The Science of Adhesion
Insights to Understanding Adhesive Performance

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Abstract

The continued integration of smaller, higher-functioning devices in the Aerospace, Defense & Space sectors is making it more challenging than ever to minimize assembly failure, especially where reliability is top priority and fail-safe processes, and materials are the standard. Assembly failures due to poor adhesive bonding tend to linger causing excessive manufacturing downtime, scrap, costly rework, and delays.

This paper introduces the science behind adhesion. Regardless of the application, the market or the adhesive technology being used, such as epoxy, silicone, urethane, paste or film, achieving a proper assembly bond is critical for application success. Adhesion is achieved via two mechanisms, mechanical and chemical bonding. To optimize this the adhesive must flow (or wet) across the substrate. This maximizes the interaction between the adhesive and substrate allowing flow into microscopic substrate pores for enhanced mechanical bonding as well as interaction between adhesive and substrate for chemical bonding. The molecular force of attraction between an adhesive and the substrate is determined by the surface energy of the substrates. The substrate surface energy influences the ability of the adhesive to flow and wet the substrate impacting adhesion. Measuring substrate water contact angle is an easy method to determine the relative surface energy thereby gaining information about the pending adhesive bond.

This paper reviews these key factors for adhesion and presents results of an application study aimed at understanding the sensitivity and relationship of substrate water contact angle versus substrate cleanliness. The goal is to be able to use substrate water contact angle measurements as a predictive tool for adhesion.

Key words

RF power devices, thermal management, chip-scale cooling, adhesives, RF grounding, surface energy, water contact angle, bonding

I. Introduction

The continued trend towards high powered, higher-functioning devices in the Aerospace, Defense & Space sectors is making it more challenging than ever to minimize assembly failure, especially where reliability is top priority and fail-safe processes, and materials are the standard. Assembly failures due to poor adhesive bonding tend to linger causing excessive manufacturing downtime, scrap, costly rework, and delays. This is evident in every market and application where adhesives are used including structural, industrial, electronic applications and others. It is critical that high impact adhesive applications, such as structural adhesives used in the body of an aircraft, industrial adhesives used in automobile engines and electronic adhesives used on circuit boards used to power satellites or radar systems, all perform at their best, meeting specifications, every time.

For a consistent and successful adhesive bond, there are three critical parts which must work in unison including: (1) well manufactured, high quality adhesive meeting specifications, (2) clean and properly prepared substrate surfaces and (3) appropriate processing and handling of the adhesive during its application. Failure to properly execute in any of these areas may result in a poor adhesive bond resulting in part failure (Figure 1).

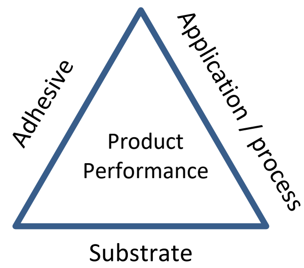

Fig. 1: Three Critical Inputs to Successful Bonding

Common issues that may occur when using adhesives and inadequate execution with any of these three inputs include delamination, poor adhesion, drying and brittleness of the adhesive, excessive flow of the adhesive, PCB warpage, parts moving on the PCB, and poor electrical conductivity. To understand the root cause of these common adhesive issues, it is beneficial to understand some of the science critical for adhesion.

II. The Science of Adhesion

An adhesive bond is created mainly by two separate mechanisms, chemical bonding, and mechanical bonding. Chemical bonding produces strong covalent, ionic, and metallic bonds by sharing or swapping electrons between the functional groups of the adhesive and a substrate. "It is the strongest mechanism of adhesion." [1] Mechanical bonding is the physical interlocking between two dissimilar materials such as an adhesive flowing and curing into microscopic pores and cracks of a substrate. "It also serves to increase surface area, increasing total contact between adhesive and substrate." [1] This increased surface area also promotes additional chemical bonding. Chemical and mechanical bonding are the methods of developing strong adhesive bonds.

