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Short Review on Laser Texturing and Cleaning Carbon Fibre Composites for Aerospace Applications

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ABSTRACT

Carbon fibre reinforced polymer composites are increasingly being used in aircrafts especially for wing and tail components and automotive applications. Surface wettability of these thermoplastic composites is poor due to low surface energies causing difficulty in the surface painting process where necessary. To achieve durable painting the composite surface needs pre- treatment to modify the surface wettability, to remove surface contaminants, and loose, friable surfaces for better paint adhesion. Conventional surface treatments such as sand blasting, mechanical abrasion and chemical etching may cause delamination defects and damage to the brittle fibers affecting service life of the bulk composite. These methods also present occupational health, safety and environmental risks. This article reviewed texturing and cleaning of polymer, composites and metallic surfaces for enhancing adhesion performance in general and, in particular, the laser texturing and cleaning which is a potential substitute to conventional surface modification techniques of composites.

Key Words: **laser texturing, surface treatment, carbon fiber composites.**

1. INTRODUCTION

Paint deposition onto a substrate is important for a number of industrial processes protecting the substrate from corrosion and wear. Painting and many other coating processes such as electrolytic and chemical plating, physical deposition and chemical vapor deposition (CVD) require the substrate surface to have a texture to allow the deposit firmly held and enhance adhesion. This is particularly necessary for polymer matrix carbon fibre composites as many polymers exhibit low adhesion characteristics [1, 2]. Texturing can provide increased surface area and provide a bond through mechanical locking of the paint to a composite. The ultimate goal of the surface treatment is to modify a thin layer at the surface to obtain more favorable chemical and morphological structure for paint adhesion without affecting the bulk properties.

Wide range of contaminants can be found on the composite surfaces and by their nature may form weak boundary layer under the paint [3]. Various techniques have been used to clean contaminants and provide a textured surface such as sand or grit blasting, chemical cleaning or treatment to etch the surface with acid and other corrosive type materials. Many of these cleaning and/or texturing processes are not commercially suitable due to high cost and serious environmental concerns owing to the use of dangerous substances which often require safe handling and environmental disposal after use. Once the surface has been cleaned and structured, the desired deposition material is normally applied by any conventional method including brushing, spraying, dipping, roll coating, electrostatic coating or immersion.

Laser texturing is a potential substitute to conventional surface modification techniques in some applications. Virtually any type of material can be processed using short pulsed lasers without contamination and damage to the substrate. In laser texturing process a focused laser beam is used to ablate a microlayer of the surface in a controlled way in order to alter the surface morphology or produce local melting and controlled surface microwaviness. The latter is particularly valuable since previous studies have demonstrated that controllable micro- or nano-roughness enhances the adhesion of subsequntly applied layers. This article reviews texturing and cleaning of polymers, composites and metallic surfaces for enhancing adhesion performance in general and the laser texturing and cleaning of composites in particular.

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2. SURFACE PREPARATION FOR ADHESION PERFORMANCE

Objectives in surface treatment for improved adhesion of surfaces can be described as follows:

1. Cleaning of surface contaminants
2. Increasing surface free energy for improved wettability
3. Increasing surface roughness for improved mechanical interlocking or bondable surface area

Contaminants can be found on the composite surfaces and by their nature form a weak boundary layer in a bond. These contaminants include silicones from release agents and bagging materials, fluorocarbon release sprays and films, machining oils, fingerprints and components in the composite itself which have migrated to the surface, such as calcium stearate from self-releasing formulations, water and plasticizers. Table 1 gives evidence of chemical contamination by fluorine species (30%) for epoxy/carbon composite surface [4].

