RAPID DEVELOPMENT OF SURFACE TREATMENT PROCESSES FOR BONDING DISSIMILAR MATERIALS

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INTRODUCTION

A recent concept in automotive lightweighting is that of the ‘joining of dissimilar materials’. The purpose is to allow tailoring the materials in a structure so as to ensure that each part of the structure has the optimum mechanical properties and the minimum weight. An example would be the bonding of aluminum stiffening ribs to a polymeric body panel.

The concept of ‘joining’ has many subtleties. The purpose of the joint (or interface) between the components is to transfer the applied load from one component to the next. If the means of joining is by welding, the stress distribution is evenly distributed throughout the joint. However, dissimilar materials are almost never able to be welded, and mechanical fasteners (bolts or rivets) are frequently used. All of the transferred stress in a structure joined with mechanical fasteners is concentrated in the fasteners and the holes through which they pass. To resist fracture, the material must be made thicker and heavier in order to sustain these stress concentrations, which negates much of the advantage to be derived from multi-material structure design.

From a structural standpoint, adhesive bonding provides the advantages of welding with the ability to use multiple materials. Stresses in bonded structures are uniformly distributed and allow the absolute minimum gage materials while retaining excellent mechanical properties such as strength, stiffness, and impact resistance. However, adhesive bonding processes bring a distinct set of challenges to manufacturing.

At first glance, bonding operations appear to be straightforward mechanical processes which involve various combinations of washing or wiping, abrasion, surface treatment, adhesive application, positioning and fixturing components, and curing, perhaps through application of some combination of heat and pressure. The perception of bonding as a mechanical process has resulted in a failure to appreciate the fact that creating a successful bond between an adhesive and a substrate is actually a multistep *chemical* process. The first step occurs at the manufacturer of the adhesive, where the resin is synthesized. The second step occurs on the shop floor of the end user, where a bonded *interface* is synthesized from the reactions of the adhesive with the prepared surface. Whereas the bulk properties of the cured adhesive depend on the manufacturer’s control of the quality of the coating or adhesive and on the ability of the technician to properly execute the cure cycle, the properties of the interface are established on the shop floor by the technician during the bonding process. The quality of the established interface depends on generating a prepared surface of identical chemical composition and structure time after time [**1-8**]. This is more difficult than it may seem at first glance, because the properties of a surface are determined by the composition and structure of only the uppermost 2 to 3 molecular layers. By way of contrast, a fingerprint leaves a layer of oils and fatty acids that is around 1000 molecular layers thick. The residue from a human’s breath is 100’s of molecules thick. What might seem to be insignificant changes in incoming material, storage and handling, processing or environment can actually result in large changes in the properties of a surface, and therefore the properties of an adhesive bond.

The most sensitive factor in control of a bonding process is control of the structure and composition of the interface between the adhesive and the substrate. It is also one of the most difficult factors to control, because it is vanishingly thin (therefore delicate) and is created by technicians using manual processes in an environment that typically has marginal controls over temperature, humidity, and airborne contaminants. As a point of reference, another industry whose products’ performance and quality depend equally heavily on the structure and composition of surfaces is semiconductor device manufacture. Because of this industry’s appreciation of the delicate nature of surfaces and interfaces, semiconductor device manufacturing is performed by highly trained workers in stringently controlled clean rooms. Furthermore, manual processes are avoided as much as possible because of the difficulty in control.

The properties of a structure that includes an interface are usually determined by destructive testing. This can lead to slow and inefficient process development cycles. Developing and evaluating cleaning procedures and surface treatment processes requires multiple iterations of sample fabrication and testing to quantify process and materials effects. Once a process is established and scaled up to manufacturing, it must be continuously evaluated and controlled. Process evaluation and process control based on feedback from destructive testing of bonded components makes real time quality control of bonding processes essentially impossible.

