COMPARISON BETWEEN LASER TECHNOLOGIES AND ALTERNATIVE PROCESSES ON PAINT AND POLYMER LAYER REMOVAL ON COMPOSITE SUBSTRATE

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Abstract

The application of composites and in particular CFRP (Carbon Fiber Reinforced Polymer) for lightweight construction is a booming market. This material tends to gradually replace metals and alloys in many applications such as automotive, renewable energies, aerospace... Indeed, composite materials combine high mechanical performances, low weight and good corrosion resistance. However this highly technical material requires innovative processes in its manufacture, its machining and its maintenance. Laser processes such as cutting, drilling, surface activation and cleaning can compete with conventional and alternative processes. In this paper, we report on paint and polymer layer removal on CFRP substrate with several laser technologies. In addition we make a comparison with alternative processes such as high pressure waterjet, cryogenic pellet and sodium bicarbonate.

In order to determine the specific advantages and drawbacks of different laser technologies, we compare different laser/matter interaction, thermo-mechanical and photochemical processes. For thermo-mechanical processes, we used IR and green fiber laser, Nd:YAG, CO_2 TEA and a hand-held laser tool used for cleaning paint on metal and pollutants on stone. For photochemical processes, we used and UV fiber laser and an Excimer source. With these, we can compare the results between the use of high pulse energy (J) at low repetition rate (<100Hz) and the use of low pulse energy (µJ-mJ) at high repetition rate (>10kHz). Results are evaluated in terms of feasibility and damage characterization of carbon fiber or epoxy resin.

Introduction

The process of laser cleaning is one of the most popular applications in industry and in the field of architectural preservation or artworks. Indeed, laser technology can remove paint on metal [1-5], traces of pollution on buildings or stone carvings [6-7], the corrosion or oxidation of metals [8-9] and even tile grout [10].

In the scientific literature, few publications are related to the laser cleaning of paint and polymer layer especially on Carbon Fiber Reinforced Polymer (CFRP) [11-12].

In comparison to metals, carbon fiber reinforced plastics (CFRP) are very different material. The close ablation thresholds for the selective ablation of layer (paint and polymer) on CFRP substrate, lead to a technological challenge.

In this regard, the ongoing studies at Alphanov investigate the feasibility of paint and polymer removal on CFRP, their efficiencies with different pulsed laser systems and alternative techniques (high pressure waterjet, cryogenic pellet and sodium bicarbonate).

Many data such as operating parameters, processing speeds, the chemical composition of the paint or polymer film and their thicknesses are subject to confidentiality. We will assess the feasibility of each technique and we compare their effectiveness of their processing speeds.

Experimental

Laser removal processes

For coating removal, the mechanism varies depending on the laser beam characteristics and laser delivery method. However, there are two basic laser coating removal mechanisms: thermo-mechanical and photochemical processes.

<u>Thermo-mechanical</u>

Laser removal can be achieved with pulsed lasers, which create bursts of high intensity energy. One advantage when compared to the continuous wave laser paint stripping process is that the depainting can occur at lower average temperatures. There are different variations of the ablation mechanisms that can be observed depending on the laser beam characteristics, which include power, wavelength, pulse width, pulse frequency, beam profile, and operating parameters.

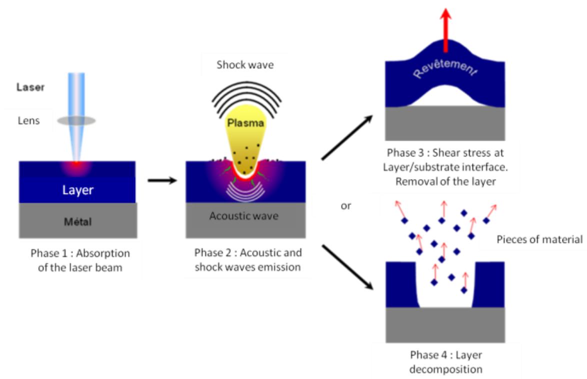

Figure 1. Thermo-mechanical process

On the one hand, the energy is absorbed by the valence electrons, then heat conduction take place and the energy of this "heated electron" to the atomic network. This heat localized, intense and prolonged causes melting and vaporizing the material. The expelled material is mostly in the form of vapors and melted droplets that are found partly on the periphery of the workpiece area. The heat-affected zone (HAZ) extends beyond the dimensions of the laser spot.

