

Investigation of the adhesive-bonded aluminum-polyamide hybrid joints

Master of Science in Materials Science and Engineering

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Investigation of the adhesive-bonded aluminumpolyamide hybrid joints

Abstract

Today, environmentally friendly, high-strength and lightweight engineering materials are becoming increasingly important for the automotive and aviation industries. For this purpose, it is critical to combine different materials correctly and to create a reliable hybrid structure. Adhesives have a huge market share among the joining methods due to their low-stress concentration, high formulation possibility, good fatigue resistance, and sealing advantages. However, surface properties and surface treatments play an active role in determining joint performance.

In this thesis, the effect of roughness, plasma treatment, and adhesive type on adhesivebonded aluminum and polyamide samples were investigated. In this context, three different grit size ratios (120, 500, 1200), three different plasma methods (only aluminum, only polyamide, both surfaces), and three different adhesives (cyanoacrylate, epoxy, MS polymer) were used. Roughness, contact angle, lap joint shear strength and scanning electron microscopy tests were carried out. As a result of the data obtained, the increase in grit size decreased the Ra, Rq, and Rz values and the abrasive trace size in the samples sanded with P120, P500, and P1200 grit size. The decrease in Ra caused a decrease in the contact angle and an increase in the shear strength of the lap joint. Plasma treatment effectively increased the contact angles of the aluminum and polyamide surfaces, and the shear strength of the lap joint highly increased. Applying the plasma treatment on both sides did not increase the effect. The lap joint shear strength of the adhesive types is listed as epoxy>cyanoacrylate>MS Polymer. The lap joint shear strength value order of the observed failure modes is substrate > adhesion/cohesion > adhesion > cohesion.

Keywords: Adhesive, roughness, contact angle, lap shear strength, failure type

Yapıştırıcı ile birleştirilmiş alüminyum-poliamid hibrit bağlantıların incelenmesi

Öz

Günümüzde çevreci, yüksek mukavemetli ve hafif mühendislik malzemeleri otomotiv ve havacılık sektörü için giderek önem kazanmaktadır. Bu amaçla farklı malzemelerin doğru şekilde biraraya getirilmesi ve güvenilir bir hibrit yapı oluşturulması kritiktir. Yapıştırıcılar düşük gerilim konsantrasyonu, yüksek formülasyon imkanı, iyi yorulma direnci ve sızdırmazlık avantajları nedeniyle birleştirme yöntemleri arasında oldukça büyük pazar payına sahiptirler. Ancak yüzey özellikleri ve yüzey işlemleri bağlantı performansını belirlemede etkin rol üstlenmektedir.

Bu tezde, yapıştırıcı ile bağlanmış alüminyum ve poliamid numunelerinde pürüzlülük, plazma işlemi ve yapıştırıcı tipinin etkisi araştırılmıştır. Bu bağlamda, üç farklı kum boyutu oranı (120, 500, 1200), üç farklı plazma işlemi (sadece alüminyum, sadece poliamid, her iki yüzey) ve üç farklı yapıştrıcı (siyanoakrilat, epoksi, MS polimer) kullanılmıştır. Pürüzlülük, temas açısı, bindirmeli bağlantı kayma dayanımı ve taramalı elektron mikroskobu testleri gerçekleştirilmiştir. Elde edilen veriler sonucu P120, P500, P1200 kum boyutu ile zımparalanan numunelerde grit boyutu artışı Ra,Rq ve Rz değerlerini ve zımpara izi boyutunu düşürmüştür. Ra' nın azalması temas açısının düşmesine ve bindirmeli bağlantı kayma dayanımının artmasına neden olmuştur. Plazma işlemi alüminyum ve poliamid yüzeylerin temas açılarını etkin bir şekilde bindirmeli bağlantı kayma dayanımı yüksek oranda arttırmıştır. Plazma işlemini çift tarafa uygulamak etkiyi arttırmamıştır. Yapıştırıcı türlerinin bindirmeli bağlantı kayma dayanımı değeri sıralaması, substrat > adhezyon/kohezyon > adhezyon > kohezyon şeklindedir.

Anahtar Kelimeler: Yapıştırıcı, pürüzlülük, temas açısı, bindirmeli bağlantı kayma dayanımı, hasar modu

To the curious child inside me and to my family who always helped me.

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List of Abbreviations

FSW	Friction stir welding
FSSW	Friction stir spot welding
РР	Polypropylene
СРО	Chlorinated polyolefin
EPR	Ethylene-propylene rubber
TI	Thixotropic Index
RTV	Room-temperature-vulcanizing
MS	Modified silicone
SPUR	Sily-modified polyurethane
ToF-SIMS	Time-of-flight secondary ion mass spectrometry
XPS	X-ray photoelectron spectroscope
AFM	Atomic force microscope
SEM	Scanning electron microscope
ATR-IR	Attenuated total reflectance infrared spectroscope
SE	Secondary electrons
BSE	Backscattered electrons
EDS	Energy-dispersive X-ray spectroscopy
3D	Three-dimensional
PLA	Polylactic acid
HDT	Heat deflection temperature
Rpm	Revolutions per minute
CAD	Computer-aided design

List of Symbols

C=O	Carbonyl group
(-OH)	Hydroxyl group
А	Angstrom
Wc	Work of cohesion
Wa	Work of adhesion
γ	Surface energy
θ	Theta
k	Contact coefficient
cP	Centipoise
η	Viscosity
°C	Celcius
MPa	Megapascal
kJ	Kilojoule
μm	Micrometer
kV	Kilovoltage
kHz	Kilohertz

Chapter 1

Introduction

1.1 Metal – polymer joining techniques

There are several methods for joining metals and polymers. These are summarized in Figure 1.1



Figure 1.1: Classification of joining process

1.1.1 Adhesive

It is one of the most used joining methods in the industry. Its most important feature is the transfer of load by shear (1). The mechanical properties of the bonded joint depend on the properties of the adhesive and the joint configuration. While the load distribution is evenly distributed in the center of the connection, peak values can be found around the edges. Compared to mechanical fastening and welding methods, it has advantages such as the ability to join different materials, low-stress concentration, improvement in fatigue resistance, sealing, weight reduction, good surface finishing, assembly of thin or flexible substrates, and no need for holes. However, it has drawbacks such as being difficult to remove, requiring good surface preparation, low design security, withstand shear loading only, bond failure is difficult to predict, temperature sensitivity, high purchase cost, hazardous chemical and solvent emission (2,3). Automotive, rail systems, and furniture, are some of the adhesive applications (4).



Figure 1.2: Adhesive Failure Modes. (a) Adhesion Failure, (b) adhesion/cohesion failure, (c) cohesion failure, and (d) substrate Failure (5)

1.1.2 Welding

Metals can be joined with thermoplastics and composites by welding using heat and pressure. For combining metals with polymer hybrids, several forms of welding, such as friction stir welding (FSW), laser-based welding, friction stir spot welding (FSSW), and ultrasonic welding, are viable approaches (6). In most cases, the welding procedure consists of three phases. These include the production of molten material,

the development of bonds, and the cooling of molten material over time. In the laser welding method, narrow and deep welding can be obtained with a concentrated heat source without filler material (7). Steel structures, engine parts, vehicle body pieces, and interiors are all great candidates for this joining technique. (8). Due to the lower heat used in solid-state welding, the base metal does not melt and is ideal for joining aluminum alloys and polymers. In the FSW method, which is a type of solid-state welding, heat is generated by friction between a rotating probe and the workpiece. Thanks to the low temperature, less cracking and degradation are observed in the base material (9). It is used in aviation, maritime and automotive industries to produce lighter and more economical structures and long straight welds (10).



Figure 1.3: Laser-beam-welding of aluminum and polyamide (11)

1.1.3 Mechanical Fastening

Mechanical fastening includes methods such as press-in fastening, self-tapping screws, inserts, boss caps, press-on fasteners, panel fasteners, blind riveting, and clinching. The following are some of the advantages of these methods (12,13):

- reopenability of the assembled pieces,
- easy technology and machinery
- controllable volume capability
- joint of dissimilar materials
- ease of joint inspection

- assurance of structural integrity by well-known prediction methods and analysis
- little surface preparation and cleaning are required
- repair or replacement of pieces is facilitated

The disadvantages are as follows (12,13):

- augmented stress concentration
- loosening of fasteners due to creep, moisture, and stress relaxation
- notch sensitivity and crazing (beginning of cracking) of the polymeric partner
- reclosure limitation (polymer does not withstand torque from inserted fasteners)
- differences between the thermal expansion coefficient of plastics and metallic partners may increase residual stresses
- loss of properties due to moisture
- need to access both sides of the part
- increased number of process steps,
- weight penalty due to thicker sections (for reducing the effect of hole stress concentration) and fasteners.