Development of surface preparation processes can frequently be streamlined by using wetting measurements to evaluate the response of a surface to treatment. This initial screening can then be followed by more abbreviated fabrication and testing of bonded or coated test specimens. The result is a significantly more efficient process development cycle that also can establish process control parameters for quality assurance when these processes are transferred to manufacturing. This paper discusses the use of contact angle measurements using the Surface Analyst™ to speed up evaluation and development of several representative surface preparation processes while providing quality assurance measurements that are easily transferred to manufacturing for monitoring and quality control. The Surface Analyst is a fast, easy, accurate, and non-destructive instrument used by manufacturers with critical surface requirements, a common concern in lightweighting.

Wetting measurements via contact angle goniometry can be an excellent and practical probe of factors that affect surface energy, such as cleanliness and treatment level [**1-4, 6-10**]. These measurements show monolayer sensitivity and when coupled to appropriate instrumentation can be readily operated by manufacturing personnel in shop environments.

Critical cleaning processes

A critical cleaning process is one that has a specific and quantifiable outcome crucial to the product performance. These processes form a vital component of many surface preparation and treatment procedures. Evaluation of the quality and effectiveness of a cleaning process may involve multiple iterations of cleaning followed by fabrication of bonded or coated specimens and mechanical and/or environmental testing. In the work presented here, contact angle measurements were used to rapidly identify optimum cleaning procedures for several materials, which varied from material to material depending upon the particular surface properties.

Surface treatment via abrasion

Abrasion of composite and metal surfaces can be extremely effective as a pretreatment for adhesive bonding. For metal surfaces, thick, weak oxides are removed to create a high-energy surface that can establish an excellent interface with adhesives or coatings. Composite materials respond to abrasion in a very different manner than metals, however. Whereas metal abrasion begins with plastic deformation and work hardening followed by fracture and removal of metal particles, composite matrix resins fracture in a brittle manner during abrasion with little or no deformation. Abrasion can remove insoluble contaminants such as mold releases and create a high-energy surface via microscopic fracture of the brittle matrix resin to establish a bondable surface. This work presents an example of rapid process evaluation using wetting measurements via contact angle to establish an effective composite abrasion process which maximized surface energy. Subsequent fabrication of adhesive specimens validated the quality of pretreatment and demonstrated achievable control limits for manufacturing.

Surface treatment via plasma

Plasma treatment of composite surfaces prepare surfaces for adhesive bonding have been investigated for many years but have not yet seen widespread adoption. The development of atmospheric pressure plasma treatment systems over the past decade have removed the previous constraints of batch processes performed in vacuum chambers, greatly improving the practicality of these treatments. However, the equipment still represents a significant capital expense. Perhaps more importantly, there is a general lack of understanding in the aerospace industry about the advantages and limitations of these treatment processes. This has made process development difficult and has hindered their proliferation.

Chemical surface treatments such as flame, corona, and plasma are all different classes of plasma reactions. They all function through oxidation of organic compounds. There are many competing reactions occurring during the oxidation process, the fastest of which is usually the creation of free radicals through electron and ion bombardment of the surface. These free radicals then react with oxygen to form compounds such as peroxides which then decompose to form species of increasing oxidation level including hydroxyls, ketones, and carboxyl compounds. These oxidation reactions are accompanied by fragmentation and chain scission. Given enough reaction time (i.e. long enough exposure), small molecules such as organic contaminants are converted to CO_2 and H_2O vapor, which is the basis for plasma cleaning.

In the case of plasma treatment of metals, once the underlying oxide is exposed through contaminant removal, continued plasma exposure will dehydrate and densify the oxide. This can be beneficial for adhesive bonding and coating. Overtreatment is virtually impossible.

When polymeric substrates (composite materials, injection molded plastics, polymer films) are treated using plasmas, continued plasma exposure after contaminant removal will oxidize the polymer substrate. This is generally desirable as is creates high energy, reactive sites that enhance adhesion of coatings and adhesives. However, overtreatment is of significant concern as polymeric substrates will be reduced in molecular weight through chain scission and become physically weakened. Although such a surface will be readily wettable in surface energy measurements, it will result in poor performance when bonded or coated due to failure in the weakened near-surface regions of the substrate. When developing plasma treatment processes for polymers it is important to identify the endpoint of cleaning and activation so that overtreatment can be avoided. This generally corresponds to the treatment conditions that just minimize contact angle.