This type of interaction was tested with the following sources:

Laser	EOLITE BOREAS IR80	EOLITE BOREAS G30
Wavelength	1030nm	515nm
Pulse width	ns	ns
Energy	µJ-mJ	µJ-mJ
Rep. rate	kHz	kHz

Table 1. Lasers used for ablation process

These laser sources deliver energies below 1 mJ per pulse but can deliver up to 100,000 pulses per second. We try to control the energy deposition to gradually remove the coating while attempting to preserve the composite substrate.

On the other hand, the shock wave can remove the coating and create a crack network in the remaining coating. There are different variations of the ablation mechanisms that can be observed depending on the laser beam characteristics, which include power, wavelength, pulse width, pulse frequency, beam profile, and operating parameters. This type of process requires very high pulse energies.

We used the following laser sources:

Laser	4JET CO_2-TEA	QUANTEL LaserBlast
Wavelength	10,6µm	1064nm
Pulse width	µs	ns
Energy	mJ-J	mJ-J
Rep. rate	Hz	Hz

Table 2. Lasers used for shockwave process

These laser sources deliver pulse energies below 6J but can deliver up to several hundred pulses per second.

<u>Photochemical</u>
The interaction between UV radiation and a polymer organic compound results in a photochemical decomposition of the material, known as photoablation. The energy of the photon is comparable to the covalent bonds of the target material, the absorption of a single photon by an electron valence allows "breaking" a molecular bond.

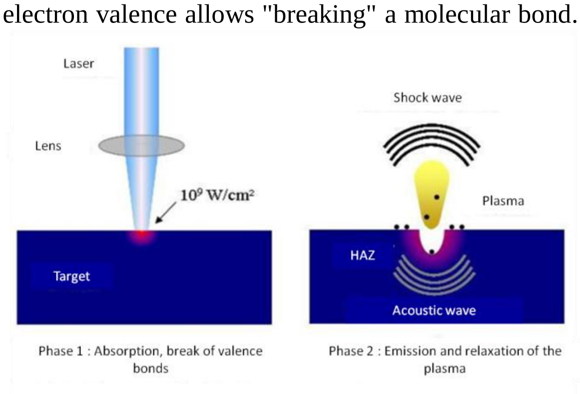

Figure 2. Photochemical process

Beyond a certain number of broken bonds per unit volume, material detaches from the surface and explodes and as a gas of molecular fragments. The expulsion of material at supersonic speed can evacuate the excess energy as kinetic energy and minimize collateral effects on the target. The thickness ablated (0.1-5µm) is precisely controlled according to the wavelength, the fluence and the absorption coefficient of the material.

Depending on the level of absorption of the polymer, the phenomenon photo ablation will get more or less in competition with radiative phenomena or nonradiative relaxation can lead themselves to a local heating of the material.

Most materials absorb more in the UV than in the IR field, the interaction with a UV laser is confined to a thin layer, which provides a better control of the thickness ablated. Finally, the UV is more conducive to a selective ablation because the ablation thresholds are more differentiated between the materials.

This type of interaction was tested with the following sources:

Laser	**EOLITE BOREAS UV14**	**SPECTRA-PHYSICS Excimer**
Wavelength	343nm	248nm
Pulse width	ns	ns
Energy	µJ-mJ	µJ-mJ
Rep. rate	kHz	Hz

Table 3 . Lasers used for photochemical process

It should be noted that the UV nanosecond laser is a laser source delivering pulses at high repetition rate (> 10 kHz), but low energy (<mJ) while Excimer laser sends pulses of high energy (> 100 mJ) but at slower rate (<100Hz).

Alternative processes

Some alternative processes had been evaluated in order to compare with laser-based techniques.

High Pressure Waterjet:

Waterjet stripping uses the impact force of pressurized water to remove a variety of coatings ranging from paints, rubbers, sealants and aerospace adhesives. These coatings may be removed from many different types of substrates including metals, plastics, concrete...

