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Ultraviolet Light Surface Treatment of Polymer Composites For Enhancement of Adhesion

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Lawrence T. Drzal
Major professor

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ULTRAVIOLET LIGHT SURFACE TREATMENT OF POLYMER COMPOSITES FOR ENHANCEMENT OF ADHESION

By

Praveen Tummala

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ABSTRACT

Ultraviolet light Treatment of Polymer Composites
for Enhancement in Surface Adhesion
By
Praveen Tummala

In spite of having desirable bulk mechanical properties suitable for all engineering applications, polymers and polymer composites are limited for their use in certain areas it is essential to adhesively bond them. This is due to their poor surface adhesion. Hence, they require some kind of surface preparation before they can be bonded. Ultraviolet light treatment has emerged out to be an efficient technique in order to prepare the polymer surfaces for adhesive bonding. It is simple to construct, easy to operate, faster and environmentally benign. The current research involves the use of ultraviolet light from two different sources *viz.* a lamp and an excimer laser, to treat the polymer surfaces. The polymer composites investigated are polyethylene terepthalate/polypropylene – glass fiber composites. Significant enhancement in surface adhesion was obtained as a result of the ultraviolet light treatment. This is due to a combination of cleaning the surface and functionalizing the surface by the ultraviolet light. To explore the practicality of the ultraviolet light treatment process, automobile engine valve covers from Daimler Chrysler have been UV treated, adhesively bonded and tested. The test results show a tremendous increase in the surface adhesion properties of the valve covers and the failure modes are completely cohesive. Thus this technique has all the potential for being applied in an industrial scale for treating massive and large number of parts that are to be bonded.

ACKNOWLEDGEMENTS

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Chapter One

INTRODUCTION

The versatility of polymers and polymer composites is creating a growing worldwide demand for these materials in a wide variety of applications. Polymers and polymer composites are very extensively used in today's industry due to their superior and excellent balance of material properties. They are attractive for various engineering and manufacturing applications. They are highly competitive with the traditional metals and alloys due to easy and excellent processability by high-volume/high-rate techniques such as extrusion and injection molding and an inherent lack of corrosion related problems. Their low cost and less weight are added advantages. An attempt to minimize the number of materials employed in various applications in order to facilitate recycling is another important reason for the interest in these materials. In spite of their desirable bulk properties, the use of many polymers is hindered by their poor surface adhesion properties. Strong and stable adhesive bonding of polymers and polymer composites plays an important role in extending their applications in various fields of industry. Adhesive bonding has also been in practice to overcome the drawbacks of mechanical fastening. Polymers may have very poor adhesive properties because they are inert and hydrophobic due to various other reasons. Therefore they require some kind of surface preparation before they can be bonded adhesively. There are various techniques available to modify surfaces and thereby enhance adhesion. Mechanical abrasion, chemical treatment, flame treatment, corona discharge and plasma treatment are the some of the surface pretreatment techniques that are

being used extensively. Each of the above has its own limitations. This work focuses on a new surface treatment technique using Ultra-violet light. This technique overcomes the scientific, technological, environmental and economical limitations of the traditional treatment processes.

Ultra-violet light is capable of chemically modifying the surfaces by adding polar groups onto the surface, if the correct wavelengths, intensity and ambient environment are chosen. This process can not only add the desired functional groups to the surface, but also remove the surface contaminants thereby cleaning the surfaces. This is a very versatile process where a supplemental gas or a solution can also be added to the treatment process depending on the chemical groups desired on the surface. UV treatment is a highly controlled and reproducible surface modification technique. The following work primarily focuses on understanding the treatment process in terms of the process parameters.

The sources for the Ultra-violet light used in this work are a pulsed UV lamp and an Excimer Laser. The lamp generates UV light over a range of wavelengths whereas the Excimer Laser generates UV light at a particular wavelength in the UV range. Studies are made in comparing the two UV treatment processes.

Two polymeric composite materials are mainly emphasized in this work. One of them is a glass fiber reinforced polyethylene terepthalate (GF-PET) and the other is a glass fiber reinforced polypropylene (GF-PP). These materials were

chosen due to their advantageous commercial potential in the durable goods, construction and transportation industries. Their applications can be extended provided their adhesion properties are improved.

Apart from using the UV light for modifying the surfaces, silanes are also used in the work. It has been shown that chemically grafting coupling agents like silanes onto a surface not only act as a protective coating but can also functionalize the surface thereby improving its adhesion properties. Even though the UV treatment improves the adhesion of the polymers, in many cases it is required to further enhance the adhesion to the point of cohesive fracture of the substrate. But untreated polymeric materials are non-receptive to these coupling agents due to the absence of the required surface functionalities. Therefore a pretreatment is required for the polymeric materials in order that the coupling agents can be grafted on top of their surface. This work discusses the functionalization of polymers using both UV light and silanes.

Adhesion tests are performed on the UV treated polymeric materials to assess the improvement in surface adhesion. The adhesion test is called a PATTI (Pneumatic Adhesion Tensile Testing Instrument) test, where an aluminum stub is bonded to the substrate using a room temperature curing adhesive and the tensile strength for pulling the stub from the substrate is measured. XPS (X-Ray Photoelectron Spectroscopy) is used to study the chemical changes introduced by the treatment on the polymeric surfaces. ESEM (Environmental Scanning

Electron Microscopy) is used to characterize the failure surfaces as well as to find out if the UV light has abraded the surface.

