PLASMA SURFACE ENGINEERING OF FIBER REINFORCED COMPOSITES FOR THE REMOVAL OF CONTAMINANTS AND IMPROVEMENT OF ADHESIVE JOINT STRENGTH

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Abstract

Over the past few decades, the automotive and aerospace industries have shown increased interest in carbon fiber reinforced plastic composite (CFRP) materials due to their light weight and low production cost. However, these composite materials exhibit poor performance in structural applications due to the weak interface when bonded to other dissimilar materials, such as adhesives, metals and polymers. As carbon-based materials, CFRPs have low surface energy that presents bonding challenges. Surface residual contaminants originating in mold release materials or handling also contribute to poor adhesive joint strength.

Treatment under atmospheric pressure plasmas (APPs) has emerged as an alternative solution to engineer composite surfaces without affecting the bulk properties of the materials. The technology utilizes a dry gaseous medium and does not involve any harsh liquid solvent chemistries. APPs contain gaseous species that can react and remove organic surface contaminants very rapidly. Furthermore, they can be instrumental in the chemical functionalization and activation of the surface through the grafting of oxygen-based polar groups. Literature references report the increase of surface energy, improved fracture toughness and increase of adhesive strength due to the APP treatment. In this paper, the details of the application of atmospheric-pressure plasma processes on fiber reinforced composites and results from the improved mold release and adhesive strength due to the application of Openair® plasmas are presented.

Background

The materials used in the automotive industry can be very complex and involve the synergy of several types of dissimilar materials. In the past, some of these materials were mechanically bonded but recent requirements for light-weighting have led to the adoption of adhesive materials. Besides the reduced structural weight, adhesively bonded materials offer many advantages, such as increased joint stiffness and improved resistance to fatigue. Specifically, adhesively bonded joints in polymeric composite structures are capable of bonding thick layers to thin layers without distortion, reduce the levels of localized stress forces that are present in mechanical joints and allow the bonding of different types of materials [1]. Overall, the cost advantage is significant due to lower material cost and reduced manual labor.

Factors Affecting Surface Adhesion in Polymer Composites

Surface Energy

The selection of the optimum adhesive for a particular set of materials that need to be joined together, as well as the interfacial properties are critical for its performance. The ability to form a bond between two materials is mainly dependent on the chemical composition of the two components as well as their surface topography. The chemical bonds that are formed can be either primary (covalent, ionic, metallic) or secondary (van der Waals, London dispersion, or hydrogen).

The adherends' surface energy is also critical, as it is an indicator of all intermolecular forces that are applied on the surface of a material and the degree of all attraction or repulsion forces that a material surface exerts on another material. Most polymers exhibit low levels of surface energy, thus the formation of adhesive joints between polymer-polymer and polymer-adhesive materials can be challenging. The following table lists the surface energy of a few commonly used polymers [2]:

Table I: Typical Surface Energies of Polymers

Polymer	Surface Energy (dynes/cm)
Polyethylene (PE)	30
Polyethylene Terephthalate (PET)	41
Polypropylene (PP)	30
Polytetrafluoroethylene (PTFE)	20
Nylon	39
Acrylonitrile butadiene styrene (ABS)	38
Polyimide	40
Polyvinyl Chloride (PVC)	39

A plethora of literature papers have been published describing the effect of polymer surface energy on adhesive bonding. Toyama et al. [3] studied the peel strength of a poly (n-butyl acrylate) bonded to a variety of other polymeric adherends. The study concluded that the highest peel strength was observed when: (a) the surface energy of the adherend was higher than that of the adhesive surface tension and, (b) in the case where the surface energy of the adherend was comparable or higher than that of the adhesive, the influence of surface forces on the measured adhesion was relatively small compared to the effect of the viscoelastic losses in the adhesive layer [4].

Surface treatments are also beneficial in eliminating the presence of weak boundaries layer at the interface. For an adhesive to perform satisfactorily during a stress event, the fracture should occur in the material that was bonded and at the interface [9].