Adhesive failure is categorized into three categories, adhesive, cohesive and substrate failure. Adhesive strength is the interfacial strength between adhesive and substrate and failure results at the adhesive-substrate interface. [2] Cohesive strength is the internal strength of the adhesive, and a fracture allows a layer of adhesive to remain on both substrate surfaces. [2] Finally substrate failure is the ability of the substrate to stay together. Depending on the failure mode, insight into the original quality of the bond is gleaned. In general, failure within the adhesive or within the substrate indicates bonding between the adhesive and substrate is ideal and maximum bonding has occurred. Adhesive failure, also called interfacial failure, generally indicates a non-optimal surface preparation, and process improvements are likely required to achieve maximum bond strength and performance.

To further understand chemical and mechanical bonding, additional insight of the behavior of adhesives during the cure process is beneficial. After adhesives are applied to a substrate, a curing process typically ensues. This is true of both paste and film adhesives where the adhesive is exposed to heat for a certain time during which the adhesive changes from its liquid phase to a solid/harden phase. This is known as curing. Figure 2 displays a viscosity curve for a typical adhesive as it is put into an oven to cure.

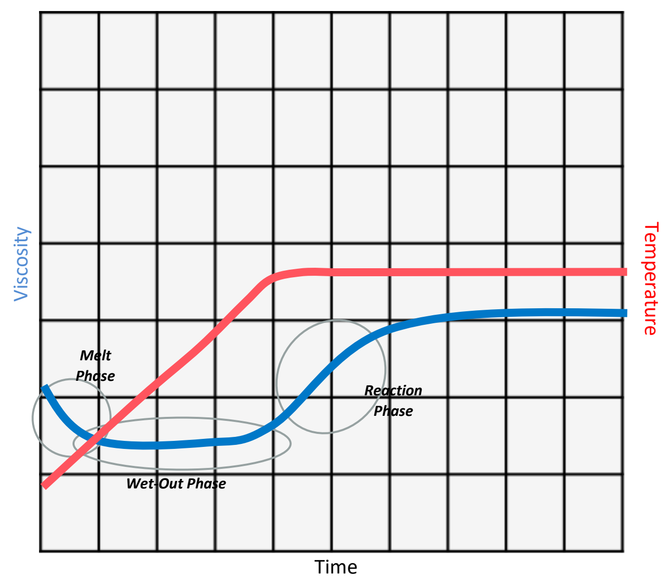

Figure 2: Viscosity of an Adhesive While Curing
(viscosity = blue line, cure temp = red line)

When a part is placed into a hot oven, the part itself will experience a temperature ramp-up from its original room temperature to the oven set temperature. The length of time required for this temperature ramp-up is dependent on many factors such as the size of the part being placed into the oven, the number of parts being placed into the oven, the actual temperature of the oven and the quality and size of the oven itself.

Upon exposure to high temperature, the viscosity of the adhesive decreases immediately. This is known as the melt phase during the curing process. Ultimately, this drop in viscosity stabilizes for a short time and this phase is known as the Wet-Out phase. During the Wet-Out phase, because the viscosity of the adhesive is lower, the adhesive is prone to flow. Adhesive flow is necessary to ensure adequate wetting of the substrate which facilitates bonding. Please note that excessive adhesive flow can also be an undesirable occurrence that may lead to poor bonding. As the adhesive remains in the oven with continued exposure to the high temperature, the adhesive will begin to molecularly crosslink and increase in viscosity. This is known as the reaction phase. Eventually, the viscosity of the adhesive will stabilize as it reaches full cure. This adhesive viscosity cure is shown as the blue line in Figure 2. Note the initial viscosity drop (melt phase) followed by the lower viscosity (wet-out phase) then finally the molecular crosslinking and viscosity buildup (reaction phase).

Understanding adhesive behavior during cure and the concept for the need of substrate wetting is critical. This helps provide insight to what is needed for good adhesive bonds. With this understanding, one can then begin to assess factors that may impact adhesive bonding. As previously outlined, these factors can be categorized into three groups, (1) performance and quality of the adhesive, (2) clean and properly prepared surfaces to be bonded, and (3) well developed application processes.