Chapter two presents a review of the literature. A summary of traditional methods for modifying surfaces is provided. The UV treatment process is described and compared with the older techniques. Some results from the literature are discussed. Chapter three discusses the experimental methods right from sample preparation to the testing. Chapter four includes the results and a discussion of the results. Chapter five discusses the UV treatment of a production composite part – a Daimler Chrysler valve covers along with the bonding, testing and analysis of the effectiveness of the process for this material. Chapter six draws conclusions and gives suggestions for future work.

Chapter Two

LITERATURE REVIEW

2.1) Importance of Adhesive Bonding

Adhesives are a critical part of many manufacturing processes. A large number of adhesive formulations are available to cover a broad array of applications. Adhesive bonding is a widespread joining method in industrial applications of polymers and polymer composites. With this technique satisfactory joints can be produced. This has been in practice to overcome the drawbacks of mechanical fastening. Adhesive joining, properly done creates strong stable joints with superior mechanical and durability characteristics to mechanically fastened structure. It has been discussed in the literature that the creation of covalent bonds across the substrate/adhesive interface is sufficient for creating viable adhesion in composites. The use of adhesives not only increases the joint strength but also distributes the load more evenly, and enables alternating joining methods to be reduced or eliminated. Dissimilar materials can be joined together by bonding even where it is impossible to gain access to either side of the joint, thereby increasing design flexibility.

The adhesive bond is continuous. On loading, there is a more uniform distribution of stresses over the bonded area. The local concentrations of stresses present in spot-welded or mechanically fastened joints are avoided. Moreover, its not possible to weld thermoset polymers. Bonded structures can consequently

offer a longer life under load. The bonded joint being continuous produces a stiffer structure. Alternatively, if increased stiffness is not needed, the weight of the structure can be decreased while maintaining the required stiffness. Adhesive bonding gives a smooth appearance to designs: there are no protruding fasteners such as screws or rivets, and no spot-weld marks. The bonded structure is a safer structure because, owing to the fewer and less severe concentrations of stresses, fatigue cracks are less likely to occur. A fatigue crack in a bonded structure will propagate more slowly than in a riveted structure or even in a machined profile because the bond lines act as a crack stopper. Adhesive bonding does not require high temperatures. It is a suitable means for joining together heat sensitive materials prone to distortion or to a change in properties from the heat of brazing or welding. Complex assemblies that cannot be joined together in any other way are feasible with adhesives. Adhesives can join different materials together, materials that may differ in composition, moduli, coefficients of expansion, or thickness. The continuous adhesive bond forms a seal. The joint is consequently leak-proof and less prone to corrosion. Adhesive joints are impermeable to air and water. The adhesive bond can provide an electrically insulating barrier between the surfaces. Bonded joints tend to be damage tolerant due to high damping behavior of adhesive layer. This capacity may be useful for reducing sound or vibration. Adhesive bonding can simplify assembly procedures by replacing several mechanical fasteners with a single bond, or by allowing several components to be joined in one operation. Adhesive bonding may be used in combination with spot welding or riveting techniques in order to improve the

performance of the completed structure. All these advantages may be translated into economic advantages: improved design, easier assembly, lighter weight, and longer life in service.

Insufficient joint strength and lack of durability have been major obstacles to the adhesive bonding. However, these limitations of adhesive bonding are being addressed by the photochemical surface modification method explored in this research.

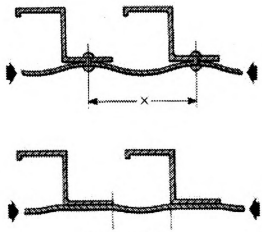


Figure 2.1

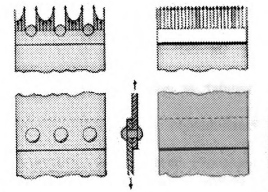


Figure 2.2

Figure 2.1: Stiffening effect-bonding and riveting	**Figure 2.2: Stress distributions in loaded joints**
The diagram shows how a joint may be designed to take advantage of the stiffening effect of bonding. Adhesives form a continuous bond between the joint surfaces. Rivets and spot-welds pin the surfaces together only at localized points. Bonded structures are consequently much stiffer and loading may be increased (by up to 30-100%) before buckling occurs.	The riveted joint on the left is highly stressed in the vicinity of the rivets. Failure tends to initiate in these areas of peak stress. A similar distribution of stress occurs with spot welds and bolts. The bonded joint on the right is uniformly stressed. A continuous weld joint is likewise uniformly stressed but the metal in the heated zone will have undergone a change in strength.