The rear door of the vehicles is joined by clinching. Several automobiles' automatic gearboxes are fitted using aluminum screws. Aluminum panels and sandwich composites are also held together using fasteners (4).



Figure 1.4: (a) Bolt, (b) screw, and (c) stud fastener joints (14)

1.2 Adhesion Theories

The interaction between atoms and molecules at the interface of two surfaces is called adhesion (15). The source of these interfacial forces may be van der Waals forces, chemical bonds, or electrostatic attraction forces (16). Adhesion is a relatively complex multidisciplinary research field that combines surface chemistry, physics, rheology, polymer chemistry, stress analysis, polymer physics, and fracture analysis (17).

There is no single universal theory that explains the reasons for adhesion. Various adhesion theories based on diffusion, mechanical, molecular, and thermodynamic adhesion mechanisms in the literature are still controversial. Combinations of these mechanisms often coexist for an adhesive joint system. The first theories developed were mechanical interlocking, electrostatic, diffusion, and adsorption/surface reaction theories (16).

Especially in the aerospace and automotive industries, the surface properties of the material significantly affect the adhesion performance. In recent years, the need for the adhesive sector has increased due to the increasing demand for light, durable and inexpensive metals, and metal alloys in these two sectors. Therefore, it has become increasingly important to understand the adhesion behavior and interfacial interactions of polymers (18–22).

For example, in the process of coating the PP fender part with paint, the adhesion performance between the polymer surfaces and the paint varies depending on the number of chemical groups present at the interface. By adding chlorinated polyolefin (CPO) (21) or ethylene-propylene rubber (EPR) to the polymer material with low adhesion property (21,23), by increasing the amount of polar functional groups on the surface by methods such as flame treatment (24)/plasma, adhesion performance can be improved. The plasma process creates Carbonyl (C=O) and Hydroxyl (-OH) groups with a high desire to bond on the surface, increasing the amount of chemical bonding of adhesive molecules with the surface (25–28).

1.2.1 Mechanical Interlocking

This simplest bonding theory, which was produced by MacBain and Hopkins in 1925 (29) is based on the idea that adhesion fills up spaces and defects in the adhesive's substrate surface. The most obvious example of this effect is the increase of mechanical adhesion by embedding the fiber ends of the textile fabric into the rubber (30).

The glue must be attached to both the gaps of the upper and lower surfaces for good adhesion, and the adhesive employed should limit the creation of air at the interface. With uneven surfaces, adhesives establish stronger bonds than flat surfaces. However, the source of increased adhesion after surface etching may also be mechanical locking, formation of a clean surface, formation of a highly reactive surface, or an increase in the contact surface area. Therefore, it is controversial whether mechanical locking or a mechanism caused by the increase in the adhesive contact surface is caused by these strong bonds.

It is known that as the surface area increases, chemical bonding and wetting increase. Although the theory predicts that the strength should increase with the increase of the rough structure on the surfaces of fibrous materials such as paper, leather, and such as paper at the macro scale, it has been observed that increasing the roughness on the surfaces of wood decreases the adhesion strength. The fact that good adhesion is also observed between smooth surfaces is proof that this theory cannot be universally accepted. (31).



Figure 1.5: Demonstration of adhesive filling into the rough surface. (a) Good wetting, (b) poor wetting behavior (32)

1.2.2 Electrostatic

According to this theory, which was developed by Deryaguin and Krotova in 1948 (33), a separation-resistant double layer is observed at the interface of the adhesive and the adhered material after bonding. The substrate behaves like a capacitor and electron transfer takes place between opposite poles (material and adhesive). As a result of the separation of these layers during the failure, a potential difference occurs, and this difference continues until the discharge occurs. These interactions, which are very small and negligible compared to chemical bonds (34), have been observed especially between polymer surfaces and thin metallic films sprayed on them (35).



Figure 1.6: Illustration of the electrical double layer at the polymermetal interface (32)

1.2.3 Diffusion

This theory, developed by Vojvutskii in 1949, explains the adhesion between two identical polymers (36). Two macromolecule interdiffusion with each other causes the formation of a transition zone (interphase). The interface layer thickness is between 10 A-1000 A. This interlocking state takes place at the ends of the chains of macromolecules. There are certain conditions for adhesion to occur. The adhesive and the adhered material (adherent) must be polymers, be soluble in each other and be compatible. In addition, sufficient temperature is needed for macromolecules to have high mobility (37). The variation of diffusion over time is shown in Figure 1.7.



Figure 1.7: Interdiffusion across the interface (32)

1.2.4 Weak Boundary Layer

According to this theory developed by Bikerman in 1961, the diffraction propagation in the assembled parts does not occur exactly at the interface (38). The strength of the bond varies with the bulk properties of the adherences and the amount of cohesive fracture propagated on any of the surfaces in contact. Alternatively, the fracture moves through a weak interfacial layer between the two materials.

The formation of air gaps due to the inability of the adhesive polymer to wet the surface sufficiently, contaminants on the surfaces, defects on the surfaces, the movement of low molecular weight molecules in the adhesive or adherents at the interface, the reaction products between air and adherents or between adherents, are the factors that affect the formation of the layer and the durability of the joint. Figure 1.8 shows Bikerman's classification of factors that cause weak layer formation (32).



Figure 1.8: Model of weak boundary layers. The Bikerman classes: (1) air pores, (2,3) impurities at the interface, (4-7) and the reaction between components and medium (32)

1.2.5 Chemical Bonding

The chemical bond theory is the most well-known and oldest theory. Molecular bonds (dipole-dipole interactions, van der Waals forces) and chemical bonds (ionic, covalent, metallic bonds) are considered determining factors to explain the adhesion between two surfaces. The formation of these bonds requires close contact between the two surfaces and surfaces free from defects, cracks, and air bubbles (21). With the diffusion effect that occurs with thermal activation, solid solution and compound formation with a certain thickness can occur at the interface because of the transport of atoms or molecules. This region is called the reaction region and contains covalent, ionic, or metallic bonds.

By using coupling agents or applying chemicals with different oxide stoichiometry to the surface, the bond strength between adhesive and adherents can be increased. Chemical agents act as a chemical bridge by attaching one end to the substrate and the other end to the polymer. Chemical agents containing silane molecules are the most used adhesion-promoting components for joining organic (polymers) and inorganic materials (glass fibers, mineral fibers, metals) (39).

The general structure of silane coupling agents is $X_3Si(CH_2)_nY$. X is a hydrolyzable (mostly alkoxy) group that reacts with the substrate, while Y represents an organofunctional group that binds to the polymer. The structure of the silane molecule is shown in Figure 1.9. The silane coupling agent forms oxane bonds by bonding with the hydroxyl group of the inorganic surface. In addition, it binds with the reactive functional groups of the polymer to form covalent bonds or interpenetrating polymer networks (39). Since the bond density between the oxide and the surface will increase significantly with high temperatures, these bonding agents cause an increase in strength and moisture resistance in the joint (40). Performing surface oxidative treatment on carbon fibers, and increasing the bonding with polymer matrix are examples of using coupling agents (39).



Figure 1.9: Organo-functional silane molecule basic structure and silanization of ceramic surfaces (41)

1.2.6 Adsorption (Wetting) Theory

If a sufficient tensile force is applied to the bulk material, the material will break, creating two new surfaces. For brittle materials, the work done on the sample is only equal to the new surface formation. The cohesive fracture occurs in material with equal composition on both sides. This work of cohesion is expressed in Equation 1.1 (35).

$$W_c = 2\gamma \tag{1.1}$$

The energy consumed in separating the adhesive from the material is equal to the sum of the surface energy of these two surfaces (γ_1 and γ_2). However, due to the interfacial energy (γ_{12}) caused by the molecular forces between the adhesive and the material before separation, the work of adhesion is calculated as in Equation 1.2 (35).

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} \tag{1.2}$$

Equation 1.2 was revised in 1869 and the Dupre equation given in Equation 1.3 was derived (42).

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \tag{1.3}$$

To provide a strong adhesive bond, the adhesive must contact the entire surface and exhibit effective wetting properties. Wetting refers to the ability of a liquid to spread over a solid surface. It is important to achieve high wetting to prevent the formation of voids and loss of performance because of bonding. Wettability is explained by Young's equation given in Equation 1.4.



Figure 1.10: Representation of the contact angle between a droplet and the surface.

In this equation valid for the equilibrium state, γ_{sv} is the surface energy at the solidvapor interface, $\gamma_s l$ is the surface energy at the solid-liquid interface, and γ_{lv} is the surface energy at the liquid-vapor interface. θ represents the wetting angle. Adhesive wetting is derived by adapting the work function in the first law of thermodynamics (Law of Conservation of Energy).