Surface Wetting and Roughness

Typically, good bonding requires complete and uniform wetting of the adherend surface by an adhesive. Wetting is promoted by polar secondary forces between the adhesive and substrate. Therefore, non-polar polymers -like PTFE- or polymers having low polarity exhibit poor adhesive properties. Wenzel [5] proposed that wetting can be improved by increasing the effective surface area available to interact with the liquid through surface roughening. He derived the ratio of the true surface area divided by the projected geometric area (Wenzel's roughness factor, r) and used this to provide an expression for the contact angle between a test liquid and the wetted material as:

$$\cos\theta = r \cos\theta_{smooth}$$

where θ is the stable equilibrium state surface/liquid contact angle and θ_{smooth} is the Young contact angle as defined for an ideal surface. The roughness ratio, r, is a measure of the effect of surface roughness on a homogeneous surface.

Surface Treatments for the Improvement of Adhesive Bond Strength of Polymer Composites

Mechanical surface treatments of polymer composite components aim to remove surface contaminants and increase roughness. Grit blasting and abrasion are two commonly used mechanical surface preparation methods. Other methods like solvent cleaning, result in surface cleaning without altering the surface morphology. Recently, the application of energetic media such as flames, lasers and plasmas has attracted a lot of attention and has yielded positive results in improving adhesion strength. Table II shows the comparison of the treatment efficacy using different methods:

Table II: Surface Treatments and their impact on bond strength [6]

Treatment Type	Material	Bond Strength Increase
Abrasion and solvent wipe	Thermoset	2.2x
Grit blasting	Thermoset	2x
Acid etching	Thermoset and thermoplastic	1.75x
Corona discharge	Thermoplastic	3x
Plasma treatment	Thermoplastic	10x
Flame treatment	Thermoplastic	2.7x
Laser treatment	Thermoset and thermoplastic	1.3x

Treatments involving the use of chemical agents, like solvent wipe and acid etching, result in a two-fold increase of the adhesive bond strength. More energetic treatments (corona discharge, plasma, flame) exhibit better performance that can be attributed to the cleaning and combined physical and chemical modification of the treated surfaces. Overall, the impact of the various surface modification methods is dependent on the type of materials being treated and the formulation of the adhesive.

Atmospheric-Pressure Plasma Processing of Composite Materials

Plasmas are known to have a positive effect on tailoring the surface properties of polymers exposed to such environments. Whereas vacuum based plasmas have been used for the cleaning and activation of polymeric materials [7] for several decades, plasmas operating under atmospheric pressure conditions have been gaining a lot of traction due to the high throughput and the potential of becoming part of inline processing at manufacturing levels.

Figure 1 shows the basic design and components of an atmospheric-pressure plasma jet (APPJ). A gas is fed at high flow rates (>1 slpm) and is subjected to the electric field that is generated between a metal electrode and the grounded housing of the system. While most APPJs utilize helium or argon gas for plasma generation, the Openair® plasma jet is designed to operate with air or nitrogen to minimize the process cost and is tailored to be used in industrial settings where high throughput is critical.

Figure 1: Schematic (left) and picture (right) of Openair® plasma jet system.

The gas becomes partially ionized leading to electron-induced excitation of the nitrogen and oxygen molecules that compose the air. Depending on the nozzle-head used, the plasma glow can have a diameter ranging from a few millimeters to several centimeters enabling the system to be used in either very localized, narrow treatment areas or larger areas. The jet is typically connected to a 6-axis robot that allows the movement of the plasma over large areas and the continuous or selective treatment. The effect of these APPJs can be controlled via the control of the jet speed and the gap between the plasma source and the treated substrate.

The impact of atmospheric pressure plasmas can be summarized as cleaning and functionalization of the exposed surfaces through the removal of surface residual impurities, grafting of new functional groups and improving the surface wettability. In air-based plasmas, the presence of nitrogen ions (N^+, N_2^+), NO, N_2O, NO_2, NO_3, oxygen and nitrogen atoms, OH radicals and excited atomic and molecular species produce a very reactive phase where these radicals are allowed to react with the activated polymer surfaces. Therefore, plasma surface treatments lead to improved printability, dyeability, and increased surface energy. This is achieved through the mild oxidation of the surface mainly due to the presence of the above-mentioned oxygen-based free radicals generated in the plasma phase, which are grafted on the surface during the plasma exposure. Depending on the process conditions, a mild etching effect might also promote changes in surface morphology and induce microroughness. However, the plasma-induced increase of surface roughness does not cause any degradation of the bulk material properties since it the treatment is surface specific and affects only the top 10nm of the material [8].

