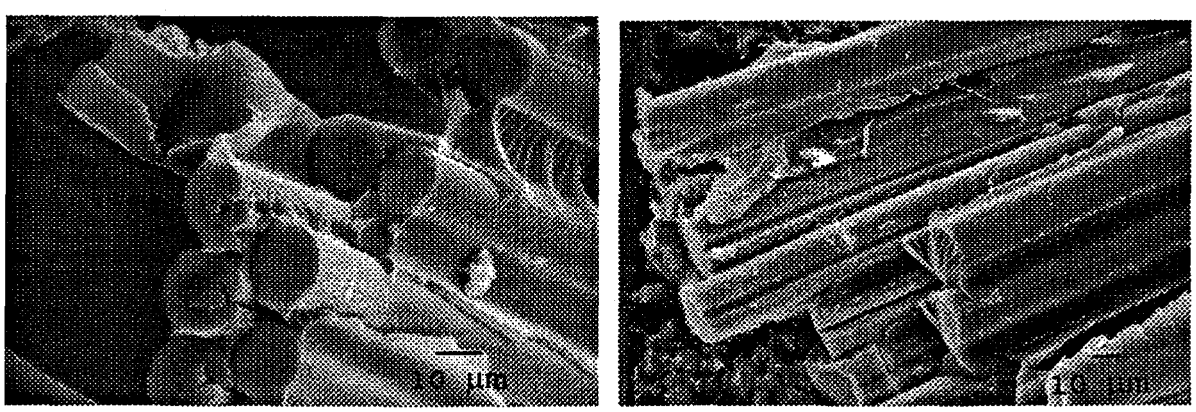
Evaluation of the fracture surface of the sanded and cleaned sample revealed that the failure mode was a mixture of fiber tear of the composite, failure of the interfacial bond and transfer of the near surface resin rich layer. Results for the laser ablated samples are demonstrated in Figure 6. The depth of the ablation obviously increases with the number of pulses as does the amount of adhesive that remains embedded around the fibers. In these micrographs there are very deep canyons created by the ablation which appears to have allowed the adhesive to partially encase the fibers. Upon stressing, failure occurred by a mixture of adhesive being transferred to the composite surface and extensive transfer of glass fibers to the adhesive surface. Since the ablation process seems to have weakened the fibers, lower ultimate strengths were obtained than were achieved with mechanical surface preparation. Samples that received more laser pulses displayed more damage along the failure surface than samples that received fewer pulses.



(A) *(B)*

Figure 7A-B. Failure scar of the composite showing the fiber bundle was penetrated by the adhesive. Failure was often at the fiber - resin interface.

By examining the fibers in the failure coupons several interesting things were noted. Figures 7A-7B show fibers protruding out from the adhesive after being mostly encased by adhesive during the bonding operation demonstrating that fiber exposed by ablation can be used to reinforce the adhesive/adherend interface. Many fibers were found that had transferred from the composite to the adhesive leaving the underside which had been damaged by the ablation visible for inspection.



(A) *(B)*

Figures 8A-B. Transferred fibers embedded in the adhesive. Original surface fibers show cracking. Non-surface fibers do not. Fibers often split.

Consistent with all ablated samples was damage to the top and bottom of surface fibers, however, fiber strands that lay just below the top layer showed no damage (Figure 8A). Also consistently throughout all samples, the damage was limited to a straight line groove cut lengthwise along the axis of the fiber. This is demonstrated in Figure 8B.

CONCLUSIONS

1. Removal of surface contaminates including mold release, grease and particulates can effectively and rapidly be achieved using laser ablation. Removal of the resin rich surface layer of the composite was also demonstrated. These two benefits can be combined to improve the chemical bonding between the adherend and adhesive.

2. Laser ablation is able to increase the surface roughness of the adherend and thus provide a greater contact area.

3. Fiber bridging occurred which allowed composite matrix fibers to extend across the adherend/adhesive interface and thus reinforce the contact plane. This is directly related to the increase in surface roughness.

4. Since glass fibers are mostly transparent, it is possible to ablate the resin while leaving the fibers intact. The laser energy is focused by the glass fiber which acts as a lens concentrating the energy near the back of the fiber. This creates three distinct regions below the fiber. (a) A shielded region of resin which is not ablated. (b) A groove cut into the fiber which runs parallel to the axis of the fiber and along the rear side. (c) A heavily damaged plane of composite resin which extends parallel to the fiber axis beginning at the groove cut in the fiber.

5. It is expected that ablation would work better with carbon or graphite reinforced composites since those fibers would not focus the energy near the fiber surface.

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