2.2) Reasons for Poor Adhesion of Polymers

Adhesion problems are commonly encountered in the commercial use of polymers and polymer composites. Adhesion is largely controlled by the conditions on the surface of the adherend. Surface factors such as wettability, surface free energy, the functional groups on the surface, surface contaminants and surface roughness influence the adhesion properties of a material. Processed polymers and polymer composites can also contain undesirable compounds or environmental or processing additives that can reduce or limit adhesion. In addition, the inherent low surface energy of polymers makes it difficult to bond these materials. Polymer surfaces are highly inert and exhibit good chemical resistance. The absence of polar chemical functional groups on the surface adds to the poor adhesion of polymers. They are water repellant and have very poor wetting properties, which make them hydrophobic. Polymer surfaces can be very smooth which means that they lack surface roughness which can enhance mechanical interlocking and adhesion. Due to all the above reasons, polymers exhibit very poor affinity to adhesives, paints and printing inks, which frequently limit their applications unless they are surface treated.

2.3) Various Methods to Enhance Surface Adhesion

It is necessary to pre-treat the polymer surfaces prior to their bonding, printing or painting. There are various methods to improve the adhesion properties of the polymers. The prominent ones are mechanical abrasion, chemical treatment, flame treatment, corona discharge, plasma treatment and ultraviolet radiation treatment.

2.3.1) Mechanical Abrasion: Mechanical abrasion is the process of roughening the surface of a polymer by mechanical means to improve the adhesion. This includes grit blasting, wire brushing, sanding, abrasive scrubbing, scraping or filing. Mechanical abrasion creates valleys and crevices on the adherend. An adhesive must fill these valleys and crevices of the adherend and displace trapped air to work well. The mechanical interlocking of the adhesive and the adherend together creates a strong bond between them, and the overall strength of the bond is dependent upon the quality of this interlocking interface. Abrading the adherend enhances the mechanical interlocking and increases the bonding surface area. Though it improves adhesion, mechanical abrasion is a surface destructive technique.

2.3.2) Chemical Treatment: Chemical treatment commonly includes acid or alkaline etching of the adherend surface. Etching the adherend removes stubborn oxides and roughens the surface on a microscopic scale. The desired functional group can also be added to the surface by treating it with an acid. For example, oxidation of surfaces can be done in chromic acid and sulfonation in

chlorosulfonic acid. Wet chemical and solvent treatment, if effective, often add numerous additional processing steps such as neutralization, washing, rinsing and drying. These solvents and chemicals are usually hazardous or designated hazardous, constituting a toxic waste disposal problem and cost.

2.3.3) Flame Treatment: Flame treatment is ideal for treating polymer films. Flame treatment involves exposing the surface of the substrate to a suitable oxidizing flame for a period of time. This treatment brings about a change to the polymer surface that makes it wettable and permits a strong adhesive bond between the surface and the adhesive. During treatment, one side of the polymer film is exposed to a laminar gas air flame while the back side is cooled by contact with a water-cooled aluminum roll. The flame burner is usually a stainless steel ribbon mounted in a cast-iron housing. Dust filtered compressed air is premixed with natural gas in a venturi mixer. The flame power is quantified and is simply a function of the volume of natural gas burned per minute. The input energy to the substrate is a complex function of the flame power, the exposure time and the burner to flame gap.

No detailed mechanism of the process has yet been developed. However, the specific flame properties are responsible for the observed changes in the characteristics of the polymer. The optimization of the flame treatment process is to be done with control of variables such as fuel flow rate, film treatment velocity, choice of fuel, non-fuel additives, substrate to flame separation distance and the burner configuration.

2.3.4) Corona Discharge: Corona treatment of a material for better adhesion is accomplished by exposing the air near the material surface to a high-voltage electrical discharge, a corona that causes the oxygen molecules in the discharge area to divide into their atomic form. These oxygen atoms are then available to bond with the molecules on the surface of the material being treated, thereby changing the surface molecular structure to one that is extremely receptive to inks, coatings, and various adhesives. Corona treatment, in effect, chemically modifies the surface (raising the surface tension), allowing it to grab onto the ink, coating, or adhesive being applied.

The components of a corona treating system include a power supply, a high-voltage transformer, and the treater station through which the material to be treated passes. The station itself typically comprises an electrode, an electrical insulator or dielectric, and a return path (ground), and it can be configured in a number of ways to accommodate different materials.

The power supply has a very simple function: to raise the frequency and voltage of the incoming power to levels sufficient to generate a corona in the station. Power supply needs to be monitored and controlled because delivering the proper energy level is important to the characteristics of the resulting corona discharge and the surface-energy level attained on the surface of the material. In general, the higher the frequency (kHz) rating of the power supply, the lower the voltage required to deliver a given power to the corona discharge. A high-frequency/low-voltage combination is ideal, as a lower-voltage corona is less

damaging to the insulators and dielectrics in the station and to the material being treated.

There are several basic corona treatment system configurations used for treating materials. They are defined essentially by the location of the dielectric material in the station: conventional, bare roll, double dielectric, and convertible. The configuration that is best for a given application depends mainly on the material being processed. Corona treatments work best on flat surfaces. Control of the treatment is by time of exposure.

2.3.5) Plasma Treatment: The physical definition of plasma is a partially ionized gas consisting of electrons, ions and neutral atoms or molecules, with an essentially equal density of positive and negative charges. These species in plasma exist at many different levels of excitement. Plasma can exist over an extremely wide range of temperatures and pressures. The solar corona, a lightening bolt, a flame and a "neon" sign are all examples of plasma. The plasma atmosphere consisting of different excited particles depends on the gas used in the system. By changing the gas used, plasma surface treatment can be used to modify the chemical and physical structure of a material. Because of its properties similar to both liquid and gas, plasma is often referred as "fourth state of matter".