Atmospheric plasma treatment of polymer textiles can also improve surface properties such as wicking, dyeing, printing, surface adhesion, mechanical, fracture, and ballistic impact properties in a cost-efficient way. Roughness increase accompanied with the increase of surface area available for reactions can enable mechanical interlocking of the adhesive to the adherend. It has been reported that because of the high stability of the fresh oxide layer durable bonds can be achieved by surface roughening [9]. Some bonding may occur purely by the mechanical interlocking of two surfaces. According to this theory, when a liquid adhesive is placed between two surfaces, it penetrates the crevices and pores and then solidifies and further interlocks with the surface layers on both sides and provides a mechanical bond. In general, mechanical bonding is a low-energy bond in comparison to a chemical bond.

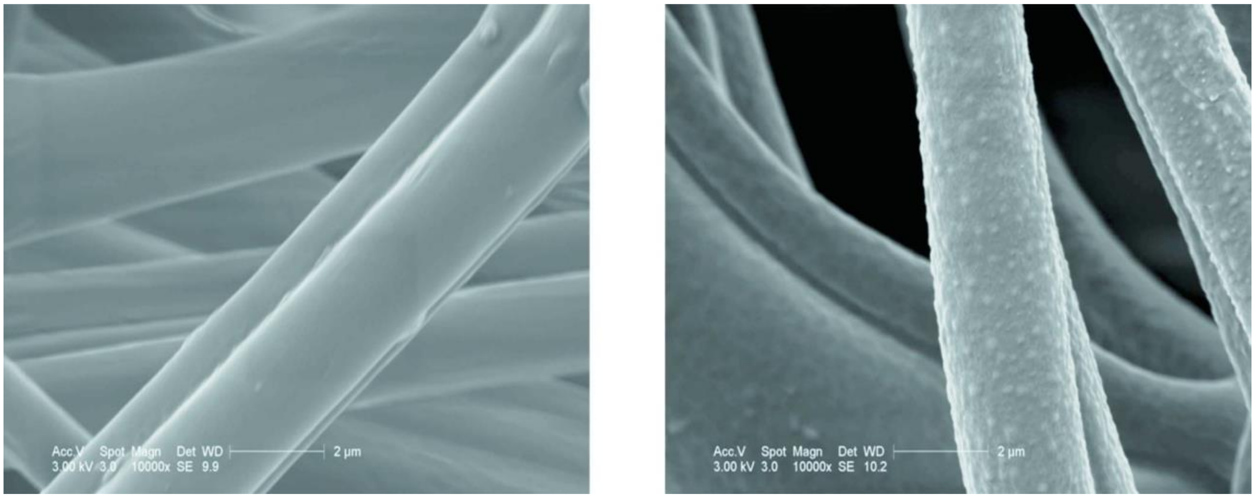

Figure 2: Scanning Electron Microscopy (SEM) images of untreated (left) and atmospheric plasma-treated polypropylene fibers (Courtesy of Ya Liang, Drexel University).

Figure 2 shows the impact of atmospheric plasmas on the surface morphology of polypropylene fibers. The diameter of the fibers was about 2μm and remained unaffected after the plasma treatment [8]. The plasma treated surfaces appear to be rougher and of textured morphology which makes them ideal candidates for composite systems as mechanical interlocking is promoted and frictional energy dissipation is enhanced when bonded to another substrate.