EXPERIMENTATION

Cleaning process evaluation

Several substrates were ordered from McMaster-Carr and received in an unknown state of cleanliness. Water contact angle measurements were obtained using the Surface Analyst SA3001 (BTG Labs, LLC). Measurements were taken in the as-received state and after several cleaning processes, including solvent wiping with isopropanol, acetone, and Dysol DS-108 (a mixture of ethyl lactate, aliphatic petroleum distillates, and propylene glycol n-propyl ether, Dysol, Inc.). Some samples were manually washed in detergent and hot water (Dawn, P&G, Inc.). Other samples were washed in an automated parts washer using an industrial alkaline detergent (Cuda SMP-1000 detergent, Hotsy Equip. Co. Inc.).

Abrasive surface treatment

Carbon fiber reinforced epoxy composites were prepared to model different levels of surface preparation: solvent wipe only (referred to as ‘No Prep’), solvent wipe followed with a light sanding (“Under Sand”), preparation per customer’s internal standard (“Spec Sand”), and solvent wipe followed by an aggressive sanding to expose carbon fibers (“Over Sand”). Substrates were solvent cleaned prior to sanding using acetone, ethanol and Kim Tech Delicate Task Wipers. A clean wipe was soaked in acetone and applied directly to the composite surface for a unidirectional wipe, followed immediately by a dry wipe in the same direction with a clean wiper. This was followed with a similar ethanol wipe and a five-minute dry time to allow solvent to flash completely off of the surface. Surfaces were then abraded with 3M 7447+ Scotchbrite pads with linear abrasion parallel to the long axis of the specimen. After desired level of abrasion was reached, substrates were subjected to an additional solvent cleaning with acetone and ethanol using the previously described unidirectional wipe method. Table 1 outlines the experimental matrix.

Table 1. Experimental test matrix.

Substrate	Adhesive	Surface Preparation	Lap Joints (ASTM D1002-94)
T300 Fabric, tool side	EA 9309 Paste	No Prep	5
		Under Sand	5
		Spec Sand	5
		Over Sand	5

Bonding. Adhesion strength and failure modes were evaluated using single lap joints corresponding to ASTM D1002-94 with a ½” overlap using Loctite EA9309. Bonded substrates were placed under uniformly dispersed static load and allowed to cure at room temperature for seven days. The natural bondline thickness established was approximately 0.2mm (0.008”).

Plasma treatment

Plasma treatment processes proceed on a molecular layer-by-layer basis from the free surface towards the interior. The amount of exposure time required to perform an effective surface treatment will depend on the amount and identity of any contaminant present on the surface. More highly contaminated surfaces will require more exposure time to a plasma to reach the same level of treatment as a lightly contaminated or uncontaminated surface. Because of this, it is important to control for the state of the surface prior to plasma treatment.

For this study, polypropylene samples were precleaned prior to surface treatment and analysis by washing with detergent and warm water (Dawn), followed by a DI water rinse in order to establish a baseline surface condition. Using the Surface Analyst, contact angle measurements were taken on these surfaces both prior to and after plasma treatment (Plasmatreat RD1004, Plasmatreat NA). Treatments were performed using a standoff height of 13.4mm with various traverse speeds: 50mm/s, 100mm/s, 150mm/s, 250mm/s, 350mm/s and 500mm/s.

Treated and untreated samples were then primed with 2 coats of DPLF Epoxy Primer applied according to technical data sheet with adequate times allowed for drying between coats. Black Envirobase High Performance (EHP) waterborne basecoat automotive paint was then applied to the samples within 30 min of primer coats. Paint was allowed to dry for 24 hours prior to adhesion testing.

Adhesion testing was done in accordance with ASTM standard D3359-09, Standard Test Method for Measuring Adhesion by Tape Test. In this method, crosshatch lines are scribed into the paint film, adhesive tape is applied and then removed. Adhesion is evaluated by visual evaluation of the amount of paint adhered by the tape.