Table 1. Chemical composition (%) of carbon/epoxy composite surface [4]

	C	O	N	F	Si	S	O/C
Carbon/Epoxy	56.4	8.1	1.5	32.2	1.8	-	0.14

Table 2. Roughness and surface free energy of bare surfaces [4]

	Roughness Ra (µm)	γ^{LW} (mJ/m^2)	γ^{AB} (mJ/m^2)	γ^{TOT} (mJ/m^2)
Glass/Epoxy	0.79 (±0.08)	31.6 (±1.11)	2.36 (±0.42)	33.96 (±1.51)
Carbon/Epoxy	0.81 (±0.17)	38.54 (±0.9)	1.13 (±0.17)	39.67 (±1)

Composites usually have very smooth and glossy moulded surfaces due to the use of fluorinated film as mold release agent in manufacturing, Table 2 [4]. Surface energies of composites tend to be low, Table 2, especially for the thermoplastic matrices making wetting of the surfaces difficult. To achieve durable painting the composite surface needs pre- treatment to modify the surface wettability and morphology and remove surface contaminants for better paint adhesion.

2.1. Surface Treatment Methods

Various chemical, mechanical and energetic surface treatment methods have been evaluated for the treatment of plastics and metals for bonding. These evaluations may also give indication of feasibility of their application to the surface preparation of fibre reinforced composite for painting process. Some techniques are summarized in Table 3.

Table 3. Surface pretreatment methods

Mechanical	Energetic	Chemical
Alumina grit blast	Corona discharge	Solvent Cleaning
Cryoblast	Plasma	Detergent Wash
Sodablast	Flame	Acid Etch
Peel ply	Excimer Laser	Primer
SiC abrasion		

2.1.1 Energetic Treatment Methods

Corona discharge technique uses energetic species in an electrical discharge produced from ionized air by applying high voltage between two electrodes above the treated surface. This process introduces chemical modification of the thermoplastic composites surfaces and increases wettability [5]. The aim is to improve interfacial contact and intrinsic adhesion for bonding using adhesives technology. The surface energy level and consequently the wettability of the electrical discharge treated thermoplastic composite can be increased (80º to ~5º water contact angle decrease) giving improved adhesion. The improved bond performance is related to chemical modification of the surfaces by increased type and concentration of oxygen containing groups released by X-ray photoelectron spectroscopy [5].

Plasma treatment has been increasingly used to modify the surface characteristics producing hydrophobic or hydrophilic surfaces on polymers and metals. Plasma is an ionised gas containing both charged and neutral particles, such as electrons, ions, atoms, molecules and radicals. The treatment of composite materials by means of cold plasma increases surface wetting properties as well as improving mechanical strength in terms of adhesion between fibres and matrix [6]. The method used for surface activation of polymers allows the modification of surface characteristics to obtain improved bonding without affecting bulk properties [7]. Plasma causes ablation of both molecular layers and organic residues from the polymer surfaces and reported to produce an increase in surface's roughness [8]. This important phenomenon has been exploited for adhesive purposes through roughening the surface to increase the number of chemical links between coating and substrate. The cold plasma treatment of polupropylene surfaces to improve wettability and adhesion properties have been widely studied topic. The water contact angle of the cold plasma treated samples using air gas can be reduced by 30 %. Samples painted with or without without using a primer can give a good adhesion of the paint film. Therefore, it represents an efficient, clean and economic alternative to activate polymeric surfaces.

Various other studies have shown reactive energetic species in plasma such as ions and electrons formed from the gas interact with the surface and cause chemical changes [9,10]. The oxygen plasma treatment to improve adhesion bonding performance of the thermoplastic matrix composites gives much better bonding as compared to sand blasting using 150 µm particles, but comparable to chromic/sulphiric acid etching [9]. Figure 1 shows analysis of the plasma-treated surface, by SEM. The main effects of the treatment is increased surface roughness and carbonyl content. The plasma will not remove silicone release agent. The plasma treatment is more controllable than acid etching because the chromic acid is very aggressive and can rapidly etch away the composite surface, Figure 1.