To enable the gas to be ionized in a controlled and qualitative manner, the process is carried out under vacuum conditions. A vacuum vessel is first pumped down using rotary and roots blowers, sometimes in conjunction with high-vacuum pumps to a low to medium vacuum pressure in the range of 10^{-2} to 10^{-3} mbar. The

gas is then introduced into the vessel by means of mass flow controllers and valves. Although many gases can be used, commonly selected gases or mixtures of gases for plasma treatment of polymers include oxygen, argon, nitrous oxide, tetrafluoromethane, and air. A high-frequency generator, which can be in the kHz, MHz, or microwave range is then used to ionize the gas into a plasma, forming an environment that has been referred to as "the fourth state of matter" (i.e., in the presence of sufficient energy, a solid can be melted to a liquid, a liquid vaporized into a gas, and a gas ionized into a plasma). The formed reactive particles, mainly free radicals react in a direct way with the surface without damaging the bulk properties of the treated part. The surface modification is limited to the outermost 10 to 1000 Å of the substrate. One distinguishing characteristic of plasma is a visible glow discharge, with colors ranging from blue-white to dark purple, depending on the type of gas. This visible glow is caused by the relaxation of excited gas particles that emit UV radiation.

Plasma systems generally consist of five main components: the vacuum vessel, a pumping group, a gas-introduction and gas-control system, a high-frequency generator, and a microprocessor-based system controller. Various optional parts can then be added to adapt a base system to handle particular applications or substrates.

2.4) UV Treatment of Surfaces

Ultra Violet light has been in use for many years to clean organic contaminants from various surfaces. It has also been proved successful in modifying surfaces by introducing polar groups on the surface. The traditional use of UV light for cleaning surfaces combined with the newly discovered surface modification technique using UV light makes it more advantageous.

Light is the most common form of electromagnetic radiation. Electromagnetic radiation is characterized by its wavelength and frequency. The electromagnetic spectrum covers a broad range, from radio waves with wavelengths of meter or more, down to X-rays with wavelengths of less than a billionth of a meter. UV light is part of the electromagnetic radiation with wavelengths ranging from 100nm to 400 nm approximately. The UV band lies between the X-rays and the visible light in the electromagnetic spectrum. Figure 3 depicts the optical portion of the electromagnetic spectrum.

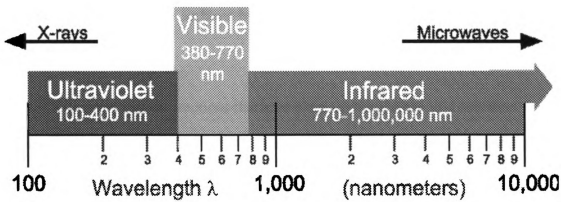


Figure 3.1: Elecromagnetic Spectrum

light can be divided into three categories. UV-A which ranges from 315-400nm, UV-B which ranges from 280-315nm and UV-C which ranges from 100-280nm. There are various sources that generate the UV light which will be discussed in the following chapters.

The entire UV range produces photons of varying energies that can be useful in modifying various surfaces. A variety of interactions take place between the UV photons and substrate as well as between the UV photons and the surrounding environment. Traditionally UV light is used to clean surfaces in presence of an inert gas. This inert environment can be replaced by a very oxidative environment. The various reactions initiated by the UV light will be discussed in detail.

UV light has photons of sufficient and varying energies that can break almost all the bonds on the surface of a polymer thereby creating active sites on the surface. These active sites are highly receptive to the reactive species in the environment surrounding the surface. The desired functional groups can thus be attached onto the polymer surfaces by UV irradiation in the presence of reactive gases.

There are various reactions that take place on the surface of a substrate in presence of UV light. Photooxidation, photosubstitution, photografting, photocrosslinking and photodegradation are the important ones.

Photoablation: Photoablation is the ability of UV light to break the bonds on the surface of the polymer by bombardment with high-energy photons. This affects the outermost surface molecular layers exposed to the UV light. As a result of this, the organic contaminants on the polymer surface are oxidized to CO_2 and H_2O. Ablative photodecomposition is the etching of the polymer surface to a depth of 1000A° or more. This occurs if UV light of very high intensity, higher than the ablation threshold energy of a polymer strikes its surface. When photons of high intensity are delivered onto the surface it results in spontaneous ejection of fragments into the gas phase. The ablated material carries away a high percentage of the energy of the photon that is not consumed in the bond breaking. Ablative photodecomposition takes place mainly when the UV light source is an excimer laser operating in the UV range. This causes roughness on the surface, which in turn enhances adhesion.

Photocrosslinking: Photocrosslinking is the formation of chemical links between the molecular chains of polymers in presence of UV light. When the surface of a polymer is exposed to UV light in presence of inert gases, crosslinking occurs on the surface of the polymer. Crosslinking produces a stronger and harder substrate microsurface. Under certain circumstances, crosslinking through UV treatment can also render additional wear or chemical resistance to a material. Photocrosslinking of polymers finds its application mainly in the field of photolithography.