Ultrahigh pressure waterjet stripping involves the use of water at pressures <1200 Bars to mechanically remove coatings. High-pressure pumps force water through specially designed nozzles (diameter 330µm) that direct the high-velocity stream to impinge upon the coated substrate. The kinetic energy of the waterjet physically erodes the coating to expose the underlying substrate surface.

Cryogenic pellet:

Dry ice blasting involves projecting dry ice with high pressure on coated surface.

Cryogenic cleaning is the result of three effects:

1 - Impact effect - caused by the pressure of the air, accelerating the dry ice pellets, can penetrate the coating up to the substrate.

2 - Thermal shock - the difference of temperature between the projected dry ice at -78 ° C and the substrate induce cracks on the coating, without any impact on the cleaned surfaces.

3 - The blast, is the result of passage of solid dry ice in the gaseous state called "sublimation". During impact, the volume of gas generated by the ice is multiplied by 600.

Sodium bicarbonate:

Bicarbonate of soda (or sodium bicarbonate) is a soft blast medium with a less hardness than most plastic abrasives. Compressed air delivers sodium bicarbonate media from a pressure pot to a nozzle. The sodium bicarbonate impacts the coating and removes it.

Experimental protocol

Due to confidentiality agreements, we cannot describe in detail the experimental setup (optical elements, cleaning strategies...).

In order to study the effects of each cleaning techniques, the experimental protocol is based on the following parameters:

- The repetition rate of the laser
- The energy per pulse
- The speed of the laser beam
- The number of passes of the laser beam

It may be preferable to use low repetition rates (i.e. at low average power) to prevent excessive heating that can degrade the quality of cleaning processing and the integrity of the CFRP substrate.

In the case of our study, we firstly used low rates in order to optimize the quality of stripping. Then, we increase the rate to reduce the cycle time (if the high rate does not damage the composite substrate).

The speed of the laser beam is an essential parameter (as the number of passes). This allows adjusting the amount of energy deposited on the coating. The optimal speed is directly related to the laser repetition rate, the pulse, the diameter of the focused beam and the material's ability to react to the amount of energy.

The speed of the laser beam determines, together with the repetition rate and beam diameter on its focus position, determines the overlap between consecutive laser pulses.

We must point out that the study of the influence of each process parameters has led to make several hundred trials for each etching solution. We present only successful results, where the epoxy matrix of the substrate is not damaged. If the removal process cannot keep the integrity of CFRP substrate (damaged on epoxy matrix, melted zones or broken fibers), we present typical results of processed area.

Coated samples

As for the experimental setup, we cannot describe neither the exact composition of the layer we have to remove nor their thicknesses. We can only note that paint layer is much thinner than polymer one.

The samples of our experiments are composed by:

- Substrate : carbon fibers into an epoxy resin
- Layer : Paint or Polymer film

Figure 3. Thermo-mechanical processing

The paint and the polymer film are composed by organic polymer (as the substrate). So the ablation thresholds of these layers are very close compared to metal or stone as a base material.

The main objective of this study is to find the best compromise between the different operating parameters (laser, energy, speed) to obtain a complete stripping of the substrate without altering the surface.

Results with thermo-mechanical laser processes

Cleaning by ablation processing

On this part, we discuss on paint and polymer removal with laser sources able to deliver energies below 1 mJ per pulse but can deliver up to 100,000 pulses per second. We try to control the energy deposition to gradually remove the coating while attempting to preserve the composite substrate.

Both of these laser sources are nanosecond pulsed laser.

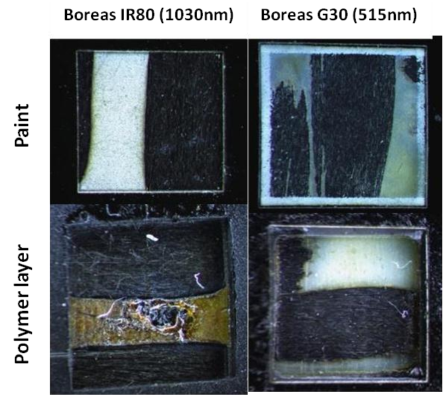

Figure 4. Paint and polymer stripping on CFRP by ablation processing – 5x5mm² processed area (binocular microscope)

We can notice on this picture that both of these lasers have given good results on paint removal on CFRP. The substrate was not damaged by the laser beam. However, some fibers were affected during stripping with IR wavelength (1030nm).