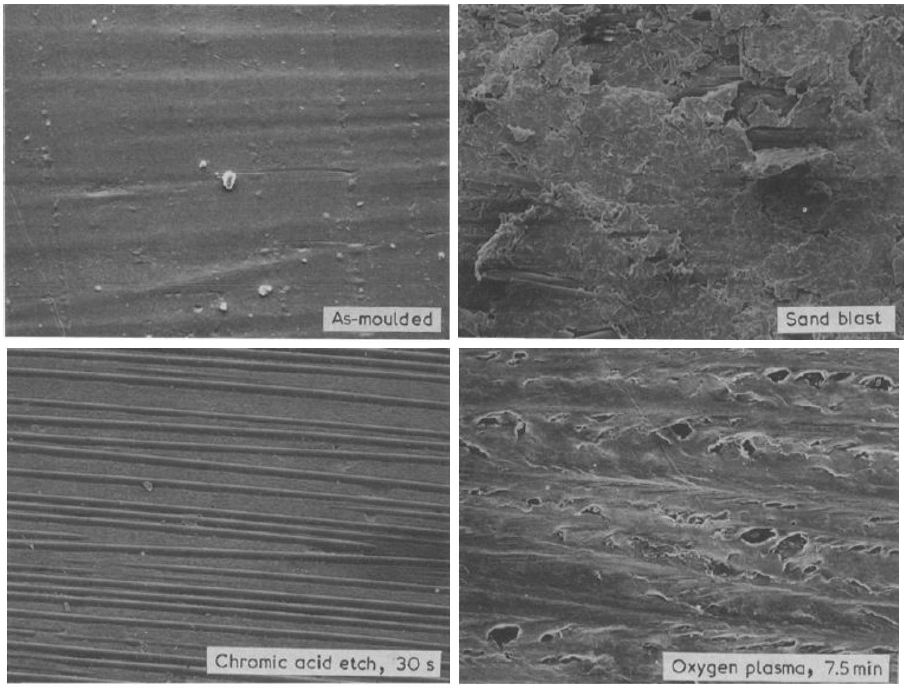

Figure 1. SEM images of the surface before and after treatment [9]

Surface modification of polyolefin automobile bumpers by using microwave technology with plasma treatment has also been shown to enhance wettability and paint adhesion properties [11]. The surface is degreased in detergent solution followed by cleaning with propanol before oxygen plasma treatment and microwave power. Figure 2 demonstrates the oxygen plasma treatment induced hydrophilic effect where the water contact angle is decreased significantly (from 70 to 30º) for the oxygen plasma-treated polyolefin samples. The hydrophilic effect is attributed to increased oxygen functional groups such as O-H and C-O-C on the polyolefin surface with microwave plasma treatment using oxygen gas. Adhesion tests of the plasma treated samples painted without the use of a primer showed improved adhesion [11].

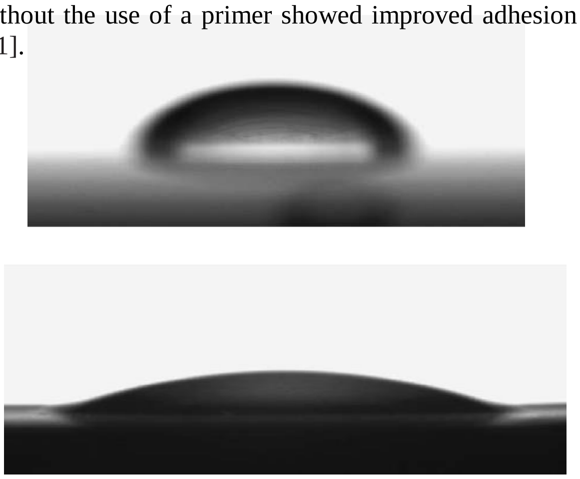

Figure 2. The contact angle of a water droplet on non-treated (a) and plasma treated polyolefin samples [11]

2.1.2. Mechanical Treatment Methods

Of the mechanical surface treatment methods peel ply is one of the more common surface pretreatments for composite bonding [12, 13]. A peel ply is a layer of nylon or polyester fabric incorporated in the surface of a composite during its manufacture stripped off the surface immediately before bonding giving a rough and clean surface [13]. Several peel plies have allowed increase in surface roughness and surface cleaning efficiency and chemical modification [4]. Contact angle values also exhibited a sharp decrease resulting from peel ply use corresponding to increase of surface free energy, mostly due to the roughening of the composite surface as well as surface cleaning. Common surface contaminants like fluorinated or siliconed species are completely removed from the composite surface after peel ply treatment [4]. The surface cleaning and roughening lead to improved adhesion as evidenced by an increase of single lap shear values correlated with the increase in surface free energy.