Photosubstitution: Photosubstitution is the introduction of the desired functional groups onto the surface of the polymer using reactive gases. For example sulfonic acid groups ($-SO_3H$) can be introduced onto the surface by using SO_2 as a reactive gas. The reaction can be depicted as follows.

$$R - H + SO_2 + 1/2\ O_2 \rightarrow R - SO_3H$$

Similarly chloride groups, amino groups, cyanide groups, nitride groups, boride groups can be added to the surface in presence of the respective reactive gaseous atmosphere.

Photografting: Photografting is the introduction of hydrophilic functionality to a hydrophobic polymer surface by treating with UV light and using dilute aqueous or solvent based mixture solutions. Organosilanes and other coupling agents like isocyanates can be grafted onto the polymer surface in presence of UV light. Untreated polymeric materials are not receptive to these due to the absence of the appropriate active sites. Another example of photografting is the introduction of acrylic groups using UV light in presence of a photoinitiator like benzophenone. Similarly epoxy and amino functionalities can be grafted using appropriate aqueous chemical solutions.

Photooxidation: Photooxidation is the introduction of oxygen-based functional groups onto the surface of a polymer using UV light. This reaction takes place when the surface is treated with UV light in presence of either air or oxygen or ozone. UV light creates a very high oxidative environment around the substrate in

presence of any one of these gases. Ozone formation and ozone decomposition are the important reactions in this process. For this reactions to occur UV light having wavelengths of 184.9 nm and 253.7 nm are essential.

Molecular oxygen absorbs the 184.9 nm light to form an excited oxygen molecule.

$$\mathbf{O_2 + h\nu\ (184.9\ nm) \rightarrow O_2^*}$$

The excited state can then dissociate to form two ground-state oxygen atoms.

$$\mathbf{O_2^* \rightarrow 2O}$$

The ground state oxygen atom then reacts with molecular oxygen to form ozone.

$$\mathbf{O + O_2 \rightarrow O_3}$$

The quantum yield for ozone formation is approximately 2, which means that for every photon absorbed, two ozone molecules are formed.

Ozone has a strong absorption at 253.7 nm and two weak ones at 305 and 440 nm. Ozone absorption at the 253.7 nm is responsible for its decomposition.

$$\mathbf{O_3 + h\nu\ (253.7\ nm) \rightarrow O + O_2}$$

The quantum yield for ozone photolysis at 253.7 nm is approximately 0.9, which means that for each ozone molecule destroyed, there is one oxygen atom formed. These are the main pathways of ozone formation and decomposition. The overall

quantum yield of ozone taking into account both formation and decomposition reactions are 0.5, meaning that it takes two photons of light to generate one ozone molecule.

UV light not only interacts with these gases but also oxidizes the surface organic contaminants and creates receptive sites on the surface by breaking the molecular bonds on the surface. The oxygen related species like ozone and nascent oxygen generated by the UV light interact with the surface. The combined effect of UV light and ozone thus functionalizes the surface with oxygen related groups like OH, COOH, CHO and CO. Photooxidation using UV light is a very effective and economical technique for modifying polymer surfaces in order to improve their wettability and increase adhesion.

Although Ultra Violet light by itself, has been in use for many years to clean organic contaminants from various surfaces, usually the time of exposure has been long, several tens of minutes. The traditional use of UV light for cleaning surfaces combined with the newly discovered surface modification technique using UV light makes it more advantageous.

2.4) Sources of UV Light:

The sources for UV light can be divided into three categories. They are 1) UV lamps generating UV light in the entire UV range, 2) Monochromatic UV lamps and 3) Lasers operating in the UV range.

1) UV Lamps – UV lamps generate light in the entire UV range. These lamps operate over a range of wavelength from approximately 100 nm to about 1000 nm. They have varying light intensities and energies. The operating medium can be different in different lamps. Mercury vapor lamps and Xenon lamps are the most commonly used ones.
2) Monochromatic UV Lamps – These lamps generate incoherent UV radiation that has a unique wavelength. Depending on the type of gas (operating medium) used, different lamps generate monochromatic UV light at different wavelengths. The operating medium is usually an excimer (excited dimmer) in these lamps. For example lamps operating in pure xenon (Xe_2) generate light at 172 nm, in a gas mixture of krypton/ chlorine (KrCl) generate light at 222 nm and in a gas mixture of xenon/ chlorine (XeCl) generate light at 308nm.
3) Lasers – The lasers that operate in the UV range are the excimer lasers. Similar to the excimer UV lamps, the excimer lasers also operate at different wavelengths depending on the gas used in the laser. The light from the lasers is of higher intensity and smaller cross section when compared to that from lamps. Examples are Kr_2 laser operating at 146 nm,

Xe_2 laser operating at 172 nm, ArF laser operating at 193 nm, KrF laser operating at 248 nm, XeF laser operating at 351 nm, KrCl laser operating at 222 nm, XeCl laser operating at 308 nm etc.

2.6) Advantages of the UV Process over the Traditional Techniques:

UV surface treatment process can have numerous advantages when compared to other surface modification techniques. Some of them are listed below.