Sizing or finish coatings are often applied on fibers to improve easiness of handling and to protect against abrasion. Different types of polymers are used as sizing chemicals: modified starch, polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), and acrylates. As mentioned above, the polymeric character of sizing can limit the adhesive properties of the coated fibers, yarns or tows. In a literature report published by Xu et at. [10], it was confirmed that atmospheric-pressure plasmas can also be effective in removing sizing agents from fiber surfaces. Commercial T700-grade high-strength carbon fibers (Toray Co., Ltd, diameter of 7 mm) were used in this study. The fibers were processed with sizing agents but without any sizing extractions. The fibers were subsequently embedded in a polysulfone resin to produce a composite structure. X-ray photoelectron spectroscopy results showed that the carbon fibers that were treated under a dielectric barrier discharge- a type of atmospheric pressure plasma- were etched and part of the sizing was removed making them more compatible with the resin.

Applications Using an Openair® Plasma Jet

Removal of Mold Release

The manufacturing process of composites utilize mold release agents to separate the matrix material from the mold. Several methods have been presented which are used to remove mold release from the surface in preparation for the next process step, whether that be application of an adhesive or paint. Complete removal of the mold release without compromising the surface is the goal. In some cases, the surface is cosmetically altered or damaged to the point of affecting the mechanical properties. Solvent wipes and mechanical surface treatments can be a time-consuming process step compared to plasma treatment.

The application of treating composite surfaces with Openair® plasma to remove mold release has been shown to improve adhesion. Law et al. studied the removal of a 5-8 nm layer of FreKote 719-NC from a CFRP using Openair® plasma compared to methanol wipe and grit blasting cleaning methods. Lap shear samples were bonded using a heat cured epoxy adhesive. Comparison of the plasma process against a standard grit blasting process revealed that the plasma cleaning process yields approximately 7% improvement in adhesive composite-to-composite bond strengths. Additionally, plasma offers a significant advantage as a more environmentally friendly surface treatment technique compared to the use of aluminum oxide grits. Also, the ability to automate the process show that Openair plasma treatments can be a viable alternative [11].

Surface Functionalization of Carbon Fibers

Improvement of the mechanical properties of the composite can be achieved through the treatment of the fiber component prior to the fabrication of the composite. By increasing the hydrophilicity of the fiber, adhesion to the matrix material is increased. Erden et al. studied the effect of Openair® plasma treatment on carbon fibers used in the fabrication of single fiber composites [12].

The study applied Openair plasma to polyacrylonitrile (PAN) based carbon fiber. Several techniques were used to characterize the plasma treatment. X-ray photoelectron spectroscopy (XPS) was used to find the elemental composition of the carbon fiber surface. The percentage of oxygen increased up to 8.9% and the oxygen: carbon ratio increased 12%. The increased oxygen content at the surface indicates that the functional groups present at the surface are responsible for the increased surface energy and wettability. A modified Wilhelmy technique was used to measure the advancing and receding water contact angles. An average decrease of 18.9° from 77.2° to 58.3° was seen for the treated fiber. The characterization techniques were used to show that the surface of the carbon fiber had been modified chemically can explain the improvement in mechanical properties of the composite.

The carbon fibers were used to reinforce a Polyamide 12 (PA12) matrix to make single fiber composite samples. Tensile tests were performed on the single fiber composite samples to measure the interfacial shear strength (IFSS). The IFSS increased from 40.2 to 82.7 MPa due to the plasma treatment. The single fiber composite samples are a good representation of the interfacial bond strength between the fiber and matrix.

Similar results were reported by Sanchez Serrano et al. [13] in a study involving the bonding of Hexcel 8552/AS4- ethylene-tetrafluoroethylene (ETFE) aerospace prepreg laminates using EA9695 K.05 (Loctite Hysol, Henkel) epoxy adhesive. The group conducted mechanical testing such as single lap shear (SLS) and bond line toughness. The Openair® treated composites showed improved performance: bond line toughness of 762 J/m^2 and single lap shear of 34 MPa.

Summary

High performance carbon-based fibers can be effectively incorporated in reinforced composites due to a new surface modification method involving air plasmas operating under atmospheric pressure conditions. The fiber surface properties can be tuned through the control of the plasma process parameters allowing the tailoring of surface chemical composition and morphology. Also, plasma surface engineering of composite materials does not require harsh chemical agents and does not produce environmentally harmful byproducts. As the method does not require the use of a vacuum plasma system, industrial upscaling is feasible and can be beneficial to the automotive, aerospace and defense industry.

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