Crane et al [12] studied the effect of a variety of mechanical surface treatments, including a peel ply, on the wetting and bonding behaviour of carbon/epoxy composite surfaces. The treatments investigated included nylon and Nomex peel ply, and silicon carbide paper abrasion. It was found that the surface energy of the composite was approximately doubled from 30 x 10^{-5} to around 60 x 10^{-5} mJ m $^{-2}$. A 25% improvement in lap shear strength over untreated carbon/epoxy was noted for the sanded samples, but no improvement in strength' was shown for the peel ply treated composites indicating no direct correlation with surface energy. Main problems with peel plies is the cross-transfer of contamination or release agents on the ply to the composite. The morphology of the surface obtained using a peel ply is a very regular imprint of the weave of the fabric used, Figure. 3.

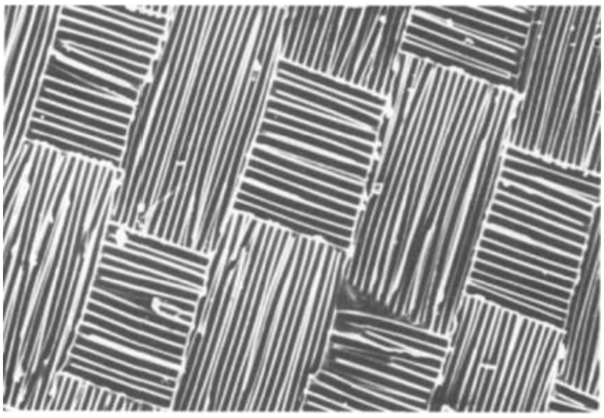

Figure 3. SEM micrograph of peel ply treated carbon/epoxy composite [14]

Alumina grit-blasting has also been suggested as a good mechanical surface treatment for carbon/epoxy composite [15]. The effect of alumina gritblasting is to modify the morphology of the surface and also to remove some surface contamination. The roughness introduced by the treatment will also affect the wetting of the composite. The variables in grit-blasting are the size of alumina grit, the blast pressure, the treatment time, theblast angle and the distance from the blast nozzle to the surface. Fibre damage can occur with most carbon- and glass-reinforced composites, even at low blast pressures and short treatment times as shown in Figure 4 [14]. Similarly silicon carbide abrasion also causes visible damage to carbon and glass fibres in the composite.

Figure 4. SEM micrograph of alumina gritblasted carborVepoxy composite (magnification 300X) [14]

Parker and Waghorne have studied the effectiveness of mechanical treatments at removing chemical contaminants such as fluorocarbons and silicones from carbon/epoxy surfaces [16]. Alumina gritblasting and silicon carbide abrasion were found to be superior to Scotchbrite abrasion but no technique completely removed all contaminants. The direct effect, therefore, of the mechanical treatments on adhesion properties was confused by the detrimental effect of residual contamination, although the best joint strengths were obtained for grit-blasted substrates.

3. LASER SURFACE TREATMENT

Lasers have been used for cleaning polymer surfaces, micro-fabricating of polymers by ablation, precise cutting. The geometry and dimensions of laser produced features are highly controllable using process parameters, including laser intensity, pulse length and shape, scanning speed and laser shot superposition. In order to optimize the surface characteristics, laser treatment allows partial or complete removing of the superficial polymeric layer without affecting the fiber reinforcement [17-20]. By selecting suitable laser parameters (number of pulse, laser fluence), a fully controlled ablation of the superficial polymer layer can be obtained.

Laser texturing can be performed by individual laser shots or by a mask with a desired pattern. The intensity and interaction time of the laser beam determine the textured volume at the surface which usually changes from a few nanometres to micrometers. Ultrashort pulsed lasers are mostly used, since they facilitate surface modification without changing the bulk properties of the base material. Laser texturing also offers competitive advantages over conventional sandblasting and chemical treatments due to ease of automation, elimination of effluent, lack of contamination and ability for processing three-dimensional parts.

UV lasers are more suitable for polymers as most organic materials adsorb UV radiation, creating photochemical reactions on the surface of the polymer only several molecular layers deep without damaging the bulk polymer [14]. The UV laser etching was, thus, used as a pre-adhesion surface treatment [9, 17-20] with the advantages of chemical and morphological modification and cleaning of the polymer surface with minimal fiber damage.