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \tag{1.4}$$

By combining Equation 1.3 and Equation 1.4, the Young-Dupre equation (Equation 1.5) is derived.

$$W_a = \gamma_{lv} \left(1 + \cos\theta \right) \tag{1.5}$$

 W_a represents the spreading coefficient or work function. According to Equation 2.4, for good wetting (θ <90°), the liquid should have high surface tension. As the angle value goes from 90° to 180°, there is a trend from partial wetting to nonwetting. If the molecules of the liquid are bonded to each other more strongly than at the surface, the liquid will not diffuse on the surface (Figure 1.11a). Conversely, if there is a greater attraction to the surface, the liquid will spread more (Figure 1.11b).

$$W_a = k \left[\gamma_{sv} \left(1 + \cos\theta - \gamma \iota \right) \right] \tag{1.6}$$

Surface roughness is a parameter that changes the contact angle. At contact angles greater than 90 degrees, the roughness of the surface adversely affects wetting and increases the contact angle. However, the increase in roughness at contact angles less than 90 degrees increases wetting. For example, the high roughness seen because of sandblasting the silicon surface caused poor wetting. Polishing the silicon surface mechanically increased wetting compared to solder. Thick-film gold conductors require light sanding to improve adhesion performance (43). For all these reasons, Equation 1.6 was derived by adding the "contact coefficient", which is a function of the surface roughness, to Equation 1.5.



Figure 1.11: (a) Weak and (b) strong attraction between liquid and surface

Wetting behaviors and surface properties according to contact angle are summarized in Table 1.1. It is known that metal oxides show wetting behavior ($\theta < 90^\circ$), while nonoxide metals show non-wetting behavior ($\theta > 90^\circ$). In addition, non-polar organic polymers such as Teflon and surfaces containing hydrophobic contaminants such as silicone, oil, and grease also exhibit non-wetting behavior (44). According to Equation 1.2 and Equation 1.3, an adhesive with high surface tension should be chosen to ensure good adhesion. For example, epoxies often have a surface tension of 89 dynes/cm. The surface tension of pure water used in contact angle analysis is 72 dynes/cm. Therefore, as a rule, epoxy is expected to wet a surface wetted by water (45).





In addition to contact angle, surface energy, and surface tension, pot life and gel time are also factors affecting wetting. "Pot life" refers to the period of use without decomposition after the one-component adhesive is removed from the container (first application). For two-component adhesives, it represents the time that the two components can be reused without decomposition after mixing. It can also be defined as operating time or usable life. If the pot life is passed, an excessive increase in the viscosity of the adhesive is observed. This makes the adhesive difficult to dispense and does not flow. Manufacturers take the viscosity values as a criterion in determining the pot life of the adhesives. For example, one manufacturer may accept a viscosity value of 25% as the limit, while another manufacturer may set a different limit value for a similar product (45). It has been observed that for an increase of 10 degrees Celsius at temperatures above room temperature, the viscosity of the epoxy decreases from 20% to 80%. Partial gelation and partial polymerization expressed as "B-staged" or "Bstaging", can also be seen in adhesives exceeding pot life. The adhesive that reaches the gelling point becomes unable to wet the surface. For example, in an epoxy adhesive that can be used for 48 hours, an increase in viscosity that causes serious gelation can be observed from below 6,000 cP to 16,000 cP in the next 24 hours (45). In addition, the temperature is also a factor affecting the gelation time. It can be applied at relatively high temperatures to reduce the viscosity of the adhesive and increase wetting.

Component separation or displacement in the resin or hardener parts due to excessive wetting is expressed as bleeding. This is a common problem with low molecular weight and reactive diluent resins and solvent-based adhesives. Porous surfaces can increase bleeding due to capillary action (45). Bleeding can be minimized by removing surface contamination with plasma. Applying too much adhesive to the surface, excessive adhesive thickness (the thickness that will require minimal tightening for adhesion is ideal) increases bleeding. Thixotropic (the fluid that takes a finite time to reach equilibrium viscosity when subjected to a steep change in shear rate) pastes that can be dispersed and cured quickly, are ideal for applications where bleeding is not desired. The thixotropic index (TI) of the adhesive is used for the best adhesive distribution on the surface. TI can be calculated as in Equation 1.7 (46). Adhesives with an index of 2 to 5 are suitable for automatic dispensing.

Thixotropic Index (TI) =
$$\frac{Viscosity at 0.5 rpm, \eta 5.0}{Viscosity at 5.0 rpm, \eta 0.5}$$
 (1.7)

1.3 Surface Preparation for Adhesion

Surfaces must be clean for good adhesion. For example, the deposits formed because of insufficient cleaning of the metals used in electronic components cause corrosion and adversely affect the adhesion. The material, which is exposed to processes such as coating, soldering, and etching, must be cleaned of impurities before adhesion by using suitable solvents. These contaminants are divided into three particulates, highly polar (ionic) residues, and nonpolar (grease-like) residues. Since these three pollutants are often found together in production environments, more than one solvent and cleaning stage is needed. As a rule, polar solvents dissolve polar impurities, while non-polar impurities are dissolved by non-polar solvents. Polar solvents such as water, isopropyl alcohol, ethanol, and methyl ethyl ketone are used for cleaning chloride, salts, acids, acid fluxes, and alkalis. Greases, oils, silicones, rosin flux, and low molecular weight impurities are cleaned with solvents such as hydrocarbons, Freons ®, hydrochlorofluorocarbons, xylene, terpenes, and naphtha (47). Cleaning methods are divided into three solvent cleanings (wet), plasma (gas) cleaning, and CO2 (dry ice) cleaning. These methods are summarized in Figure 1.12.



Figure 1.12: Pre-adhesion surface cleaning methods

In some conditions, cleaning operations are not sufficient for the best adhesion performance. Inert surfaces such as gold, noble metals, Teflon, and non-polar plastics such as polyolefin need additional surface treatment because they have low surface energy. Abrasion, etching, and ion spraying can be applied to remove impurities from the surface and increase wetting by increasing the adhesion surface area. In addition, high wetting and low contact angle values can be obtained on plastic surfaces with corona discharge. Solvent-based and air-drying primers are adhesion-enhancing ingredients. These are applied to the surface with the methods of spraying, brushing, dipping, or spin coating. Primers are very useful for RTV silicone adhesives. Due to the high affinity and polarity, epoxies do not require primer application because solvent-thinned epoxies are used as primers for other polymers. Solvent solutions of various silanes are one of the best primer choices. Semi-crystalline material surfaces have poor adhesion performance due to low polarity and low surface tension. To increase polarity and wetting, oxidizing methods such as corona discharge, plasma, and flame treatment can be applied (47). The plasma treatment aims to transform a lower energy surface into a higher one by removing contaminants from the surface and adding oxygen (polar) containing molecules to the surface (Figure 1.13).



Figure 1.13: Plasma working principle and plasma cleaning mechanism. (1) Electrical charging of accelerated air particles and (2) movement of charged particles to the surface

1.4 Adhesive Types

Adhesive selection for engineering applications is a difficult and time-consuming process. Trial-and-error studies are unreliable and inefficient. To solve this problem, some criteria have been determined for the right adhesive selection over the years. These are load, design (joint geometry, nature of adhesive and adherent), production process, and environment (48). As a result of these criteria, the most used adhesive types are epoxy, polyurethane, modified acrylic, cyanoacrylate, and anaerobic.

1.4.1 Epoxy

Epoxy adhesives have high strength, good high-temperature resistance, good solvent resistance, and good gap filling properties. Their wide range of formulations and relatively low cost make them attractive. However, attention should be paid to the thermal resistance of the parts to be joined as they show an exothermic reaction. They also require the exact mix ratio for correct curing and optimum properties. Exact measuring and mixing at an appropriate speed are required for two-component formulations. Single component formulations often require cold storage and high-temperature curing. In addition, they have a short pot life (49). Metal, plastic, glass, rubber, wood, and ceramic materials can be bonded by epoxy adhesive. Insulating varnish and adhesive, industrial storage tanks sealant, aerospace industry, bonding to vinyl and other plastics, and anti-corrosion sealant for metals and plastics are examples of the use of epoxy adhesives (35).

1.4.2 Polyurethane

Polyurethanes are the adhesive type with the best flexibility at low temperatures. They can be one or two components and have a wide range of curing times at room temperature or high temperature. They are tough, cost-effective, easy to apply, and bond to a wide variety of materials. However, both cured and uncured polyurethane adhesives are moisture sensitive and not resistant to high temperatures. They also have a short pot life and can be applied using special mixing and dispersing equipment (49). Especially plastic, metal, and rubber materials can be bonded by polyurethane adhesive. Lamination of clear plastic, marine, industrial applications, textiles, upholstery, electrical industry, and underwater are examples of the use of polyurethane adhesives (35).