- UV treatment is a very controllable and versatile process.
- It is capable of treating all polymer surfaces even surfaces that are temperature or vacuum sensitive.
- UV can treat three-dimensional substrates and it is adaptable to treat flat or complex geometries.
- The times of treatment are relatively shorter and are not labor intensive.
- The process produces no emission of volatile organic compounds (VOC's). Hence it is environmentally benign.
- It is simple and easy to construct and inexpensive to operate.
- This operation does not require evacuation of the surrounding environment during the treatment.
- Because of the simplicity of the process, it is inherently low in cost to construct as well as to operate.
- It is a non-destructive technique.
- It is a dry process.
- Specific functionalities can be produced on the surface.

- The UV treatment process is highly reproducible.
- Unlike other treatment processes, the UV process can be operated either as a batch or as a continuous process.
- Optimization of the surface properties can be achieved without alteration of the bulk properties.
- Surface cleaning and surface modification takes place in a single step.

2.7) Variable Parameters Influencing the UV Treatment Process:

There are various factors that influence the UV treatment process. The process needs to be optimized in terms of these factors.

Type of Lamp: The configuration of the UV lamp used plays a key role in the treatment process. The intensity of the lamp (power of the lamp), size of the lamp, and the pulsing frequency of the lamp are the influential factors in the treatment process. The type of the laser used also affects the treatment because different lasers operate at different wavelengths.

Lamp to Sample Distance: Because of the use of elliptical reflectors in most lamps, the light is focused at a particular distance from the lamp and it diverges after that. The intensity of the lamp decreases as we go far away from the lamp. Hence the lamp to sample distance needs to be optimized depending on the material that is being treated.

Gas Concentration and flow rate: The concentration of the supplemental gas supplied and its flow rate are variables that need to be optimized for treating a particular surface.

Time of Treatment: The time of UV treatment differs from material to material. So, depending on the material of the substrate, the treatment time has to be optimized.

Temperature of the Substrate: The temperature to which a substrate reaches during a treatment needs attention because some polymers are temperature sensitive. Also temperatures higher than the glass transition (Tg) in polymers may have adverse effects on their properties. Treating them for longer times or with high intensity lamps can degrade the material or affect the bulk properties.

Chemical Composition of the Substrate: The physical and chemical characteristics of the substrate play a key role in the UV treatment process. The chemical composition of a substrate determines the absorption of the light and its reactions with the surrounding environment. The type of the UV process parameters to be used for a treatment depends entirely on the surface chemistry of the substrate.

Laser fluence and pulse repetition: The energy of the laser beam is a variable quantity when the laser treatment is considered. Also the area of the rectangular laser beam is variable. Laser fluence is obtained by dividing the laser energy with the area of the beam. Both these variables are to be adjusted to attain the desired laser fluence. Since the beam is of high energy, care has to be taken while treating polymers because high-energy laser can ablate the surface away. The laser fluence was can be varied in order to optimize the polymer for the maximum adhesive performance without damaging it. The laser pulses also can be varied to achieve maximum adhesion.

Chapter Three

Experimental Methods

3.1) Experimental Materials

Two UV lamps and an excimer laser have been used in order to conduct the UV treatment experiments. The lamps are designated as RC-500 and RC-747. Xenon is the manufacturer of the UV lamps. Both the lamps are pulsing lamps. RC-500 has a total power output of 300 w and pulsing frequency of 120 Hz. Its dimensions are 5 in x 1 in. RC-747 can operate in two modes. Both the modes have the same total power output of 2000 w have the same lamp size of 16 in x 3.5 in. The only difference between the two modules is their pulsing frequency. One of them pulses with a frequency of 120 Hz and the other with a frequency of 3 Hz. A KrF excimer laser, COMPex 301 manufactured by the Lambda Physik®, has been used for the laser UV treatment. The excimer laser has KrF as the lasing medium in it. It has a rectangular pulsed beam. It operates at a wavelength of 248 nm. The average maximum power of the laser is 15 w and the maximum pulse energy is 1500 mJ. It has pulse duration of 25 ns and the pulsing frequency is variable between 1 and 10 Hz.

Figure 3.1 is the picture of the RC-747 UV lamp and figure 3.2 is the picture of the KrF Excimer Laser.

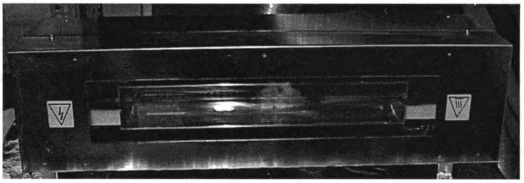


Figure 3.1: RC-747 UV Lamp

Figure 3.2: KrF Excimer Laser

The materials that are treated with UV light for increased adhesive performance are Ticona Impet EKX-215 and Hivalloy X83-21-5. Ticona is a 20% glass fiber reinforced Polyethylene Terepthalate (GF-PET). This is a thermoplastic composite material and has a T_g of 89°C. Hivalloy is a blend of Polypropylene and Polystyrene with 35% glass fibers reinforced in it (GF-PP). This is also a thermoplastic composite with a T_g of 118°C. Both these materials have got a wide array of applications, mainly in the automotive industry.