Excimer laser treatment to control the adhesion performances of glass/epoxy and carbon/epoxy composites can provide a complete cleaning of the surface can be reached after only one laser pulse, Table 4 [20]. This evidenced by the complete removal of fluorine contamination. Three different ablation stages are; weak ablation (150 mJ/m2 – 40 pulses), medium ablation (150 mJ/m2 – 400 pulses) and total ablation (500 mJ/m2 – 500 pulses).

Table 4. Chemical composition (%) of epoxy matrix surface determined with ESCA analyses [20]

	C	O	N	F	Si	S	O/C
Bare surface	56.4	8.1	1.5	32.2	1.8	T	0.14
50 mJ/cm2 – 1 pulse	80.4	12.5	5.6	0.7	0.5	0.5	0.16
150 mJ/cm2 – 4 pulses	76.4	16.9	4.2	-	1.5	-	0.22
150 mJ/cm2 – 10 pulses	78.6	15.9	3.6	-	1.1	-	0.2
150 mJ/cm2 – 40 pulses	77.8	16	5.4	T	-	0.8	0.21
150 mJ/cm2 – 400 pulses	77.4	16.9	5	-	-	0.7	0.22
500 mJ/cm2 – 40 pulses	75.3–	15.7	5.8	-	1.9	1.1	0.21

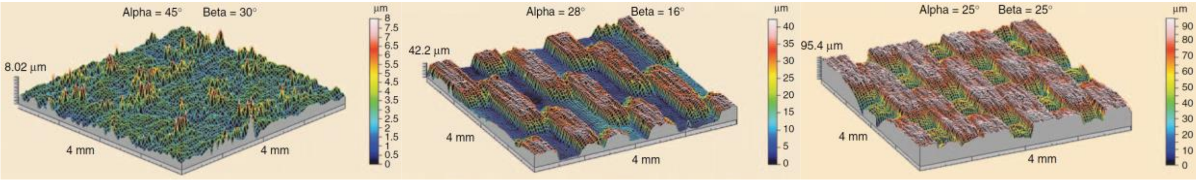

Figure 5 Surface profilometry and average roughness of glass/epoxy surfaces treated with different excimer laser beams conditions: (a) 150 mJ/cm^2 –40 pulses (Sa0.6 µm). (b) 150 mJ/cm^2–400 pulses (Sa13.1 µm). (c) 500 mJ/cm^2–500 pulses (Sa17.2 µm) [20].

The weak ablation mode only provides a surface cleaning with no protrusion of fiber reinforcement or surface roughening, Figure5. The medium ablation rate gives a rough surface which is composed of both fiber reinforcement and epoxy matrix (Figure 3(b)). Finally, the total ablation mode exhibits a complete removal of matrix; the residual surface is then composed only of the fiber reinforcement's weaving. Laser treatment of these composites exhibits high adhesion performance evidenced by single lap shear tests. The slight fiber protruding obtained on exposing the composites to UV laser irradiation leads to a great increase of lap shear value (approx 30% increase) providing a high performance quality of bonding [20]. However lap shear values decrease on the extreme laser treatment due to weak boundry layer between superficial fibers exposed to laser beam. This is evidenced by the SEM observations confirming completely ripped off reinforcing fibers. The unlinked remaining fibers causes the premature rupture for such totally ablated samples.

ArF Excimer laser operating at deep UV wavelength (i.e. 193 nm) is shown to enhance adhesion strength by 250% and 450% compared with SiC abrasion treatment and non-treated surfaces respectively [17,18]. This method can effectively be used for various thermoplastic composites and some metallic materials. Laser-treated surfaces induces have chemical changes depending on the fluence on the surface identified by FTIR spectra and XPS analysis [17]. Various contaminants such as Mg and Si present at the non-treated surfaces has been totally