1.4.3 Modified Acrylic

Modified acrylic adhesives have good flexibility, good peel, and shear strengths. They don't need mixing and they can bond to dirty surfaces. The curing at room temperature and moderate cost are advantageous for modified acrylic adhesives. However, the curing time is higher than anaerobic or cyanoacrylates adhesives. They have also low

strength at high temperatures. The drawbacks of these adhesives are that they are toxic and flammable. Dispensing equipment is required for application and care should be taken because of limited open time (49). Metal, thermoset/thermoplastic polymers, and oily surfaces can be bonded by modified acrylic adhesives (35). Developing flexible bonds in plastic and non-plastic assemblies such as office furniture and architectural laminate are examples of the use of modified acrylic adhesives.

1.4.4 Cyanoacrylate

Cyanoacrylate adhesives have high tensile strength and long pot life. They cure quickly at room temperature. Since they are a single component, they can be easily dispensed from the package. They bond metals well but have poor durability with acidic surfaces. In addition, their cost is high. Solvent resistance and elevated-temperature resistance are low. They should be used with caution as they adhere to the skin (49). Metal, plastic (except polyolefins), and glass materials can be bonded by cyanoacrylate adhesives. Closure of wounds/lacerations and quick repair of small parts are examples of the use of cyanoacrylate adhesives (35).

1.4.5 Anaerobic

Anaerobic adhesives have good solvent and elevated temperature resistance. They can cure rapidly at room temperature. They provide high strength on some surfaces (mostly metal). They don't need mixing. The pot life is uncertain. They are non-toxic and moderately costly. However, since the air must be removed for curing, permeable surfaces are not suitable for the use of these adhesives. They have also a limited gap cure (35). Metal, plastic, glass, and wood materials can be bonded by anaerobic adhesives. Bold and stud locking are examples of the use of anaerobic adhesives (35).

1.4.6 Hybrid Sealant

Polyurethane and silicone sealants belong to the family of high-performance adhesives due to their high strength, good adhesion, movement capability, and durability. Adhesives developed to combine the strong properties of more than one polymer material (such as combining the strength of polyurethane with the weathering resistance of silicone) are called hybrid sealants. Hybrid sealants are two types such as sily-modified polyether (modified silicone or MS polymer) and sily-modified polyurethane (SPUR polymer). These two polymer groups can also be called silylterminated oligomers because of their similar backbone structure. These adhesives are environmentally friendly due to their solvent-free and isocyanate-free properties. They have a variety of viscosities thanks to their formulation flexibility. Like other sealants, they can have plasticizers and fillers. Although they are usually single-component, they can also be two-component. Silicone and polyurethane sealants have a 51% share of the sealant market in the USA. Although hybrid sealants have a share of 9% and MS sealants have a share of 1.6%, hybrid sealants are expected to replace conventional sealants in the future. MS polymers are mostly used as a sealant, they can also be used as high-tack (acrylic modified MS) or adhesive with excellent toughness and flexibility (MS-epoxy blends). A detailed comparison of the properties of these three sealant types is given in Table 1.2 (50). Metal, plastic, wood, and materials can be bonded by hybrid sealants. The joining of doors and windows in the building and construction industry are examples of the use of hybrid sealants (50).

Property	MS Polymer	Polyurethane	Silicone
Environmental friendliness	10	5	9
Non-bubbling	10	6	10
Low-temperature gunnability	10	8	10
Slump resistance	10	10	10
Quick cure	10	7	10
Storage stability	10	7	9
Body (tooling)	8	10	8
Weather resistance	8	6	10
Adhesion to various substrates	10	5	8
Mechanical properties	10	10	10
Heat resistance, mechanical stability	9	8	10
Non-dirt pickup	10	10	5
Stain resistance	8	8	5
Paintability with water-based paint	10	10	3

Table 1.2: Comparison of properties of sealants (Scale: 10=excellent; 1=very poor) (51)

1.5 Surface Characterization Techniques

These methods such as Time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), secondary electron microscopy (SEM), attenuated total reflectance infrared spectroscopy (ATR-IR) are used to examine the adhesion phenomenon on the surface and interface. With ToF-SIMS analysis, elemental, isotopic, and molecular information can be obtained at extremely high surface sensitivity (monolayer) (52,53). ToFSIMS and XPS analyses are performed under an ultra-high vacuum to avoid surface contamination. In the XPS method, X-ray photons produced from the monochrome X-ray source meet the sample surface and cause photoelectron detachment from the surface. By examining the characteristic peaks in the spectrum produced by using the kinetic energies of these ejected electrons, the surface composition and oxidation state can be examined. By knowing the surface chemistry, the relationship between elemental and functional groups, surface energy, and bond strength becomes understandable. AFM is a method used to create a topographic map of surfaces. As a result of molecular interactions obtained from surfaces that are in contact with the surface or scanned with probes close to the surface, a horizontal resolution of the order of 0.01 nm can be obtained (53). In addition, the relationship between the roughness values obtained from the topography and the adhesion strength can be established. Contact angle analysis can be performed to observe the relationship between surface energy and adhesion. In addition, there are studies in the literature examining the relationship between roughness, polarity, chemical composition, and surface free energy and adhesion (17,21,24,54-60). In scanning electron microscopy (SEM), electrons are sent to the sample surface. Electrons scattered at different angles are picked up by the detectors. The image is obtained through signals processed by the microscope software. Secondary electrons (SE) provide information about morphology and topography, while backscattered electrons (BSE) provide information about atomic composition based on atomic number and concentration. In addition, the distribution of elements can be mapped with point, linear or regional qualitative and quantitative analysis with the EDS detector.

1.5.1 Surface Roughness Parameters



Figure 1.14: Graphics of the roughness parameters

The arithmetical mean roughness (Ra): the arithmetical mean height indicates the average of the absolute value along the sampling length.

$$Ra = \frac{\sum h}{n} = \frac{h1 + h2 + \dots + hn}{L}$$
(1.8)

Root mean square deviation (Rq): indicates the root mean square along the sampling length.

$$Rq = \sqrt{\frac{h1^2 + h2^2 + \dots + hn^2}{n}}$$
(1.9)

Maximum height of profile (Rz): indicates the absolute vertical distance between the maximum profile peak height and the maximum profile valley depth along the sampling length (61).

$$Rz = \frac{(p1 + p2 + p3 + p4 + p5) - (v1 + v2 + v3 + v4 + v5)}{5}$$
(1.10)
Chapter 2

Experimental

2.1 Materials

2.1.1 Adherent

PA66 and 1050 aluminum alloy were used in this thesis as the adherents. The granular U3501 NC01 low viscosity natural PA66 resin (Invista, Kansas, USA) was supplied from IMS polymers (İzmir, Turkey). Typical resin properties are given in Table 2.1. The chemical analysis of aluminum was carried out by ARL 3460 Metals Analyzer (Thermo Fisher Scientific, Massachusetts, USA) and the result is shown in Table 2.2.

Density	1.14 g/cm ³	ISO 1183
Tensile Strength at Yield	82 MPa	ISO 527
Elongation at Yield	3.9%	ISO 527
Elongation at Break	45%	ISO 527
Tensile Modulus	3000 Mpa	ISO 527
Melting Temperature, 10°C/min	264 °C	ISO 11357
Notched Charpy at 23°C	4.7 kJ/m ²	ISO 179
HDT at 0.45 MPa	199 °C	ISO 75

Table 2.1: INVISTA U3501 PA66 resin properties

Sample	Al	Fe	Si	Sb	Zn	Others
1050 aluminum alloy	99.5%	0.23%	0.17%	0.01%	0.01%	0.08%

Table 2.2: The chemical composition of 1050 aluminum alloy

2.1.2 Adhesive

Three different industrial (cyanoacrylate, hybrid polymer (MS), and epoxy) adhesives were used in this thesis. Pattex super glue gel is extra strong, flexible, impact, and water-resistant. It can fill gaps and does not drip. Apel ProSeries High Tack is a silaneterminated polymer adhesive and insulating material developed with one component MS Polymer technology (hybrid) with excellent initial adhesion. It can be used in all kinds of bonding and isolation processes in all weather conditions. It is easily used in the bonding and fixing of difficult building materials without the need for extra surface treatment. Pattex Power Epoxy adhesive is a fast setting, gap filling, two-part adhesive which produces rigid bonds with high bond strengths. The glue has also advantages such as resistance to water, fuels, grease, and diluted acids.

