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Surface modification of aircraft used composites for adhesive bonding

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ABSTRACT

Due to the inherent low surface energy of the polymer matrix portion of a given composite material, poor adhesion properties are exhibited and must be overcome in order to achieve strong adhesive bonds. Mechanical methods to improve adhesion have typically included manual abrasion like sanding or grit blasting. Energetic techniques, such as laser and plasma, are garnering continued attention towards the same end. This work describes results of recent investigations of atmospheric pressure plasma treatment (APPT) of composite materials based on glass and carbon fiber reinforced toughened epoxy resin systems for adhesive bonding. Chemical, physical and APPT treatments were compared in terms of enhancing surface energy and interfacial fracture toughness. Surface treatments were followed by characterization of wetting properties using traditional contact angle techniques as well as ballistic liquid deposition. The effects of APPT on the substrates were characterized by taking into account both chemical and morphological changes. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) were used to confirm the elimination of fluorine and the introduction of oxygen and nitrogen. Etching effects of plasma were studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The double cantilever beam (DCB) test configuration was used to investigate treatment effects on adhesive bond performance. Results exhibited the effectiveness of physical procedures in cleaning surfaces, while APPT generated a higher hydrophilic behavior. All the samples tested by DCB yielded cohesive failure mode within the laminates.

1. Introduction

The use of composites in aircraft structures presents many attractive characteristics, including resistance to corrosion, fatigue, and impact; dimensional stability; low density; and temperature tolerance [1]. Because of these features, this field has been greatly studied in recent years. Some of the advantages implied in using composite are stiffness, ability to be tailored into complex shapes [2], strength, and lighter weight. This reduction in the final weight of the manufactured structural component is essential in terms of fuel consumption reduction, which has been previously estimated at about 30–50% when working with carbon and glass fiber reinforced epoxy composites [3–5].

The great importance of these materials can be observed by considering the composition of the Boeing 787 Dreamliner, an airplane where CFRPs, carbon sandwich, and GFRP composites make up 50% of the primary structure, including fuselage and wing [6]. Along the same lines, 25% of the A380 Airbus craft is reported to be comprised of composite materials and it is projected that over 50% of the A350 will be composite-based [7].

Composites are primarily integrated in structures by means of mechanical fastening or adhesive bonding [8,9]. The choice of adhesive joints as assembly method allows for better stress distribution as well as durable, lightweight, and esthetic bonding [8,10–12]. It is essential to have the data and keys to be able to predict failure mechanisms, so diverse parameters have to be taken into account, including surface state, environmental conditions, and bonding design, among others.

One of the most important conditions to be set before performing polymer based composite adhesive bonding is the pretreatment of the surface, especially due to the low surface energy and wettability exhibited by polymers. Many researchers have studied the modification of composite surfaces by means of solvent cleaning [13], abrasion, peel-ply [14], tear-ply, acid chemical etching [15,16] or plasma treatments [17,18]. A typical goal of physical surface treatments such as solvent wipe or abrasion is the removal of contaminants and the roughening of the surfaces. By using abrasion and cleaning steps, an increase in roughness and

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bond strength has been reported for thermoset matrixes, while thermoplastics did not enhance surface energy due to their smooth and hydrophobic surface [13,19]. When a physico-chemical procedure is used, such as plasma, the aim is functionalization of the specimens in a way that increases surface energy and thus promotes adhesion by providing specific interactions across the adhesive–adherend interface. The ionized gas generated by plasma allows several effects, which are mainly cleaning, activation, and oxidation of polymeric surfaces without affecting bulk properties [20–23]. The combination of these effects results in improved adhesion properties by creating a more hydrophilic surface.

In this work, two composites based on glass and carbon fiber reinforced toughened epoxy resins used in the construction of airplanes have been subjected to different surface treatments in order to achieve robust adhesive joints. The investigation was focused on the use of various surface preparation methods such as chemical (solvent wipe), physical (sanding and grit blasting), and physico-chemical (plasma treatment). Surface treatment effects on wetting properties were evaluated through contact angle measurements as well as ballistic liquid deposition. Chemical composition changes were characterized by XPS and ATR-FTIR techniques, quantifying the removal of fluorine and insertion of oxygen in the surfaces. Topographical modifications and roughness parameters were obtained by SEM and AFM analysis, so the post-treatment state of the composites was well characterized. Finally, DCB testing was carried out to obtain fracture toughness data of the bonded systems, as well as to predict the failure mechanism, revealing the effectiveness of treatments as well as the fluorine content independence with adhesion strength.