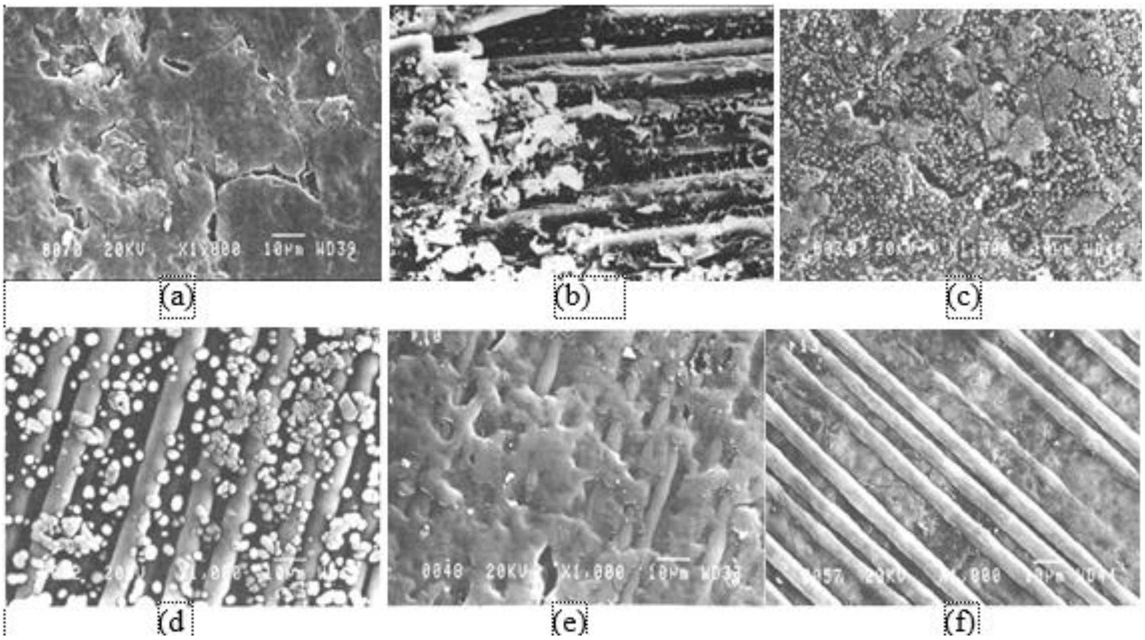

Figure 6. SEM micrographs o f PEEK composite surface after treatment at various parameters (a) non-treated. (b) Sic-abraded. (c) laser-treated: 0.18 J/ cm^2, 50 P, (d) 0.18J/ cm^2. 100 P. (e) 1 J/ cm^2, 10 P. (f) 6 J/ cm^2. 10 P [17].

removed with the laser treatment. The improved adhesion can be correlated with the roughening of surfaces, chemical modification, and removal of contaminants. The failure mode is then changed from adhesive to cohesive following laser treatment indicating the improved interfacial adhesion. However effectiveness of the treatment can be reduced above optimum energies and the number of pulses due to ablation and carbonization of the surface [18]. Mechanical properties of the laser treated substrates remains unchanged as the microstructural changes occurred only at superficial outer layers, Figure 6.

SEM micrographs of the nontreated and SiC-abraded PEEK composite adherend are shown in Figure 6.a and b. The surface of the abraded adherent 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 6c-f. Effective ablation threshold for the PEEK composite was found to be 0.42 J/cm^2 [23]. Below this value removal of the matrix in the surface region occurs and with high number of pulses rounded granules are formed on the surface. The formation of granules can significantly enlarge the surface area and contribute to better mechanical interlocking of the adhesive to the adherend [16]. Once the matrix is removed, the bare fibers are immune to etching. Above the ablation threshold the composite fibers are observed to etch smoothly. Microparticles and debris redeposit onto the surface leaving a dust-like texture. When the ablation threshold was greatly exceeded, fibers are thinned and buckled, Figure 6.

Excimer laser surface treatment of glass fiber reinforced epoxy polymer composite used by Park et al.[21] was shown to enhance adhesion. The enhanced adhesion mechanism is due to changes by oxidation (from chain of hydrocarbon to polar groups such as carbonyl and hydroxyl) in chemical structure when the treatment is carried out below ablation threshold. The increased surface roughness obtained with ablation above the ablation threshold also greatly contributes the adhesion enhancement. At high energy density, the ablation causes instant fragmentation of polymeric chains, resulting in no oxidation of the surface [24]. Dependence of ablation rate of the epoxy matrix with number of pulses and laser energy density, Figure 7, means the process can be controlled by selective ablation of epoxy matrix with optimised parameters.