Regarding the polymer layer, the results are more contrasted than for paint removal. Only the IR laser induced strong damages to the CFRP substrate. Some fibers were broken and have been found outside the polymer matrix of the substrate.

Cleaning by shockwave processing

On this part, we discuss on paint and polymer removal with laser sources able to generate pulse energies below 6J but can deliver up to several hundred pulses per second.

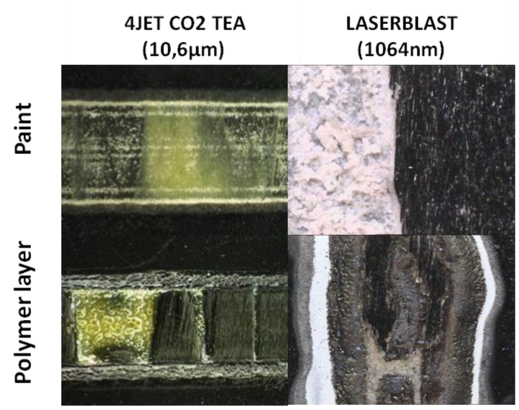

Figure 5. Paint and polymer stripping on CFRP by shockwave processing – 5mm width processed area (binocular microscope)

With these laser sources, the use of high-energy pulses has not led to form a shock wave sufficiently effective to separate the coating (paint or polymer film) without damaging the substrate CFRP. Theses layers could be removed but a lot of carbon fibres have been broken and the substrate has a high roughness.

By comparing the results of two thermo-mechanical processes (ablation and shock wave), we note that it is preferable to use lower pulse energies but at a high repetition rate (ablation process).

The boundary between damaged and undamaged CFRP substrate is very thin. A small change on process parameters may lead to get different qualitative results.

If we consider the absorption spectrum of epoxy resin, we can note that epoxy resin is almost transparent (~0%) for wavelength above 515nm.

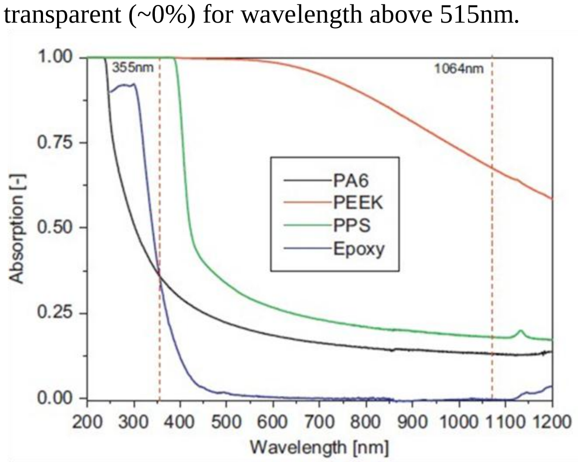

Figure 6. Absorption spectrum of epoxy resin

This means that it is the carbon fibers that absorb the entire incident laser radiation. If the carbon fiber received a huge amount of energy, the excessive heat is conduct through the fiber and destroys the polymer matrix of CFRP incidentally. Small pulse energies remove small thickness of layer. CFRP substrate is reached by multiplying the number of passes.

Results with photochemical laser processes

We focus on this part on paint and polymer removal with UV laser sources able to deliver pulses at high repetition rate (> 10 kHz), but low energy (<mJ) while Excimer laser sends pulses of high energy (> 100 mJ) but at slower rate (<100Hz).

Both of these laser sources are nanosecond pulsed laser.

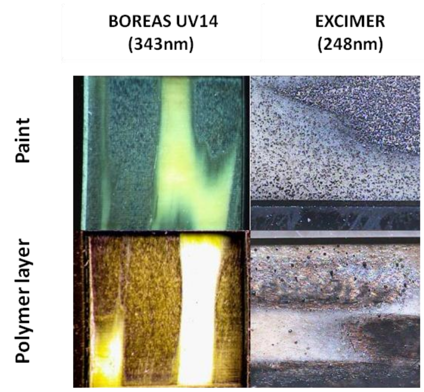

Figure 7. Paint and polymer stripping on CFRP by photochemical processing – 5x5mm² processed area (binocular microscopy)

We can note that UV laser with low pulse energies at high repetition rate gave very good results on paint as well as on polymer layer removal. CFRP substrate is not damaged.