RESULTS

Cleaning process evaluation

Figure 1 shows contact angles obtained from the various materials as a function of cleaning process. In all cases, the as-received coupons showed high contact angles (poor wettability), and the large standard deviations indicated large point-to-point variability in surface cleanliness. Solvent wiping with isopropanol or acetone in all cases resulted in at least a 15° drop in the contact angle, indicating an increase in cleanliness. There was no indication that one of these solvents was better than the other. Hand washing with Dawn detergent followed by an isopropanol wipe resulted in a significant increase in cleanliness for titanium and stainless steel surfaces but resulted in no measurable improvement on the other surfaces. Cleaning in the automated parts washer provided a significant improvement in cleanliness for the metal surfaces but was not beneficial for the composite materials. Finally, following the wash cycle with a solvent wipe was beneficial for all surfaces except the aluminum. Contact angles of around 20° represent extremely clean metal surfaces.

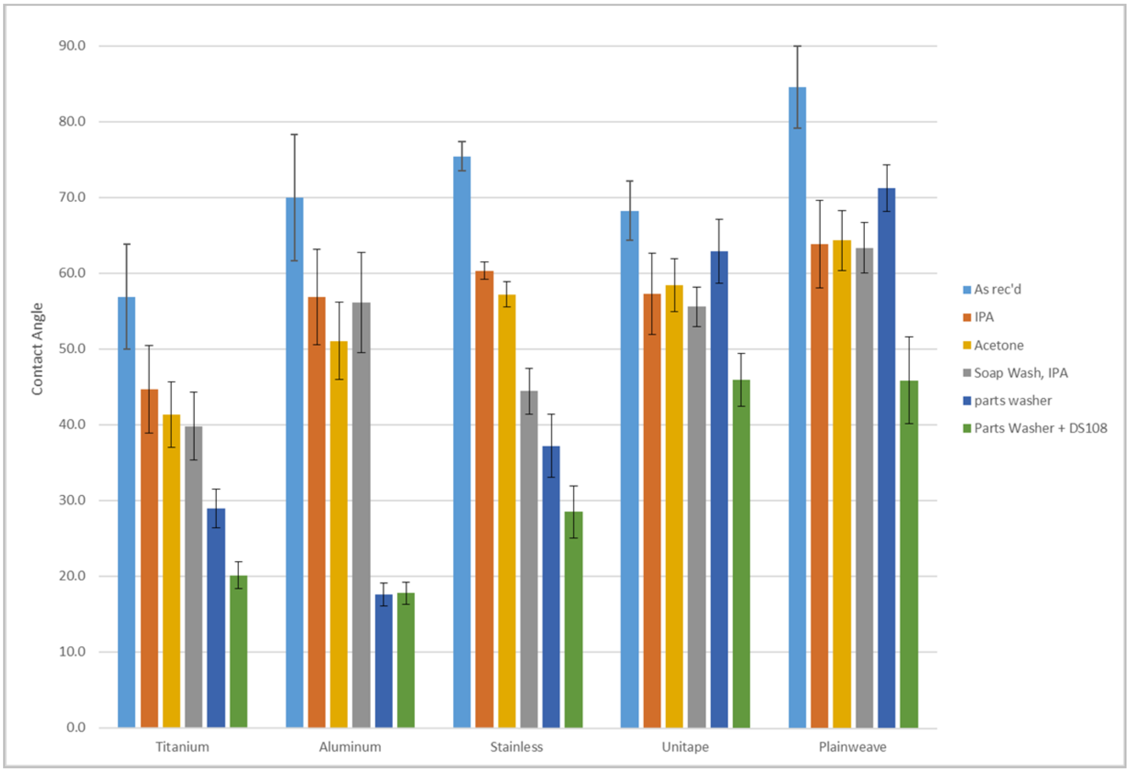

Figure 1. Water contact angle vs cleaning procedure for various materials. Low contact angles indicate higher energy, cleaner surfaces.