Four different adhesives are used for bonding the UV treated samples and testing them for enhanced adhesive strength. They are the Araldite 2015, Ashland Pliogrip 7779, Dow AH5643A (LESA) and Essex Betamate 73005. The formulations and the curing times of the adhesives are discussed in the results chapter.

The UV lamp treatment chamber is an aluminum chamber whose height is 2 inches. It has an inlet and outlet for gas flow. An ozone generator is used in order to supply supplemental ozone during the treatment process. The inlet gas flow rate to the ozone generator and the voltage can be varied. A mass flow controller is used to maintain constant inlet gas flow rate to the ozone generator. The ozone coming out of the ozone generator has the same flow rate as the inlet gas. The concentration of the ozone in the outlet stream of gas is dependent on the inlet gas flow rate and the voltage applied. The lower the gas flow rate, the higher the concentration of ozone. The higher the voltage applied, the higher the concentration of ozone. The inlet gas to the ozone generator for all the experiments is medical grade oxygen that is 99% pure.

The materials are cut to 1 in x 1 in flat samples using a band saw. The surface of the samples is wiped with isopropanol before treatment.

3.2) UV Treatment Process

The blower that supplies cooling air around the UV lamp is switched on. The power supply to the UV lamp is switched on next. The valve of the oxygen gas cylinder is opened and the flow rate is set at 10 scfh. The oxygen from the cylinder is fed to the gas inlet of the ozone generator using a Teflon tube. The ozone generator is switched on and the voltage is set at the desired value. A Teflon tube connects the outlet of the ozone generator and the inlet of the aluminum chamber. The gas flows through the chamber, over the sample and exits through the outlet. The cut and solvent cleaned sample is placed in the chamber. The time of treatment and mode of treatment (continuous or intermittent) is set on the dial of the power supply and the lamp is switched on. Once the treatment is complete, the sample is taken out of the chamber and its surface temperature is measured using an infrared pyrometer. The rest of the process parameters are kept constant and only the UV treatment time is varied for a particular set of experiments. The figure below shows a schematic representation of the UV treatment procedure.

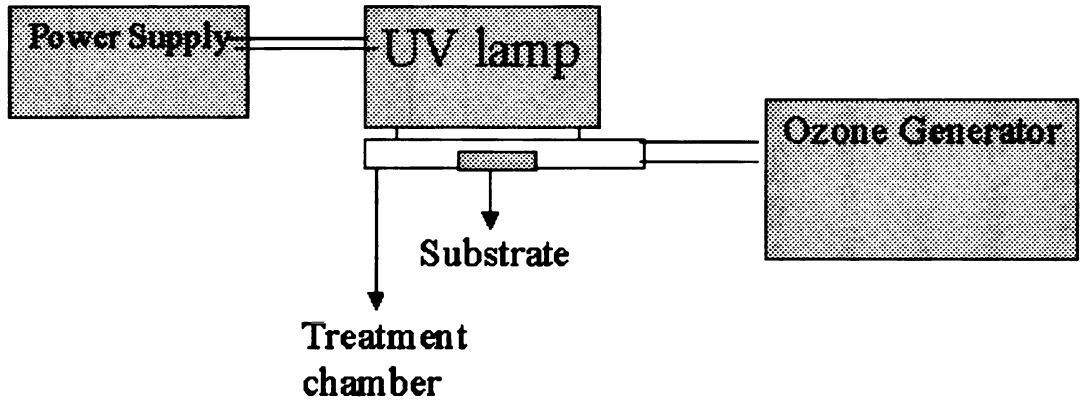


Figure 3.3: Schematic Representation of the UV Treatment Process

3.3) Laser Treatment

Laser treatment is carried out in air. The sample is mounted on the sample holder and the laser parameters are set up. The laser parameters can be controlled using a joystick. The power supply to the laser and the guiding laser (He-Ne laser) are switched on. The lens covers are removed. The pulse repetition rate is set to the desired value using the joystick. The laser energy is also set to the desired value on the joystick. Moving the sample holder up and down can change the area of the rectangular laser beam hitting the sample. The laser energy divided by the area of the beam gives the value of laser fluence. All the remaining variables are kept constant and the number of pulses hitting the substrate is varied for a particular set of experiments. Figure 7 shows a schematic representation of the laser treatment process.