Surface modification of silicon and PTFE using 4th harmonic pulsed Nd:YAG laser (266 nm) is also used to improve wettability and adhesion characteristics [25]. The surfaces treated by Nd:YAG laser irradiation is roughened and the hydrophobicity of silicon and PTFE surface is modified into hydrophilicity. The increased surface roughness proportional to the increase in wettability also improves the adhesion strength of copper spray thin film deposited using Ar$^+$ laser beam. The improved adhesion is again connected with the oxygen enrichment of the laser treated surfaces. The increased wettability and surface free energy and high percentage of oxygen functional groups through UV laser surface treatment of polymers was also observed by Gotoh et al [22]. The increased wettability and the surface free energy is primarily due to increase in surface oxygen concentration, but the topographical changes may contribute as the surface roughness of UV laser treated PET samples is observed to increase [22]. Laser texturing is also used for pre-adhesive bonding surface treatment of metallic surfaces to enhance adhesion performance by producing microscopic wavy surface morphologies and nanoscopic surface roughness [26]. Similarly texturing of denital surfaces using lasers has been reported to improve bond strength in composite bonding process to these surfaces [27].

4. Other Approaches

Gas ions has also been used for surface treatment to improve adhesion bonding for preparing the surface of a low adhesion substrates, such as a fluoropolymer [28]. A disbursed layer of fine mesh particles is applied to the surface of a polymer in a controlled fashion by dusting, brushing, or more sophisticated techniques, such as those used for microvoid latex coatings to produce masks, Figure 8.

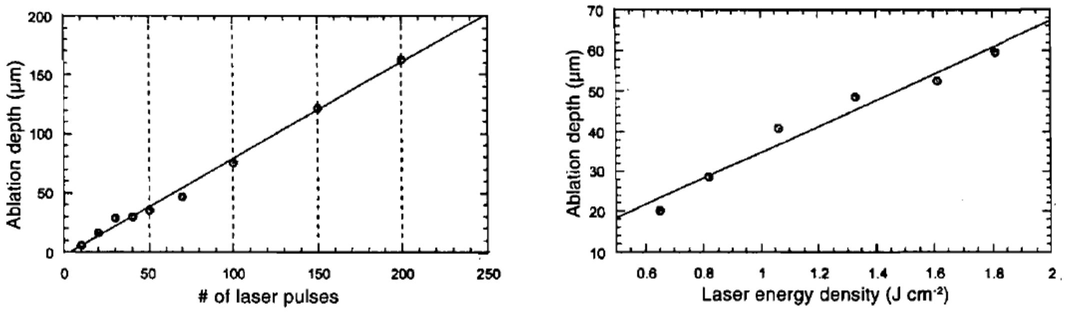

Figure 7. Depths of matrix ablation, (a) as a function of the number of pulses, energy density – 1.01 Jcm^{-2}, pulse frequency – 5 Hz and (b) laser energy density, number of pulses – 50, pulse frequency – 5 Hz, showing linear relationship [21]

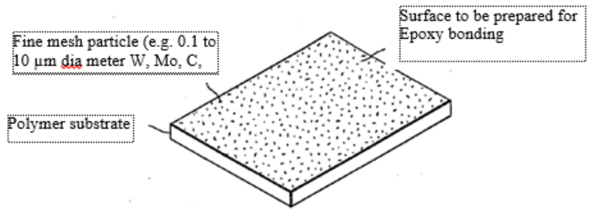

Figure 8. Schematic of polymeric material with low adhesion surface characteristics with randomly distributed surface fine mesh particles [28]

The masked surface is then treated by impinging gas ions located in a vacuum system, Figure 9. The resultant textured surface takes the form of pillars whose vertical dimensions are similar to the masking particles. The etch time ranges from seconds to hours, depending on the surface roughening desired. After ion beam processing the masked particles are removed by washing or dissolving.