Abrasive surface treatment

Figure 2 shows lap joint strength versus water contact angle for untreated and treated substrates. There is an excellent and almost linear correlation between failure load and contact angle. As the intensity of the abrasion process increased, the average contact angle decreased as well as the point-to-point variability, indicating that the more aggressive processes were increasing the average surface energy as well as the uniformity of the surface.

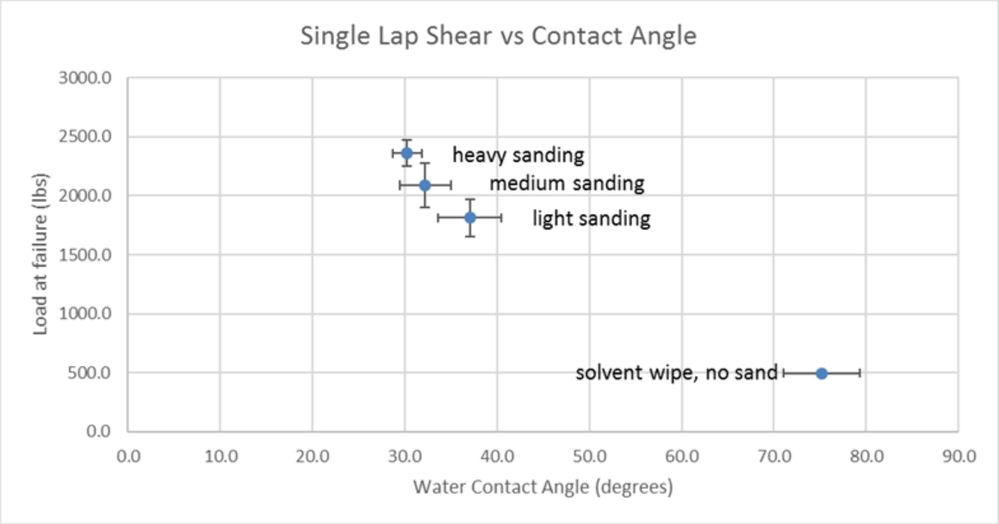

Figure 2. Failure load versus water contact angle for single lap joints prepared from manually abraded composite laminates.

Plasma treatment

Figure 3 shows the water contact angles measured before and after plasma treatments. All of the untreated, detergent washed surfaces showed contact angles ranging from about 78 to 85°, characteristic of the hydrophobic surface of untreated polyolefins. In all cases plasma treatment increased surface energy and reduced the contact angle. Increasing residence time in the plasma increased the effect. The correlation between contact angle and plasma residence time is shown in Figure 4. Contact angles of near 15° were achieved for the longer residence times, which corresponded to plasma traverse rates of about 50mm/s, quite practical treatment speeds for many processes. Finally, Figure 5 shows the good correlation of paint adhesion to the water contact angle. Excellent adhesion was obtained when treatment conditions produced contact angles on the order of 20°.