Adhesive name	Adhesive type	Adhesive properties	Image
Pattex super glue gel	Cyanoacrylate	 Physical Form: Liquid Content: 3 g Adhesive Colour: Clear Temperature resistance range: -20 - 80 °C Drying Time: 1 min 	

Table 2.3: The types of adhesives used in the thesis and their properties

Apel ProSeries high tack H660	MS Polymer	 Physical form: Liquid Content: 290 ml Adhesive Colour: White Temperature resistance range: -40 - 90 °C Drying time 5-10 min 	
Pattex power epoxy	Epoxy	 Physical form: Liquid Content: 35 g Adhesive Colour: Grey Temperature resistance range: 30 - 150 °C Drying time 5 min 	

2.2 Method

2.2.1 Adherent Preparation

PA66 resin was pressed in the form of a 15 mm thick plate using a BL70EKII injection molding machine. (BOLE, Shenzhen, China). Samples were prepared according to ASTM D1002 standards (Figure 2.3). The width of the Al pieces is 25 mm, the length is 102 mm and the thickness is 15 mm. The width of the PA pieces is 25 mm, the length is 100 mm and the thickness is 15 mm. Samples were sanded by SiC grinding paper with three different grit sizes (P120, P500, P1200) perpendicular to the bond direction for 5 seconds at 220 rpm. New sandpaper was used for each aluminum and polyamide adherent. After the grinding process, the samples were cleaned by the ultrasonic bath for 30 minutes at 50 °C.



Figure 2.1: (a) Grinding operation and (b) sanded Al and PA samples

2.2.2 Mould Preparation

The mold was designed to apply equal pressure to the bonded surface and to ensure equal adhesive thickness. Mold is printed by "Ultimaker 3" (Ultimaker, Netherlands) 3D printer. PLA was used as the filament material. Printing parameters are summarized in Table 2.4.

Layer height	0.3 mm
Wall thickness	0.8 mm
Infill	20%
Printing temperature	205 °C
Printing speed	70 m/s
Cooling	100%
Build plate temperature	60 °C

Table 2.4: 3D printing parameters



Figure 2.2: "Ultimaker 3" 3D printer



Figure 2.3: (a) CAD drawing and (b) 3D Printed adhesion test mold

2.2.3 Glue Application

Parts were cleaned using acetone and laboratory wipes before bonding to eliminate contaminants. The glue was applied to polymer adherent surfaces. The adhesive area dimensions are 12.5 mm x 25 mm. The thickness of the adhesive is 5 mm. The adhered parts were pressed with the qual load and left to cure for 24 hours at room temperature. When the curing process is complete the load was removed, and overflowing adhesives were cut off for the tensile testing. A glued sample from each group was used to take the cross-section image on SEM. Adhesively bonded samples were coded as in Figure 2.5.



Figure 2.4: The dimensions of the lap shear test specimen



Figure 2.5: Nomenclature for specimens

2.3 Characterization

2.3.1 Surface Roughness

Average surface roughness values (Ra), RMS roughness (Rq), and the average maximum height of the profile (Rz) were measured by SJ 210 profilometer (Mitutoyo, Japan) according to ISO 1997 standards with a scanning speed of 0.5 mm/s and 100 μ m interval points were selected for each grit sizes. The measuring interval is 100 μ m and analysis was performed along the line drawn from the middle at the adhesion area as shown in Figure 2.6.



Figure 2.6: Mitutoyo SJ 210 profilometer

2.3.2 Contact Angle

Average contact angle values were measured by Attension Theta Lite Optical Tensiometer (Biolin Scientific AB, Sweden) for 10 seconds after 10 microliters of distilled water were dropped on the surface of the adherend at room temperature. The pictures were obtained via OneAttension software (Biolin Scientific AB, v3.2, Vastra Frolunda, Sweden) with surface tension (Young-Laplace) analysis mode. The measurement was made at the midpoint of the adhesion area.



Figure 2.7: Attention Theta Lite optical tensiometer

2.3.3 Scanning Electron Microscope (SEM)

300VP Field Emission Scanning Electron Microscope (Carl Zeiss, Germany) was used to examine the fracture Q150R ES Gold sputter coating was performed on the samples to get a good image. SEM images were obtained under 10 kV operating mode using a secondary electron detector at 1.00 kx magnification as shown in Figure 1.14. Images were taken parallel to the sanding direction.



Figure 2.8: (a) Q150R ES - Rotary Pumped Coater, and (b) The Zeiss Sigma 300 VP SEM

2.3.4 Plasma Treatment

In this thesis, a custom-made cold atmospheric plasma is used. Before the application, the sample surfaces are cleaned with acetone. The laser pulse frequency is 20 kHz. The voltage is 30 kV. The treatment duration is 180 seconds. The treatment area is 25*12.5 mm. The distance between the sample surface and probe is 1 mm.



Figure 2.9: Cold atmospheric plasma

2.3.5 Tensile Testing

20 kN universal testing machine (Hegewald & Peschke, Germany) was used to obtain the single lap shear strength of samples. The tensile test was performed according to the ASTM D1002 standard. The loading speed of the test is 1.3 mm (0.05 in.) /min. 5 samples were tested for each grit size and average values were calculated. For failure type analysis (cohesive, adhesive, cohesion/adhesion, and substrate), the adhesion area separated after the tensile test was photographed.



Figure 2.10:Zwick Z020 universal tensile test machine

Chapter 3

Results and Discussion

3.1 Grit size - Surface Roughness

The surface roughness of pristine and sanded Al and PA samples with 120, 500, and 1200 grit were measured. The effect of grit size on surface roughness parameters and the R profile was investigated.

Their surface roughness profiles (R profile) along 4 mm (L) are shown in Figure 3.1. Along the scanned surface, the highest peak point value (hpp) was observed in Al120, and the highest valley point value (hvp) was observed in the PA120 sample. These points are shown in Figure 3.1b and Figure 3.1f, respectively. Samples with hpp and hvp values were also the samples with the highest Ra, Rq, and Rz values. An acceptable homogeneous roughness profile (Figure 3.1) and wear were created in all samples except the PA1200 sample, proving that the sanding process was optimized. It is thought that the large peak value seen in the PA1200 sample is caused by a defect on the surface due to the deformation of the sandpaper (as a result of heat and friction) during sanding, or a scratch formed as a result of the cutting process. This region is shown in the red circle in Figure 3.1h.



Figure 3.1: Surface roughness profiles (R profiles) of (a) A10, b) A1120, (c) A1500, (d) A11200, (e) PA0, (f) PA120, (g) PA500, and (h) PA1200 sample

Ra values obtained as a result of the analysis are shown in Figure 3.2, Rq values in Figure 3.3, and Rz values in Figure 3.4. For the sanded surfaces, it was observed that the Ra, Rq, and Rz values decreased as the grit size increased. It has been stated in the literature that as grit size and wheel speed increase, surface roughness and removal rate decrease (62). As grit size increases, the length of the abrasive grains and the average diameter of grain decrease (63). P120 sandpaper has an average grain diameter of 122 µm, P500 sandpaper has an average grain diameter of 30 µm, and P1200 sandpaper has an average grain diameter of 15 µm (64). Therefore, less depth is obtained. The order of Ra values measured for Al surfaces is Al10<Al1200<Al500<Al0. Rq and Rz values also have a similar order due to the peak values. The lowest Ra of Al is 0.35 µm while the highest Ra of Al is 5.18 µm. The order of Ra values measured for PA surfaces is PA0<PA1200<A1500<PA120. Rq and Rz values also have a similar order due to the peak values. The lowest Ra of PA is 0.26 μ m while the highest Ra of PA is 3.54 μ m. The reason why the surface roughness values of aluminum are higher than PA is that PA has lower hardness (65,66). For this reason, a higher amount of SiC particles penetrated the surface, resulting in a higher abrasion. Metal surfaces can also often have a high surface roughness due to manufacturing and post-production processes such as rolling, and hard polishing (67). The reason why the PA0 sample has the lowest Ra, Rq, and Rz values is that the injection process allows high quality and smooth surface formation compared to additive manufacturing methods such as FDM (68).



Figure 3.2: Ra values of pristine and sanded samples



Figure 3.3: Rq values of pristine and sanded samples



Figure 3.4:Rz values of pristine and sanded samples

Surface morphologies of Al and PA samples sanded with 120, 500, and 1200 grit sizes were investigated by SEM. It was observed that as the sand size increased, the number of pits on the Al and PA surfaces increased and a hollower structure was formed on the surface. The R profiles in Figure 3.1 also prove that as the grit size increases, shallower pits form on the adherent surfaces. In addition, as the grit size increased, the trace size due to sanding decreased on the surfaces. The abrasive trace size on the surface of Al120 (Figure 3.5a) and Al1200 (Figure 3.5c) samples were 41.87 μ m and 4.41 μ m, respectively. The abrasive trace size for PA1200 samples is 20.67 μ m (Figure 3.6a) and 10.12 μ m (Figure 3.6c), respectively. As the Ra value decreased, the surfaces became opaquer as seen in Figure 2.1.



Figure 3.5: SEM images of (a) Al120, b) Al500, (c) and Al1200 sample at 1.00 kx magnification



Figure 3.6: SEM images of (a) PA120, (b) PA500, and (c) PA1200 sample at 1.00 kx magnification

3.2 Surface Roughness - Contact Angle

Wetting performance and contact angle values of pristine and sanded samples were measured. Contact angle values and surface roughness parameters are summarized in Table 3.1. The relationship between the average roughness of the Al samples and the contact angle and the drop shape is shown in Figure 3.7, and the relationship between the average roughness of the PA samples and the contact angle and the drop shape is shown in Figure 3.8.

