Plasma Treatment for Adhesion Promotion of High Performance Materials used in Aerospace Manufacturing

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Abstract

The promotion of adhesive adhesion by plasma surface modification is widely accepted as a valuable tool in mechanical design, allowing for adhesions with superior strength-to-weight ratios. The aerospace industry is among those that use adhesion promotion techniques extensively, benefiting from the ability to join dissimilar, but highly engineered materials and simple-to-complex manufacturing processes. While the nature of adhesion promotion will not substitute for adhesive techniques, proper leveraging of atmospheric plasma-based technologies has resulted in synergies that benefit final aerospace-related products. One of these areas of benefit is component performance under high temperature. Many joints experience wide temperature ranges derived from high altitudes and speeds relative to the load the joints must sustain. This work shares data pertaining to atmospheric plasma surface modification techniques applied to high temperature performance plastics such as polyetheretherketone (PEEK - $C_{19}H_{12}O_3$), and composite matrices such as aramids, and the benefits derived from these techniques by the aerospace industry.

Introduction

Of paramount importance to the aerospace industry is the adhesion of adhesively-bonded joints. New methods for preparing high performance polymer and matrix/reinforcement composite surfaces for bonding to similar and dissimilar materials through the use of cold, atmospheric pressure plasma technology has offered recent promise for replacing prior art practices for surface preparation, such as by abrasion and batch vacuum plasma methods. Atmospheric pressure plasma regimes feature high density discharges which are highly integratable to in-line continuous production environments. Process and reactive gas components rapidly activate polymer surfaces, providing surface species which contribute to secure bonding and curing of various adhesives and promote desired cohesive failure results.

Adhesion performance is dynamic, being highly dependent upon the material type, performance-aiding additive load, surface chemistry, surface roughness, adhesive chemistry and bond stress factors to name a few. When parameters are aligned to meet performance requirements, measures such as lap shear strength can be elevated to >40%, with recent reports indicating the possibility of >65% increase in interfacial shear strength with polyolefins [1]. From the perspective of initiating initial interfacial bonding, surface wettability is key. While it is generally understood that that there is no direct correlation between bond strength and surface wettability, it has also been confirmed that sufficient increases in surface tension by plasma discharge to achieve desired wettability can reduce adhesive processing time, surface roughness, and an increase in bond strength as a result of polymer surface oxidation, acid group formation, and the polar component of the surface free energy. It is these surface activation mechanisms related to improvements in bond strength which has attracted the attention of aerospace manufacturing process engineers.

Another influencer of bond strength with high performance plastics is surface contamination. One common but not well recognized representation of such contamination is that of moisture absorbed by the substrate. Moisture uptake by materials such as nylon 6, PPTA, UHMWPE, and others can directly correspond to environmental relative humidity levels within which such materials are stored and processed. Such moisture uptake typically involves interactions between absorbed water and the polymer's surface molecules. As reported by Zhu et al [2], the rate at which plasma processing can occur can be related to the level of moisture uptake, intermolecular forces, crystallinity, and molecular structure. With most polymeric surfaces, the presence of weak boundary layers exists in the form of oligomers, grease, release agents, dust and absorbed moisture. The intensity of current state surface modification techniques with PEEK polymers, for example, can be delayed and/or reduced, as can be the amount of nitrogen or oxygen uptake and functionalities, and subsequently nitrogen/carbon and oxygen/carbon atomic ratios.

Aerospace Polymers, Composites & Surface Modification

Polymers for high performance aerospace applications are typically characterized by thermoplastics, such as PEEK. On average, high performance thermoplastics have heat-deflection temperatures > 2000C, a minimum of 50% higher than standard engineered thermoplastics. Properties such as a higher melting point, higher glass transition temperature, higher heat deflection, chemical and burn resistance, and greater wear and fatigue resistance also characterize the need for more specialized molding and surface modification technologies. High performance thermoplastics being applied to aerospace application include fluoropolymers, high-performance polyamides, polyamideimides, polybutylene terephthalates, polyetherimides, polyimides, polyketones, polysulfones, and polycyclohexane dimethyl-terephthalates. Composite structures for greater lightweighting such as carbon nanotube-reinforced polymer composites, and graphite/PEEK laminates are prevalent. Furthermore, engineering thermoplastics are applied in aerospace and offer enhanced properties designed for specific applications where a combination of mechanical and precision specifications must be met.

The surface modification of thermoplastics such as PEEK is challenged by the very high performance properties these polymers provide for servicing aerospace applications. For one, the semicrystalline structure of PEEK can impede the creation of strong autoadhesive bonds and typically require bonding pressures above the glass transition temperature and below the melting point, since the molecular chains are folded and therefore more restrictive of entanglement. Therefore, adhesive bonding of PEEK can result in joints with poor strength. Other causes can include low achievable surface energy, poor wetting the adhesives and high chemical resistance.