UV process can removed very small thickness of layer, the substrate can be reach very smoothly in order to prevent any damages. Epoxy resin absorbs ~90% of 343nm wavelength, a very small part of incident energy reaches the carbon fiber. The heat generated is not sufficient to destroy the epoxy matrix incidentally.

Excimer laser, with very high pulse energies at low repetition rate can't reach the same quality. Paint removal is more efficient than for polymer film. This is probably due to the lower thickness of the paint. Some attached residues were left on the surface of CFRP substrate.

Results with alternative media

On this last part of our results, we discussed about paint and polymer with alternative techniques such as high pressure waterjet, cryogenic pellet and sodium bicarbonate.

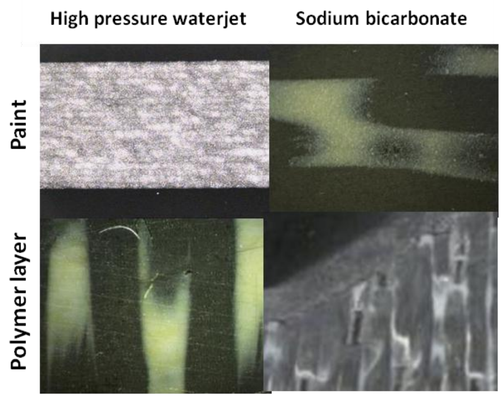

Figure 8. Paint and polymer stripping on CFRP by alternative processing

Cryogenic pellet technology was not efficient on paint and polymer film removal. The thermal shock and the impact effect were not sufficient and let coatings intact.

High pressure waterjet gave very good results only on polymer removal. The substrate is not damaged and the processing speed is one of the best of this study. Some delaminations have been reported but this is not a significant damage. For paint removal, high pressure waterjet is not efficient. Some residues still attached on CFRP.

Contrary to high pressure waterjet, sodium bicarbonate processing induce very good quality on paint removal with very smooth CFRP substrate but not efficient on polymer layer. The epoxy matrix of CFRP sample is damaged by this abrasive processing.

Conclusion

In order to summarize results of each removal technologies (thermo-mechanical, photochemical and alternative processes) in terms of quality reach (no visible damages on CFRP surface), we put it on a table:

		Paint	PU
Thermo-mechanical	BOREAS IR	☺	☹
	BOREAS Green	☺	☺
	CO2 TEA	☹	☹
	Laserblast	☹	☹
Photochemical	BOREAS UV	☺	☺
	Excimer	😐	☹
Alternative	Waterjet	☹	☺
	Sodium bicarbonate	☺	☹
	Cryogenic pellet	☹	☹

- Best results were given by laser sources with low pulse energies at high repetition rate with short wavelength (≤ 515nm). The high absorption of epoxy matrix at these wavelengths reduces heat accumulation on carbon fibers that could lead to matrix degradation.

- The more versatile solutions for paint and polymer film on CFRP sample are nanosecond fiber laser at visible and UV wavelength (515 and 343nm).

- The high pulse energies cause damage due to shock waves and are therefore not pplied for paint and polymer film removal on CFRP substrates.

- With alternative techniques, none of these technologies can remove paint <u>and</u> polymer film on CFRP samples.

- High pressure waterjet is the most efficient solution for polymer film but it is unusable for such paint. No CFRP degradation was reported.

- Sodium bicarbonate can remove efficiently paint on CFRP with no damage on CFRP samples. Nevertheless, this solution induced intense surface damage when it is used for polymer film removal.

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Meet the Author(s)

Charly Loumena studied physics and laser/matter interactions at the University of Bordeaux. Since 2008, he worked as a development engineer in laser micromachining at Optical and Laser Technological Center of the Route des Lasers Competitiveness Cluster ALPHANOV. The main topics are related to short (nanosecond) and ultrashort (femtosecond) laser processing in many fields such as thin film solar cells, ceramic matrix composite, organic matrix composite. He has collaborated on few scientific and technical papers.

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