III. Adhesive Formulation and Selection

Adhesive manufacturing today is for the most part a mature market. There has been a consolidation of the adhesive manufacturing industry over the past decades resulting in fewer manufacturers with streamlined operations with a focus on quality. [3] Most manufacturing operations are AS9100, ISO9000, TS16949, MIL 883 spec 5011 and NASA certified. While this does not guarantee perfect adhesive being shipped every time, adhesive customer complaint statistics indicate that poor adhesive quality comprise a small percentage of issues. Most issues are due to the application and substrate surface preparation.

With that said, the selection of an adhesive for a particular application is critical to the ultimate success of the part. Adhesives are formulated with specific properties such as viscosity, thixotropy, flow, and cure times. For example, resin rich adhesive systems tend to flow more than a highly filled adhesive. Special low molecular weight diluents are sometimes used to lower viscosities and increase flowability. Adhesion promotors are at times added to formulations to enhance performance on oily metal substrate surfaces. Depending on the end application, the need for any of these key adhesive properties can vary. The correct selection of an adhesive is critical for the ultimate success of a bonded part.

IV. Application and Processing

The handling, processing, and application of an adhesive at the end-user is a critical component to ensure a successful bond. Adhesive suppliers typically provide general user guidelines with the adhesive. These guidelines accommodate most applications but consideration to unique application requirements may alter the process and handling of an adhesive.

Attention to adhesive storage conditions is important as this can vary among adhesive types. While some adhesives can be stored at room temperature, other adhesives required frozen storage. Frozen adhesives typically require a very prescribed thawing procedure to minimize air bubbles from forming during thaw which can lead to dispensing issues, dot size variations, flow and adhesion issues. All adhesives have a working life during which the material is stable and can be used consistently. Material beyond its work life can increase in viscosity thus changing its dispense and flow performance.

The best scenario is close interaction between an adhesive supplier and end user to assist with the selection of an adhesive as well as providing user and processing guidelines to support an application.

V. Substrate Surface Chemistry

The condition of the substrates being bonded are critical to achieving good adhesive bonds. A substrates surface energy is linked to the condition of a substrate. The surface energy of a substrate varies depending on many factors such as the material of construction, chemical pretreatment, storage conditions, how the substrate was handled and the general cleanliness of the substrate.

Surface energy is defined as the molecular force of attraction between materials generated by the excess energy at the surface of a material. [4] “Now let us consider what happens when a liquid contacts a surface. If the molecules of the liquid are attracted to each other more strongly than to the surface than the liquid, it won’t wet the surface very well and instead will form beads. Conversely, if there is a larger attraction to the surface, then the liquid will spread out more.” [4] The classic example that demonstrates this is a freshly waxed car. A car typically has a high surface energy in an unwaxed state, indicated by a water droplet spreading across the surface. After the car is cleaned and wax is applied, the surface energy decreases and water droplets will bead up because the water is attracted more to itself than the surface of the wax coating.

A substrate’s surface energy influences the ability of adhesive to flow and wet a substrate thus impacting adhesion. Revisiting the waxed car example, the freshly waxed substrate equates to low surface energy which means the molecular force of attraction is weak between the car and the water drops.

This concept applies to all substrates. Additionally, surface energy will change over time depending on how the substrate is prepared, cleaned, stored, and handled. Take as an example a metal substrate. As soon as it is exposed to the environment, moisture in the air will begin to react with the metal substrate producing an oxide layer. As time goes on, the substrate may be exposed to other organic contamination such as dust, dirt, or fingerprints. As the substrate’s surface goes through these changes, its surface energy changes.