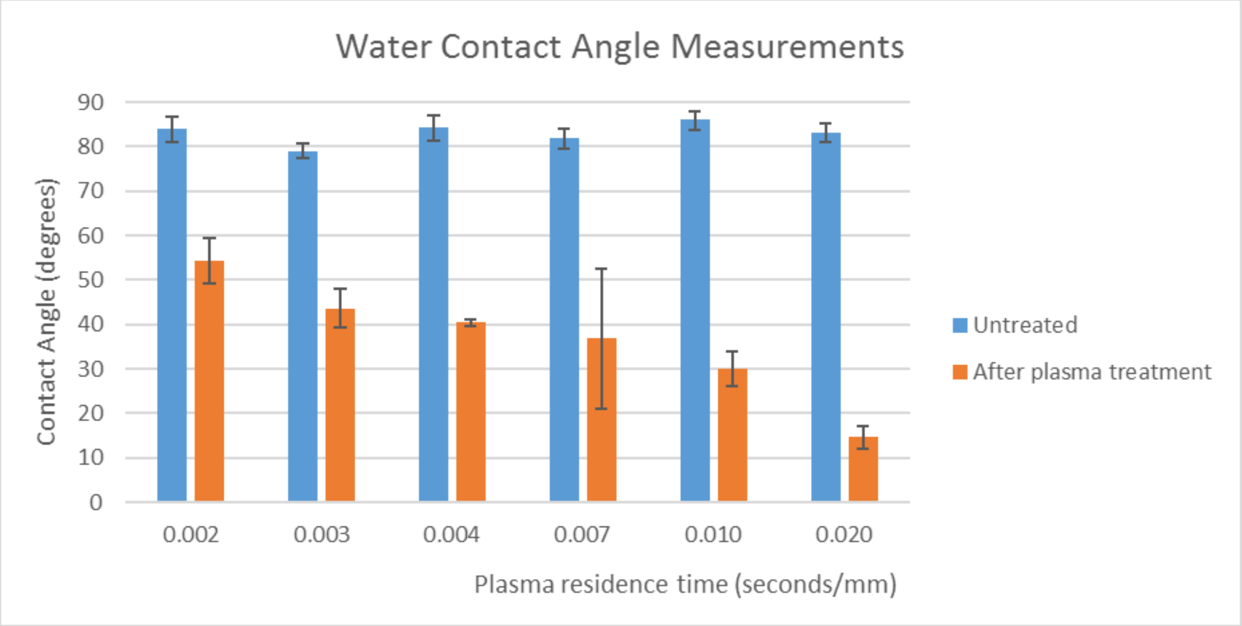

Figure 3. Water contact angle for untreated (blue) and plasma treated (red) polypropylene.

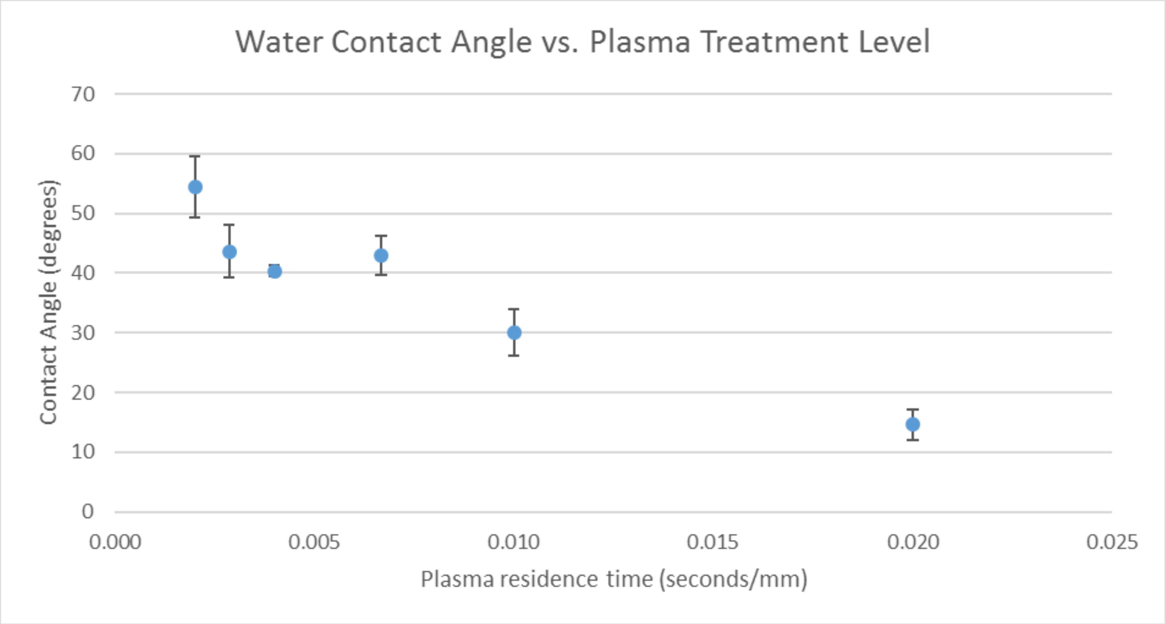

Figure 4. Water contact angle versus plasma residence time for polypropylene.