Sample name	Ra (µm)	Rq (µm)	Rz (µm)	Contact Angle (°)
A10	0.35 ± 0.03	0.48 ± 0.03	2.95 ± 0.44	78.56 ± 2.48
AL120	5.18 ± 0.63	6.38 ± 0.70	27.48 ± 2.82	90.48 ± 1.19
AL500	1.10 ± 0.14	1.37 ± 0.15	6.61 ± 0.64	87.09 ± 2.54
AL1200	0.53 ± 0.14	0.69 ± 0.16	3.91 ± 0.48	71.77 ± 3.41
PA0	0.26 ± 0.09	0.34 ± 0.11	2.11 ± 0.54	67.55 ± 3.09
PA120	3.54 ± 0.99	4.60 ± 1.26	22.99 ± 5.23	78.82 ± 3.44
PA500	0.47 ± 0.15	0.63 ± 0.17	3.69 ± 0.62	66.08 ± 3.55
PA1200	0.38 ± 0.19	0.53 ± 0.26	3.32 ± 1.47	60.48 ± 2.83

Table 3.1: Contact angle of pristine and sanded samples

Contact angle values of Al samples are listed as Al1200<Al0<Al500<Al20. The lowest contact angle value is 71.77° while the highest contact angle value is 90.48°. Contact angle values of PA samples are listed as PA1200<PA500<PA0<PA120. The lowest contact angle value is 60.48° while the highest contact angle value is 78.82°. Accordingly, the contact angle values of all PA samples were lower than the Al samples. This is because polyamide is polar and hydrophilic (-CONH) due to the amide (-CONH) functional group it contains (69,70). In addition, hydrophobic pollutants on the surface of aluminum alloys and the oxide layer formed after sanding cause an increase in the contact angle (71).

In the sanded AL and PA samples, the contact angle increased as the roughness increased, but no relationship could be established between the roughness and contact angle in the Al0 and PA0 samples. This increase in contact angle is due to the inability of the liquid to penetrate rough surfaces well and gas molecules trapped in rough

valleys. The roughness causes the formation of a discontinuous liquid-solid interface. Therefore, there is an alternation between solid-liquid and gas-liquid interfaces. The micro-geometric barrier effect prevents the liquid from spreading freely and reduces wetting (72).

Studies in the literature have reported that as the roughness increases, the contact angle increases. Boutar et al. measured the contact angle by dropping deionized water onto the pristine, P50, P180, and P1000 polished aluminum-copper alloy surface. Increasing the surface roughness increased the contact angle (72). Borsellino et al. measured the contact angle by dripping polyester, vinyl ester, and epoxy resin onto the pristine, P40 and P180 sanded aluminum AA6082 surface. They observed that the contact angle increased as the Ra value of the Al surface increased in all resins except vinyl ester (73). Ghumatkar et al. measured the contact angle by dripping epoxy resin onto a pristine, P50, P80, P120 sanded aluminum and mild steel surface. The contact angle increased continuously as the roughness increased (74).



Figure 3.7: Contact angle of sanded Al samples



Figure 3.8: Contact angle of sanded PA samples

3.3 Surface Roughness - Lap Shear Strength

LSS values of pristine and sanded samples were measured. LSS values and the Ra relationship are summarized in Table 3.2. Fracture types calculated as a percentage over 5 samples and surface images of fractured samples are shown in Figure 3.9

As the roughness increased in the sanded AL and PA samples, the lap shear strength decreased. The reason for this decrease in LSS is that the adhesive does not penetrate the cavities well before curing due to the grooves and valleys (Figure 3.1, Figure 3.5, and Figure 3.6) created by the roughness. In addition, the air formed in the spaces between the substrate and the adhesive adversely affected the effective bond formation (72).

When the fracture types are examined, adhesion failure is the most common fracture type in almost all samples. It was observed that the adhesive remained on one side (PA) after rupture. This is because PA samples show more hydrophilic properties compared to Al (Table 3.1). In addition, as the LSS value increased, it was observed

that there was a tendency from adhesion failure to adhesion cohesion and substrate. As the roughness decreases, the adhesive tends to bond better with both Al and PA.

Table 3.2: Lap shear strength of adhesively bonded pristine and sanded samples

Ra (µm) Lap Shear Sample name Al PA Strength (MPa) 0.35 ± 0.03 0.26 ± 0.09 2.2 ± 0.24 AlPA0-CA 1.54 ± 0.43 5.18 ± 0.63 3.54 ± 0.99 ALPA120-CA 1.10 ± 0.14 0.47 ± 0.15 1.77 ± 0.33 ALPA500-CA 0.53 ± 0.14 0.38 ± 0.19 2.95 ± 0.41 ALPA1200-CA



Figure 3.9: Failure types of adhesively bonded pristine and sanded samples.

Cross-sectional images taken from the midpoints of the adhesively bonded samples are shown in Figure 3.10. Dark areas represent Al and light areas represent PA.

It was observed that the heat generated during the cutting process created a welding effect. The temperature caused Al to fold over the PA. The deviation from the theoretical bonding line due to deformation (Figure 3.10a, Figure 3.10b, Figure 3.10c, and Figure 3.10d) and the fusion of Al by entering the PA (Figure 3.10c) prove this situation. When the contact angles given in Table 3.1 are examined, a very effective coupling was observed in the AlPA1200-CA sample with the lowest contact angle values. However, due to the folding problem, the adhesive thickness could not be displayed. A direct relationship between roughness and intersections was not observed.



Figure 3.10: SEM images of (a) AlPA0-CA, (b) AlPA120-CA, (c) AlPA500-CA, and (d) Al1200-CA sample at 500x magnification

3.4 Plasma Treatment - Contact Angle

Contact angle values of pristine and plasma-treated samples were measured. Results and drop shapes are shown in Figure 3.11. Plasma treatment for both Al and PA resulted in a significant reduction in contact angle. The contact angle of the Al sample decreased from 71.7° to 37.42° , and the contact angle of the PA sample decreased from 60.48° to 15.54° . Plasma caused a difference of 34.36° in Al and 44.94° in PA. The reason for this decrease in the contact angle is that the plasma treatment removes the impurities on the surface and provides the formation of polar groups that will bond with the water molecule on the surface (75). In the literature, it has been reported that the contact angle of PA decreased from 63° to 17° after low-pressure gas plasma treatment (75). It is a known phenomenon that OH groups formed on the plasma applied Al surface cause an increase in solid free energy and this reduces the contact angle (67). Altuncu et al. stated that the contact angle of plasma-made Al samples decreased from 95° to 34° . As the plasma time increased, the contact angle decreased to 10° (76).





3.5 Plasma Treatment - Lap Shear Strength

LSS values of samples made of pristine and plasma were measured. The relationship between LSS values and plasma surfaces is shown in Figure 3.12. Fracture types calculated as a percentage over 5 samples and surface images of ruptured samples are shown in Figure 3.13.

Plasma treatment provided an increase in strength independent of the side. Plasma on the aluminum side increased the contact angle by 87.12%, applying plasma on the PA side increased the contact angle by 105.42%, and applying plasma on both sides increased the contact angle by 65.42%. The reason for this increase is the decrease in the contact angles indicated in Figure 3.11. The surfaces become more hydrophilic as the contact angle decreases. It has been stated in the literature that plasma treatment increases LSS (75,76).



Figure 3.12: Lap shear strength of adhesively bonded pristine and plasmatreated samples

Higher adhesion was observed on the adhesive surfaces with plasma (Figure 3.13). Applying plasma caused adhesion failure to turn into substrate and adhesion/cohesion failure. A relationship could not be established between the conversion to substrate failure and the plasma side. In particular, the observation of substrate failure in the AlPA120-CA-ALS sample is direct evidence that plasma increases LSS.



Figure 3.13: Failure types of adhesively bonded pristine and plasmatreated samples

Cross-sectional images taken from the midpoints of the adhesively bonded samples are shown in Figure 3.14. Adhesive thickness could not be visualized due to the previously mentioned folding problem. Figure 3.14a and Figure 3.14c showed a more effective adhesion with plasma effect. The gap in Figure 3.14b was caused by the glue applied in the center not reaching the corners. Because of this gap, it reduced the effect of plasma on the LSS value.