2. Experimental

2.1. Materials and treatments

Experiments were performed on composite coupons provided by Boeing (The Boeing Company, Seattle, WA, USA). Composite adherends were prepared from MXB7701 epoxy resin reinforced with style 7781 E-glass fiber (8 harness satin fabric; referred to as GFRP) and Toray 3900-2 epoxy resin reinforced with unidirectional T800H carbon fiber (P2302-19 prepreg; hereafter "CFRP"). For this testing, a single film adhesive was used: Henkel Hysol® EA9696 (293 g/m^2, 0.06 psf). Composite samples were subjected to diverse surface treatments as described in Table 1, and divided into three main groups: solvent wipe, physical treatment (both hand sanding and grit blasting) and physico-chemical modification by APPT.

The APPT procedure was performed using a Plasmatreat single rotary plasma jet equipped with a RD1004 nozzle controlled by a FG5001 plasma generator (Plasmatreat US LP, Elgin, IL, USA). After preliminary optimization work, APPT treatment conditions were fixed at 10 mm/s raster rate and 6 mm plasma-to-sample distance [24].

Table 1
Surface treatments applied on the composite surfaces.

Treatment	Materials	Label
Cleaning	Isopropanol	IPA
	Methyl-ethyl-ketone	MEK
Physical	T-9 grit Al_2O_3 sandpaper (hand sanding)	HS
	240 grit Al_2O_3 (grit blast)	GB
Plasma	10 mm/s speed, 6 mm working height	APPT
Abrasion-Plasma	GB+APPT (each as reported above)	GBAP

2.2. Contact angle, surface energy and single fluid probe determination

Surface energies are frequently reported as a single number. However, surface energy is probably a vector quantity comprised of contributions from different classes of molecular interactions. The Owens–Wendt–Rabel–Kaelble (OWRK) model [25–27], (Eq. (1)), involves decomposing surface energies into two components: one arising from van der Waals and London type (non-specific or dispersive) interactions, and the other arising from the interaction of polar groups having permanent dipole moments (polar).

$$\frac{(1+\cos\theta)\gamma_l}{2\sqrt{\gamma_l^D}} = \sqrt{\gamma_s^P}\sqrt{\frac{\gamma_l^P}{\gamma_l^D}} + \sqrt{\gamma_s^D} \quad (1)$$

In this expression γ_l and γ_s represent the surface tension of liquid and the surface energy of solid, respectively, while the dispersive and polar fractions are identified by the D and P superscripts. The contact angle of the drop on the solid surface is represented by θ.

Attending to this definition, to completely characterize a surface energy contact angles of at least two fluids must be measured, each having a different balance of polar and dispersive components to its surface tension. In this work contact angle measurements of five fluids (distilled water, ethylene glycol, formamide, diiodomethane, and dimethyl sulfoxide) were measured using a Ramé-Hart NRL-100 goniometer (Ramé-Hart Instrument Co., Succasunna, NJ, USA). Surface energy of both pristine and APPT treated coupons was calculated by the OWRK approximation, yielding the modification in wettability due to the introduction of polar functionalities achieved by APPT.

The wetting behavior of a single liquid cannot completely characterize the energy of a surface. However, the contact angle of a single liquid can be an excellent indicator of the consistency of a surface preparation procedure, so dimethyl sulfoxide (DMSO) and water were selected for this purpose. DMSO has been suggested as an appropriate single fluid probe, because its surface tension balance between polar and dispersive components is very similar to that of many adhesives [28]. However, recent work has indicated that water functions well as a single fluid probe of surface preparation quality and consistency [29,30]. This may be due to the fact that the surface tension of water is overwhelmingly polar in nature. Because its interaction with surfaces is primarily through polar–polar interactions, water contact angles are especially sensitive to the presence of polar functional groups on the surface.

2.3. Compositional study

The surface chemical composition of both untreated and APPT composites treated at different surface depths was evaluated by ATR-FTIR and XPS analysis. The infrared spectra of the modifications produced to about 5–10 μm depth were recorded with a Bruker Tensor 27 (Bruker Optik GmbH, Madrid, Spain) spectrometer using a diamond prism with an incident radiation angle of 45°, 32 scans, and a resolution of 4 cm^{-1}. The study of the outermost surface layer (about 5 nm) modifications was achieved with a Surface Science SSX-100 XPS spectrometer (Surface Science Western, Ontario, Canada) using a monochromated Al Kα X-ray source operating at 1486.6 eV and 200 W. All binding energies were referred to the C 1s core level spectrum position for C–C and C–H (hydrocarbons) species at 284.6 eV, subtracting a Shirley background.

2.4. Morphological study

Etching effects of the plasma flux were analyzed using a Philips XL-30 FEI EUROPE SEM microscope (Eindhoven, Holland) and a