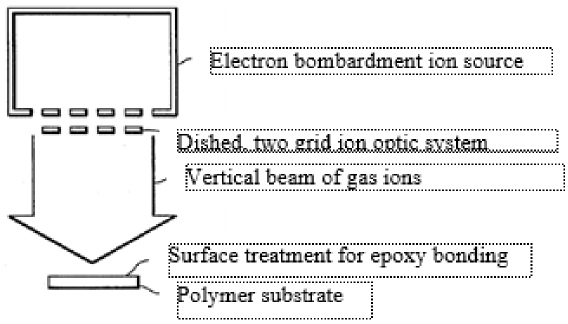

Figure 9. Schematic view of the ion beam texturing apparatus used to texture the surfaces of the polymers [28]

This methods was used to texture a fluorocarbon polymer, known commercially as Teflon [28]. The bonded joints tensile yield strengths has significantly increased (in excess of 2,000 psi) as compared to untreated Teflon (less than 180 psi). It is reported that the ion beam textured surfaces produces stronger bond joints than by chemical etch processes.

In another similar approach [29] the particles used to provide texture effects are maintained and the coating is applied on to the particles. In this process a substrate to be structured for a subsequent deposition process is initially coated with two layers of controlled size spheres where the first layer is smaller in diameter than the second layer. The substrate is then heated to melt the first layer of spheres embedding the second layer spheres. The process gives a textured surface corresponding to the shape of embedded spheres. The textured substrate is then ready for the deposition process with any suitable material to form the desired end product. The second layer spheres should necessarily have a higher melting point than the first layer spheres to avoid reflow.

RF sputtering of polymers without masking has also been used to modify surfaces for bond adhesion [30]. The surface texture, resulting from the sputtering, is controlled only by the chemical nature of the substrate, RF forward power density, and etch time. This process is referred to as natural texturing. Prior to this, Hoepfner [31] described the photolithographic process which utilizes layers or laminates for masking purposes. The masked material is removed by ion bombardment. More recently a different process [32] reported for microalloying and texturing applied on a composite material using laser beam for surface treatment. In this method an alloy micro-powder containing film is sprayed on a composite roller surface. The alloy micro-powder containing film is subsequently melted into the base material to form a new alloy material. The fused film in the substrate and forms textured pits. The method has the advantages of surface microalloying for wear-resistance performances besides deeper textured pits, increased boss height with better control of texturing as compared with the prior laser texturing method.

5. CONCLUSIONS

Different surface treatment methods to improve adhesion performance of composite materials have been evaluated. Surface contaminations originating from manufacturing process, smooth surfaces, low surface energies and wettability impairs the adhesive behaviour the composites. The surface pretreatment of composite materials is important for painting. It is necessary to limit the changes to a thin surface layer to preserve the bulk material properties whilst achieving the above objectives. Particularly composite materials require special considerations when treating their surfaces. There is a danger that some treatments may cause delamination defects just below the surface or damage to the relatively brittle fibres. These defects may result in poorer mechanical properties of the composite.

Important factors to be considered include removing surface contamination such as silicones and fluorocarbons. The bulk mechanical properties of the composite can be affected by abrasive surface treatments like alumina grit-blasting and silicon carbide abrasion. Corona discharge and plasma treatments will cause chemical changes and roughening of the composite surfaces. These methods also introduce oxygen functional groups onto the composite surface, resulting in improved wetting of the surface.

The UV laser irradiation as a surface treatment is effective and has advantages compared to other conventional treatments such as chemical etching, abrasive blasting and plasma treatments. Laser treatment allows partial or complete removing of the superficial polymeric layer without affecting the fiber reinforcement. Excimer laser treatment has been used for composite surfaces to control adhesion performances. The laser parameters (laser fluence, number of pulses) have to be carefully selected to achieve suitable surface characteristics. The general phenomena observed due to laser treatment are surface cleaning by removal of contamination and weak boundary layers through evaporation, modification of surface chemistry by imposing oxide derivatives and hydroxides, and change of surface morphology by introduction of uniform roughness. Consequently, important considerations such as cleanliness, mechanical interlocking, chemical attraction and wettability affecting the adhesion performance can all be satisfied for by laser treatment method.

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