Figure 3.14:SEM images of (a) AlPA1200-CA-ALS, (b) AlPA1200-CA-PAS, and (c) AlPA1200-CA-BOTH at 500x magnification

3.6 Adhesive type - Lap Shear Strength

The LSS values of the samples bonded with cyanoacrylate, epoxy, and MS polymer were measured. The relationship between LSS values and adhesive is shown in Figure 3.15. Fracture types calculated as a percentage over 5 samples and surface images of ruptured samples are shown in Figure 3.16. The LSS values of the adhesives are listed as E>CA>MS. A similar sequence is observed in the literature. It has been reported that epoxy can reach up to 25 MPa LSS (77), cyanoacrylate up to 17 MPa LSS (78), and MS polymer up to 1.7 MPa LSS (50). However, these values could not be obtained because brittle adhesives such as epoxy and cyanoacrylate are very sensitive to defects such as voids and microcracks (Figure 3.17c) (79).



Figure 3.15: Lap shear strength of adhesively bonded samples by adhesive type

When the fracture types were examined, it was observed that the AlPA1200-CA sample showed adhesion, the AlPA1200-E sample showed substrate, AlPA1200-MS polymer sample showed cohesion failure. As LSS increased, conversion from cohesion failure to substrate failure was observed.



Figure 3.16: Failure types of adhesively bonded samples by adhesive type The midpoints of the adhesively bonded samples were cut, their intersections were examined, and the images are shown in Figure 3.17. Two measurements were averaged for adhesive thickness. Average adhesive thickness was measured as 87.05 μ m for AlPA1200-E and 157.2 μ m for AlPA1200-MS. The reason for this is that MS polymer, which functions as a filler, is more viscous than epoxy, so it spreads more difficult. The presence of the adhesive at the interface in a smooth line has proven that the mold indicated in Figure 2.3 is effective in producing a constant adhesive thickness.



Figure 3.17: SEM images of (a) AlPA1200-E and (b) AlPA1200-MS at 100x magnification. (c) AlPA1200-E and (d) AlPA1200-MS at 500x magnification

Chapter 4

Conclusion

In this thesis, the effects of roughness, plasma and adhesive type on the contact angle, wettability, drop shape, LSS, and failure types of adhesively bonded samples were investigated.

As a result of the analysis, Ra, Rq, and Rz values decreased as the grit size increased. In addition, increasing the grit size decreased the abrasive trace size. As the Ra values of the sanded samples decreased, it was observed that the contact angle decreased, the wettability and LSS increased. Moreover, adhesion failure to adhesion/cohesion failure conversion was observed as Ra decreased in the sanded samples. This order showed a consistent association with LSS.

The plasma treatment significantly reduced the contact angle and increased the wettability. Plasma treatment decreased the contact angle of the Al sample from 71.77° to 37.41°, and the contact angle of the PA sample from 60.48° to 15.54°. Plasma treatment reduced the contact angle of the PA sample at a higher rate compared to the Al sample. Also, plasma treatment significantly increased LSS (105.42%). Applying this process to one side showed more effective results than applying it to both sides. Decreased contact angle increased LSS. Plasma treatment caused the conversion of adhesion failure into adhesion/cohesion failure and substrate failure.

As a result of the trials with different adhesives, the LSS values from the highest to the lowest are epoxy, cyanoacrylate, and MS Polymer, respectively. The MS polymer sample with the lowest LSS value showed complete cohesion failure. The order of lap joint shear strength of the failure types is the substrate, adhesion/cohesion, adhesion, and cohesion, respectively.

References

- Johnson WS (W. S, ASTM Committee D-14 on Adhesives., International Symposium on Adhesively Bonded Joints: Testing A. Adhesively Bonded Joints: Testing, Analysis, and Design. ASTM; 1988. 319 p.
- [2] Rotheiser J. Joining of plastics : Handbook for designers and engineers. Cincinnati OH: Hanser; 1999.
- [3] Baldan A. Adhesively-bonded joints and repairs in metallic alloys, polymers and composite materials: Adhesives, adhesion theories and surface pretreatment. Vol. 39, Journal of Materials Science. Springer; 2004. p. 1–49.
- [4] Amancio-Filho ST, Dos Santos JF. Joining of polymers and polymer-metal hybrid structures: Recent developments and trends. Polym Eng Sci. 2009 Aug 1;49(8):1461–76.
- [5] V. Natu A, R. Sharma A, R. Anekar N. Variation of Adhesive Strength in Single Lap Joint (SLJ) with Surface Irregularities. Am J Mech Eng. 2019 Apr 28;7(2):61–7.
- [6] Pramanik A, Basak AK, Dong Y, Sarker PK, Uddin MS, Littlefair G, et al. Joining of carbon fibre reinforced polymer (CFRP) composites and aluminium alloys – A review. Vol. 101, Composites Part A: Applied Science and Manufacturing. Elsevier Ltd; 2017. p. 1–29.
- [7] Svenungsson J, Choquet I, Kaplan AFH. Laser Welding Process A Review of Keyhole Welding Modelling. In: Physics Procedia. Elsevier B.V.; 2015. p. 182– 91.
- [8] Hong KM, Shin YC. Prospects of laser welding technology in the automotive industry: A review. J Mater Process Technol. 2017 Jul 1;245:46–69.

- [9] Nagarajan, Manoharan M. Assessment of dissimilar joining between metal and polymer hybrid structure with different joining processes. J Thermoplast Compos Mater. 2021;1–43.
- [10] Sinka V. The present and future prospects of friction stir welding in aeronautics. Acta Metall Slovaca. 2014 Aug 27;20(3):287–94.
- [11] Al-Sayyad A, Bardon J, Hirchenhahn P, Vaudémont R, Houssiau L, Plapper P. Influence of aluminum laser ablation on interfacial thermal transfer and joint quality of laser welded aluminum-polyamide assemblies. Coatings. 2019 Nov 19;9(11):768.
- [12] Parmley RO. Standard handbook of fastening and joining. 3rd ed. New York: McGraw-Hill; 1996.
- [13] Niu MCY. Composite Airframe Structures Practical Design Information and Data. 2nd ed. North Point: Hong Kong Conmilit; 2000. 1–664 p.
- [14] Shah KP. Fundamentals of Threaded Fasteners. 2019. p. 1–64.
- [15] Poisson C, Hervais V, Lacrampe MF, Krawczak P. Optimization of PE/binder/PA extrusion blow-molded films. II. Adhesion properties improvement using binder/EVA blends. J Appl Polym Sci. 2006 Jul 5;101(1):118–27.
- [16] Ebnesajjad S, Landrock AH. Adhesives Technology Handbook. Adhesives Technology Handbook. 2015. 297–338 p.
- [17] Qin RY, Schreiber HP. Adhesion at partially restructured polymer surfaces. Colloids Surfaces A Physicochem Eng Asp. 1999 Oct 15;156(1–3):85–93.
- [18] Van Der Leeden MC, Frens G. Surface properties of plastic materials in relation to their adhering performance. Adv Eng Mater. 2002;4(5):280–9.
- [19] JC R. The Chemistry of Paper. 1st ed. Cambridge, UK: RSC PAPERBACKS; 1996.
- [20] Amouroux N, Léger L. Modulation of adhesion at acrylic adhesive-silicone

elastomer interfaces. J Adhes. 2006 Sep;82(9):919-32.

- [21] Awaja F, Gilbert M, Kelly G, Fox B, Pigram PJ. Adhesion of polymers[Internet]. Vol. 34, Progress in Polymer Science (Oxford). 2009. p. 948–68.
- [22] Raghavan J, Wool RP. Interfaces in Repair, Recycling, Joining and Manufacturing of Polymers and Polymer Composites. J Appl Polym Sci. 1999;71(5):775–85.
- [23] Tang H, Martin DC. Microstructural studies of interfacial deformation in painted thermoplastic polyolefins (TPOs). J Mater Sci. 2002 Nov 15;37(22):4783–91.
- [24] Pijpers AP, Meier RJ. Adhesion behaviour of polypropylenes after flame treatment determined by XPS(ESCA) spectral analysis. J Electron Spectros Relat Phenomena. 2001 Dec;121(1–3):299–313.
- [25] Occhiello E, Morra M, Morini G, Garbassi F, Humphrey P. Oxygen-plasmatreated polypropylene interfaces with air, water, and epoxy resins: Part I. Air and water. J Appl Polym Sci. 1991 Jan 20;42(2):551–9.
- [26] Noeske M, Degenhardt J, Strudthoff S, Lommatzsch U. Plasma jet treatment of five polymers at atmospheric pressure: Surface modifications and the relevance for adhesion. International Journal of Adhesion and Adhesives. 2004 Apr;24(2):171–7.
- [27] Hegemann D, Brunner H, Oehr C. Plasma treatment of polymers for surface and adhesion improvement. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms. 2003 Aug;208(1–4):281–6.
- [28] Nihlstrand A, Hjertberg T, Johansson K. Plasma treatment of polyolefins: Influence of material composition: 1. Bulk and surface characterization. Polymer (Guildf). 1997;38(14):3581–9.
- [29] Mcbain J., Hopkins D. No Title. Phys Chem. 1925;25:88.
- [30] Borroff E., Wake W. No Title. Trans Inst Rubber Ind. 1949;25:190, 1999, 210.