A prerequisite for successful adhesive bonding is wetting of the adhesive on the PEEK adherent. Wetting will occur if the surface-free energy of the adhesive is approximately 10mN/m lower than the surface-free energy of the PEEK adherent. Standard surface energy values for adhesives are 30-50 mN/m, and 20 mN/m for plastics with poor bonding properties. Since the surface energy of PEEK is near 36 mN/m, it can be predictive that good wettability of most adhesives can take place only when PEEK is made wettable to near 60mN/m.

Surface modification is arguably the most critical process step for controlling the quality of adhesively-bonded joints such as metal-to-metal, metal-to-plastic, metal-to-composite, composite-to-composite, plastic-to-plastic, and metal-to-ceramic. Moreover, the wetting of adherend surfaces by the adhesive is critical to forming secondary bonds by the adsorption adhesion theory. To serve mechanical bonding theory, change in surface roughness (increase in surface area without an increase in void formation) to control the desired level of joint strength and the removal of weak cohesion boundary layers is necessary. For chemical bond improvement, the creating of appropriate functional layers will contribute to improved wettability and adhesion properties of the aerospace polymer surface.

Atmospheric Plasma Mechanisms

Atmospheric plasma treating systems generate an electrically charged chemical atmosphere to introduce a wide range of surface modifications to an aerospace substrate. The systems are characterized by their generation of high density reactive species for low temperature material processing. The chemical plasma process can involve surface preparation via the breakdown of low molecular weight organic materials (LMWOM) and surface decontamination, fine etching of the surface to create new topographies, grafting of new functional groups or chemical species on the surface, and the deposition of coatings on the surface. Treatment depth of atmospheric plasma discharges, assuming suitable surface exposure to effect sufficient changes in surface tension and functionalization to achieve adhesion metrics, is typically regarded to be approximately several angstroms on average. The treatment process is designed to allow the interchange of gas chemistries relative to the application requirements. With high performance thermoplastics, for example, loose surface oligomers and other residues are repetitively cleaved and degraded by atmospheric plasma micro-discharges, measuring no more than one-tenth of a millimeter across and lasting no more than nanoseconds, until they are removed largely by a combination of bombardment by ions and electrons. These organic residues are converted into water vapor, carbon dioxide, and other nontoxic gases or volatilized materials. Air, or a noble carrier gas such as argon along with a reactive component gas is typically used to initiate the breakdown of LMWOM and create surface etching for greater adhesion of coatings and adhesives. The gas species which is ionized, along with the composition and structure of the polymer itself, are the key factors that determine the degree of etching. To maximize adhesion of adhesives on plastic parts (particularly those manufactured of thermoplastic olefins), the deposition of polar functional groups from the use of oxygen and hydrocarbon reactive gases with the carrier gas can be particularly effective.

Atmospheric chemical plasma treatment systems are typically non-thermal, atmospheric-pressure, glow-discharge plasma systems which generate uniform and homogenous treatments. The level of surface tension and longevity of treatment are both typically greater than air plasma treatment effects, and similar in treatment effect to flame plasmas. The substrate is optimally treated by atmospheric chemical plasma when it is positioned several millimeters from the discharge source. Process line speed, power level, gas chemistry, gas chemistry mixtures and material composition primarily determine levels of etching and functionalization which can be achieved.

Adhesion Promotion Techniques

Atmospheric plasma treatment has been highly successful in promoting high surface wettability and chemically-adaptive conditions for promoting adhesion to aerospace polymers. The use of blown arc or blown ion air-based atmospheric pressure plasmas, or those augmented with inert/reactive components such as argon/oxygen have been highly effective in improving the adhesion of PEEK polymers to epoxy film adhesives, primarily by surface activation and functionalization. Among this adhesive's components, such as aluminum, epoxy resins, aromatic polyamines, and synthetic elastomers, it is the epoxy resin component (which consists of monomers, or short chain polymers with an epoxide group at either end) which predominantly forms the chemical bonding link with the polar chemical groups imparted by plasma treatment, and in turn with the surface functionality of PEEK. In general, atmospheric pressure plasma treatments will increase surface oxygen levels, as well as the levels of carbonyl (C=O) and hydroxyl (-OH) groups.

In advance of adhesive bonding, the use of atmospheric pressure plasmas for modifying the surface of high performance polymers is functionally effective. Materials such as polymethyl-methacrylate (PMMA) and PEEK surface-activated by atmospheric plasmas will become highly wettable (low contact angle) and promote cohesive failure via lap shear within the adhesive at between 7-10 times greater than without atmospheric plasma treatment.

References

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