A simple method of evaluating a substrate's surface condition is to measure water contact angle on the surface. A contact angle is formed when a drop of liquid is placed on a material surface and the drop forms a dome shape on the surface (Figure 3). The contact angle θ refers to the angle between the surface and the line tangent to the edge of the drop of water. (1)

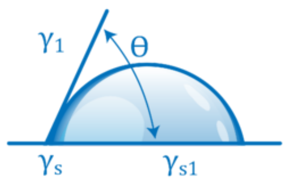

Figure 3: Water Contact Angle

As the condition of the substrate changes, the substrate's water contact angle will change accordingly. A drop of water will flow depending on the surface energy of the substrate as shown in Figure 4. "If the drop of water spreads out and becomes flatter, the contact angle is smaller. If the drop of water beads up (like on a waxed car), and becomes taller, the angle is larger." [1]

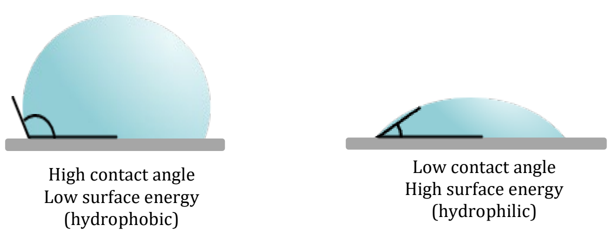

Figure 4: Hydrophobic & Hydrophilic Behavior of Liquid

Water contact angle is inversely proportional to the substrate surface energy as shown in Figure 5. This is

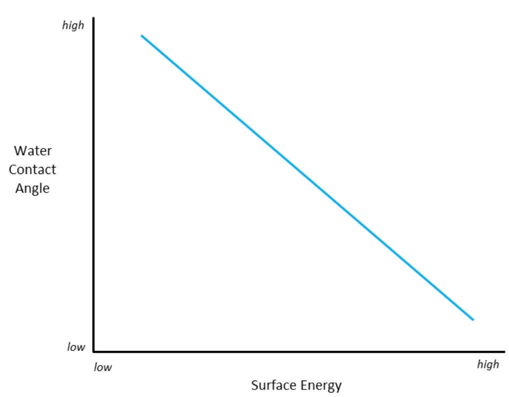

Figure 5: Substrate Water Contact Angle vs Substrate Surface Energy

because a low surface energy of a substrate, resulting in a low molecular force of attraction, will produce hydrophobic behavior where the substrate and liquid tend to repel, and the result is a drop of water that stands tall. On the other hand, high surface energy means a strong molecular attraction between the substrate and water drop. The water drop will be pulled towards the substrate and wet the surface (hydrophilic behavior). The substrate water contact angle changes accordingly in each of these scenarios inversely to the changing surface energy.

"Contact angle measurements provide an estimation of surface energy that can be related to surface cleanliness. This type of analysis is sensitive to the top few molecular layers of a surface [6]. Gilpin [7] shows that a high-energy molecule—water—with a large polar component can be used as a direct estimation of total surface energy. A clean surface with high energy will display a low contact angle: the surface tension of the water droplet will be overcome by the energy of the surface and spread out (i.e. the water molecules are more attracted to the high-energy surface than themselves). Conversely, a surface that is contaminated will display low surface energy and produce a high contact angle: the water molecules are more attracted to themselves than the surface, and the droplet will bead up." [8]

VI. Experimental Studies

As previously indicated, surface energy of a substrate can change with different surface preparation techniques. In this experiment, the adhesive and application method were held constant while the surface preparation method was varied. The experimental objective to was to determine the impact of surface conditions on adhesive bonding performance.

The adhesive used was a Defense & Aerospace industry standard epoxy film adhesive. It is an electrically conductive film adhesive filled with silver flakes. The film was 4 mil thick with a 1-mil glass fabric carrier embedded within the epoxy/silver mixture.

Lap shear specimens were built per ASTM D1002, where Alclad panels of Ti alloy with dimension of 1" x 5" x 0.062" were prepared by varying the level of surface preparation performed including no cleaning to manual IPA wipe then finally surface abrasion. The substrate water contact angle was tested and recorded for each substrate. The epoxy film was then placed between two Alclad panels overlapped 0.5 inches then cured. The samples were tested for lap shear strength then results plotted to display the relationship of lap shear strength versus substrate water contact angle.