- [31] Allen KW. Some reflections on contemporary views of theories of adhesion. International Journal of Adhesion and Adhesives. 1993;13(2):67–72.
- [32] Fourche G. An overview of the basic aspects of polymer adhesion. Part I: Fundamentals. Polym Eng Sci. 1995;35(12):957–67.
- [33] Deryaguin B., Krotova V. No Title. Dokl Akad Nauk SSRR. 1948;61:843.
- [34] Roberts AD. Surface charge contribution in rubber adhesion and friction. J Phys D Appl Phys. 1977 Sep 11;10(13):1801–19.
- [35] Petrie EM. Handbook of adhesives and sealants. 1999;896.
- [36] Voyutskii SS. Autohesion and adhesion of high polymers. Progress in Polymer Science. New York: Interscience Publishers; 1963. 272 p.
- [37] Al-Kawaz A. Paints and Adhesives Theories of Adhesion.
- [38] Bikerman J. The science of adhesive joints. Academic Press; 1961. 258 p.
- [39] Baldan A. Adhesion phenomena in bonded joints. International Journal of Adhesion and Adhesives. 2012;38:95–116.
- [40] Mittal KL. Silanes and other coupling agents. Vol. 3, Silanes and Other Coupling Agents. VSP; 2004. 1–257 p.
- [41] Treccani L, Yvonne Klein T, Meder F, Pardun K, Rezwan K. Functionalized ceramics for biomedical, biotechnological and environmental applications. Vol. 9, Acta Biomaterialia. Elsevier Ltd; 2013. p. 7115–50.
- [42] Dupré A. Théorie mécanique de la chaleur, Paris: Gauthier-Villars; 1869.
- [43] Shukla, RK. A critical-review of vlsi die-attachment in high-reliability applications. 1985;7:67-74 p.
- [44] Mittal KL. Surface contamination: an overview. In Inst of Environ Sci, Mt Prospect; 1978. p. 169–74.
- [45] Licari JJ, Swanson DW. Functions and theory of adhesives. In: Adhesives

Technology for Electronic Applications. William Andrew Publishing; 2011. p. 35–74.

- [46] Gotro J. Polymers in Electronic Packaging: What is the Thixotropic Index. Polymer Innovation Blog. 2018. p. 1
- [47] Licari JJ, Swanson DW. Adhesive Bonding Processes. In: Adhesives Technology for Electronic Applications. William Andrew Publishing; 2011. p. 143–216.
- [48] Lees WA. Overview: Adhesive selection. Mater Sci Technol. 1988;4(7):573–7.
- [49] Gauthier MM. Adhesives and Sealants. In: Engineered Materials Handbook. ASM International; 1990.
- [50] Petrie EM. MS Polymers in "Hybrid" Sealants. Construction. 2010;1–8.
- [51] Hashimoto K. Silyl-Terminated Polyethers for Sealant Use: Performance Updates. Adhes Age. 1998;41(8):18–23.
- [52] Editor JCV, Editor DB, Vickerman JC, Briggs D. ToF-SIMS : Surface Analysis by Mass Spectrometry. 2001.
- [53] Vickerman JC, Gilmore IS. Surface Analysis The Principal Techniques: Second Edition. Surface Analysis - The Principal Techniques: Second Edition. Wiley; 2009. 1–666 p.
- [54] Grundmeier G, Stratmann M. Adhesion and de-adhesion mechanisms at polymer/metal interfaces: Mechanistic understanding based on in situ studies of buried interfaces. Annu Rev Mater Res. 2005;35:571–615.
- [55] Brockmann W, Hüther R. Adhesion mechanisms of pressure sensitive adhesives. International Journal of Adhesion and Adhesives. 1996 May 1;16(2):81–6.
- [56] Komvopoulos K. Adhesion and friction forces in microelectromechanical systems: Mechanisms, measurement, surface modification techniques, and adhesion theory. J Adhes Sci Technol. 2003;17(4):477–517.

- [57] Wool RP. Adhesion at polymer-polymer interfaces: A rigidity percolation approach. Comptes Rendus Chim. 2006 Jan 1;9(1 SPEC. ISS.):25–44.
- [58] Jones R, Pollock HM, Cleaver JAS, Hodges CS. Adhesion forces between glass and silicon surfaces in air studied by AFM: Effects of relative humidity, particle size, roughness, and surface treatment. Langmuir. 2002 Oct 15;18(21):8045– 55.
- [59] Basin VE. Advances in understanding the adhesion between solid substrates and organic coatings. Prog Org Coatings. 1984 Jul 4;12(3):213–50.
- [60] Pukánszky B, Fekete E. Adhesion and surface modification. Adv Polym Sci. 1999;139:109–53.
- [61] Keyence Corporation. Surface Roughness Parameters [Internet].
 2019 [Accessed 26th April 2022]. https://www.keyence.com/ss/products/microscope/roughness/line/parameters.j
 sp
- [62] Liu W, Deng Z, Shang Y, Wan L. Effects of grinding parameters on surface quality in silicon nitride grinding. Ceram Int. 2017;43(1):1571–7.
- [63] Leite SS, Kim Jesus GM, Alves MC de S, Valarelli IDD, Bueno MAP, Magorbo FCRD, et al. Analysis of the parameters affecting the surface sanding of pinus elliottii and Corymbia citriodora wood species. BioResources. 2019;14(2):2773–83.
- [64] VSM. Grain Grading Guide [Internet]. [Accessed 26th April 2022]. https://en.calameo.com/vsm-usa/read/005029165e540cb81893f/
- [65] Aluminium Strength Hardness Elasticity Crystal Structure. Available from: https://material-properties.org/aluminium-mechanical-propertiesstrength-hardness-crystal-structure/ [Accessed 26th April 2022]
- [66] Polyamide Nylon | Properties, Price & Application | Material Properties. [Internet]. [Accessed 26th April 2022]. https://materialproperties.org/polyamide-nylon-properties-application-price/

- [67] Prysiazhnyi V. Plasma treatment of aluminum using a surface barrier discharge operated in air and nitrogen: Parameter optimization and related effects. Plasma Sci Technol. 2013 Aug;15(8):794–9.
- [68] ÖZDÍLLÍ Ö. Comparison of the Surface Quality of the Products Manufactured by the Plastic Injection Molding and SLA and FDM Method. Uluslararası Muhendis Arastirma ve Gelistirme Derg. 2021;13(2):428–37.
- [69] Solid surface energy data (SFE) for common polymers. [Internet]. [Accessed 26th April 2022] http://www.surface-tension.de/solid-surface-energy.htm/
- [70] Mittal KL, editor. Advances in contact angle, wettability and adhesion.
 Advances in Contact Angle, Wettability and Adhesion. USA: Scrivener/Wiley;
 2015.
- [71] Rahimi M, Afshari A, Thormann E. Effect of Aluminum Substrate Surface Modification on Wettability and Freezing Delay of Water Droplet at Subzero Temperatures. ACS Appl Mater Interfaces. 2016;8(17):11147–53.
- Boutar Y, Naïmi S, Mezlini S, Ali MBS. Effect of surface treatment on the shear strength of aluminium adhesive single-lap joints for automotive applications. International Journal of Adhesion and Adhesives. 2016;67:38–43.
- [73] Borsellino C, Di Bella G, Ruisi VF. Adhesive joining of aluminium AA6082: The effects of resin and surface treatment. International Journal of Adhesion and Adhesives. 2009;29(1):36–44.
- [74] Ghumatkar A, Budhe S, Sekhar R, Banea MD, De Barros S. Influence of adherend surface roughness on the adhesive bond strength. Lat Am J Solids Struct. 2016;13(13):2356–70.
- [75] Liston EM. Plasma treatment for improved bonding: A review. J Adhes. 1989;30(1-4):199-218.
- [76] Altuncu E, Tecir A, Birbaşar O. Adhesion Imrovement with Plasma Activation Between Aluminum Alloys. Acad Perspect Procedia. 2020;3(1):371–8.
- [77] What is lap shear strength in an epoxy? Fastener Engineering. Available from:
https://fastenerengineering.com/what-is-lap-shear-strength-in-an-epoxy/ [Accessed 26th April 2022]

- [78] How does heat affect lap shear strength in adhesives? Fastener Engineering. [Internet] [Accessed 26th April 2022] https://fastenerengineering.com/howdoes-heat-affect-lap-shear-strength-in-adhesives/
- [79] da Silva LFM, Rodrigues TNSS, Figueiredo MA V, de Moura MFSF, Chousal JAG. Effect of adhesive type and thickness on the lap shear strength. J Adhes. 2006;82(11):1091–115.

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