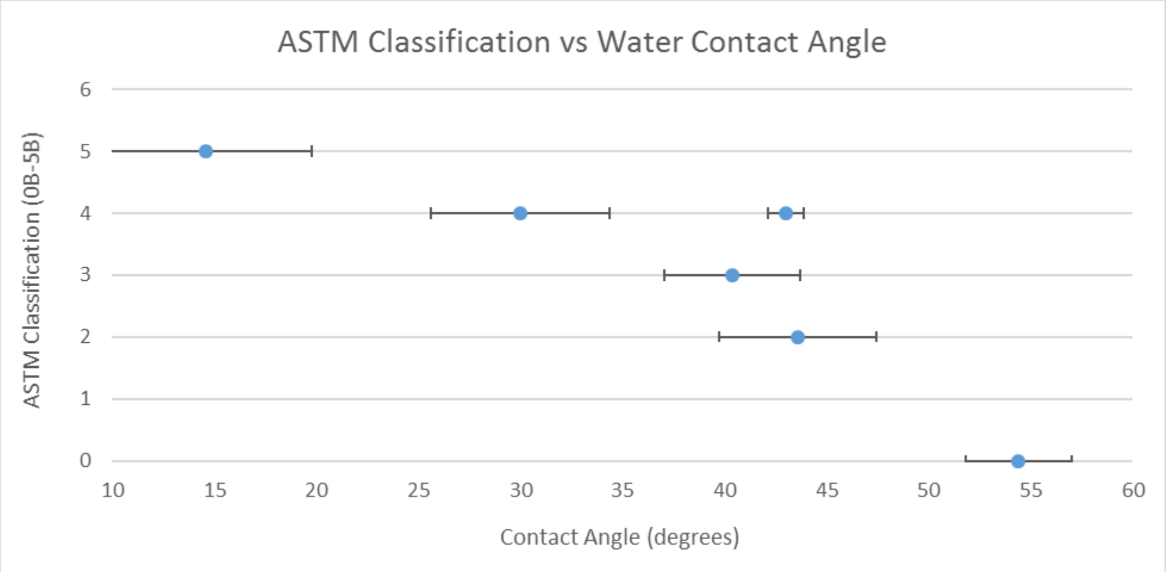

Figure 5. Paint adhesion (ASTM D3359-09) vs water contact angle.

CONCLUSIONS

Cleaning process evaluation

The Surface Analyst provided rapid acquisition of contact angles and allowed 5 cleaning processes to be quantitatively evaluated in a single day. Solvent cleaning was only moderately effective on all surfaces. Automatic parts washing was very effective on metals. The alkaline cleaner was particularly effective on aluminum, probably due to the solubility of aluminum oxide at high pH. The overall most effective cleaner was the mixture of ethyl lactate, aliphatic petroleum distillates, and propylene glycol n-propyl ether, producing the lowest contact angles on all materials.

Abrasive surface treatment

The maximum breaking load of 2400 lbs is indicative of an excellent surface treatment for adhesive bonding of composites. The strong correlation of treatment level and strength to water contact angle shows that this measurement has excellent potential as a quality assurance metric during manufacture to ensure that the surface treatment process is being performed in a reproducible and controllable manner.

Plasma treatment

Adhesion of water borne paints to polypropylene surfaces is essentially non-existent without some type of chemical modification of the polymer surface to increase the surface energy through providing chemical attachment points. Atmospheric pressure plasma treatment readily accomplishes this surface functionalization in a rapid manner. Contact angle measurements of the treated surface correlate quantitatively with the measured adhesion, showing the utility of these measurements for process development and process control.

By studying and comprehending the relationship between a contaminant surface and the effects it can have on a bond will help develop more productive monitoring and cleaning procedures for surface preparation processes. Outdated surface evaluation methods such as dyne are destructive and do not provide the reliable, precise, and quantifiable surface measurements on the factory floor that can be obtained in seconds with the Surface Analyst.

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