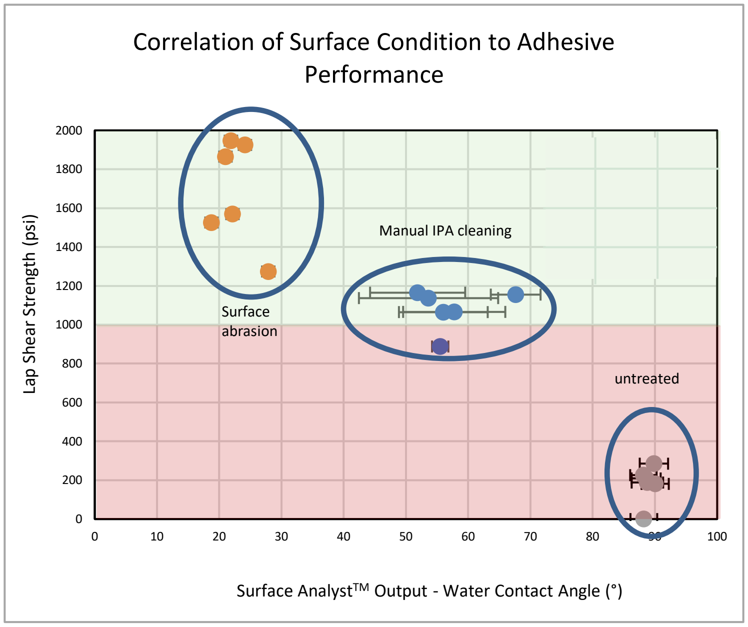

Figure 6: Correlation of Surface Condition to Adhesive Performance

The results of this experiment are presented in Figure 6. The six test samples which were not treated registered an average water contact angle of about 90°. The samples which were manually cleaned with an IPA wipe recorded an average water contact angle of 56° while the samples where the substrates were abraded logged a lower water contact angle of 22°. This trend of water contact angle decreasing with more sophisticated surface preparation techniques is consistent with general observations in practice.

Lap shear data is also presented in Figure 6. Film samples that were prepared on substrates that were not treated registered very low lap shear strength of about 200 psi. The film samples prepared on substrates cleaned with IPA registered almost a 5-fold improvement in strength of about 1,100 psi. Film samples built with substrates which were abraded had an average lap shear strength of about 1,700 psi. Higher surface energies have a higher molecular force of attraction between the adhesive and the substrate. The epoxy will be more attracted to the substrate, thus promoting more epoxy flow and wetting of the substrate. This additional adhesive flow and wetting of the substrate promotes better chemical and mechanical bonding.

An interesting takeaway from this study is manufacturing engineers may consider utilizing substrate water contact angle as both a troubleshooting tool as well as a predictive tool of adhesive performance. If substrate water contact angle is recorded at every step of the assembly process, should an adhesive fail, water contact angle data could be reviewed and may assist in identifying root cause. On the other hand, with a more proactive approach, surface preparation could be adjusted immediately at any point in the supply chain if high water contact angles are being measured prior to adhesive application. A leading adhesive supplier and the surface science industry recommends substrate water contact angles of <50° for most metals for optimal adhesive performance although tighter or looser specifications may vary depending on the adhesive system. Adhesion to polymers will vary depending on polymer type and adhesive choice. Bond performance testing should always be conducted to confirm necessary water contact angle specification for each application.

VII. Conclusion

There are three main components to achieving good adhesive bonds: the adhesive, the substrates, and the application/processing of the adhesive. Adhesive bonding is best accomplished when the adhesive can appropriately flow and wet a substrate. This promotes both chemical and mechanical bonding. Some adhesives are formulated to flow more with special diluents, filler particle shapes, loading and lower viscosity resins. The condition of substrates to which the adhesive is being bonded has large impact on the quality of the adhesive bond. Every substrate has a surface energy which is the molecular force of attraction between materials. A high surface energy indicates a high molecular attraction between the adhesive and substrate, which promotes adhesive flow and wetting of the substrate. This typically results in better bonds.

Substrate water contact angle is a method to easily gain insight into the surface energy of a substrate. Due to the ease and convenience of measuring water contact angle, there is much opportunity to incorporate this tool into manufacturing lines to be used as both predictive and troubleshooting tools.

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