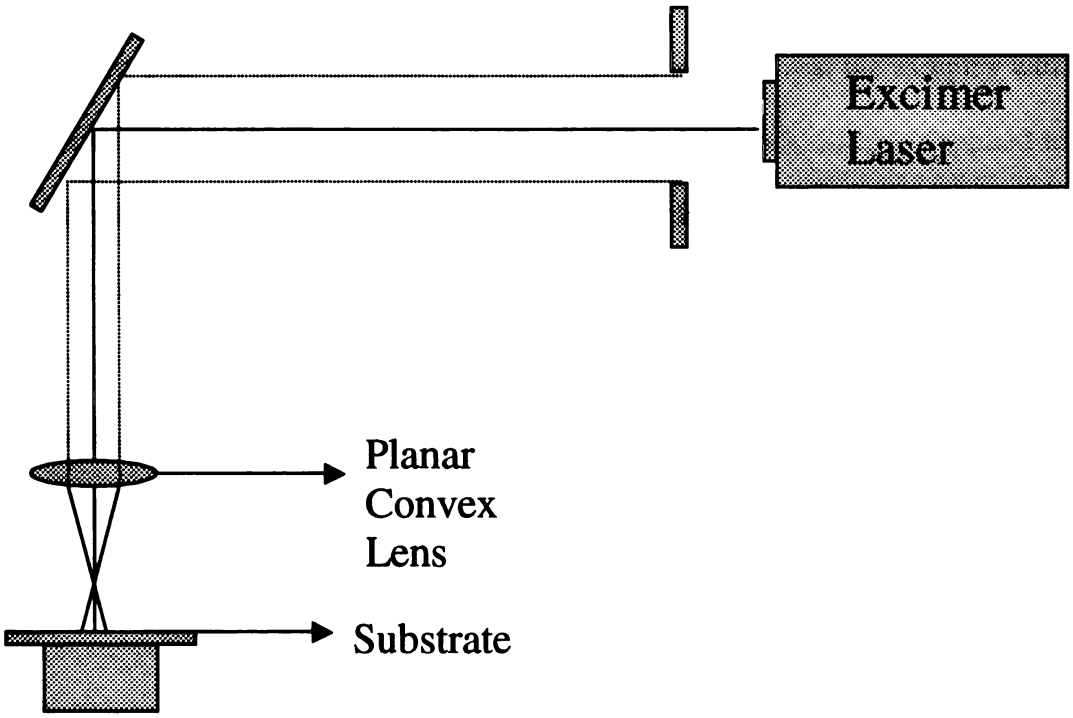


Figure 3.4: Schematic Representation of the Excimer Laser Treatment Process

3.4) Silane Treatment

Both the UV treated and laser treated samples were also treated with silane for further improvement in adhesive performance. The silane used is a Dow Corning Z-6020 silane. It is a N- (β-aminoethyl)- γ – aminopropyltrimethoxysilane. The chemical formula of the silane is $(CH_3O)_3SiCH_2CH_2CH_2NHCH_2CH_2CH_2NH_2$. The silane is hydrolyzed prior to its use for treatment. The Z-6020 silane is diluted by mixing it with deionized water in the volume ratio 1:3 (1 part silane + 3 parts D.I. water). The silane is left to hydrolyze in water over night. Then the solution is made to 1% by weight of silane by mixing it with isopropanol and left for 24 hours in a closed container before it is used.

The hydrolyzed silane solution can be applied to the samples in two ways. One way is to dip the samples in the silane solution for about five minutes after they have been treated with the UV. The other way is to treat the samples with UV with a thin layer of silane solution on top of their surface. Silane is applied to the samples in both the ways mentioned above and the results are compared. Once the samples are removed from the silane solution, they are washed in deinonized water in order to make sure there is no physical adsorption of silane onto the surface. The samples are then dried and tested or analyzed.

3.5) Adhesion Tests

The adhesion tests are carried using a Pneumatic Adhesion Tensile Testing Instrument. It will be referred to as the PATTI tester. The UV treated samples are adhered to a sandblasted aluminum pull-stub using an adhesive. These samples are called the PATTI samples. The adhesive is allowed to cure and the adhesion between the stub and the treated sample is tested using the PATTI system.

The sandblasted aluminum stubs are cleaned using isopropanol to remove any contaminants. The adhesive is mixed as recommended by the manufacturer. The adhesive is then applied to the bottom of the pull-stub and pressed against the test surface. While holding stub in place, a cut-off ring is pressed around the stub onto the test surface. The cut-off ring displaces the excess adhesive away from the stub. A light uniform clamping pressure in the form of a weight is applied on the stub during the curing time of the adhesive. The clamping weights and the cut-off rings are removed after the curing time of the adhesive. The excess adhesive surrounding the stub is scored using a knife. The PATTI sample is now ready to be tested.

The PATTI system applies a true axial tensile strength (relative to stub axis) pull test. The tensile values obtained quantitatively measure the bond strength between the adhesive and the substrate surface. The pneumatic control module of the PATTI system is connected to a pressurized gas supply (nitrogen or air) and a hose to the pulling piston. The piston is attached to the pull-stub previously glued to the test surface. Upon detachment of the pull-stub, the control

module will register and indicate the maximum pressure (burst pressure) attained in psig. This pressure is then converted into psi by using the below formula.

POTS = (BP x Ag) – C/Aps

Where:

POTS = Pull-off tensile strength

BP = Burst pressure (psig)

Ag = Contact area of gasket with reaction plate = 2 sq. in. for F-2 piston and 8 sq. in. for F-8 piston.

C = Piston contact = 0.3 pounds for F-2 piston and 0.8 pounds for F-8 piston.

Aps = Area of pull-stub = 0.196 sq. in.

The PATTI system has two different size pistons. The pistons are called F-2 and F-8. The type of piston used for testing depends on the bond strength of the PATTI sample, which in turn depends on the substrate being tested and the adhesive being used. F-2 piston is used for lower bond strengths and F-8 is used if the bond strengths are higher. The gas supply to the PATTI system is nitrogen from a cylinder. The gas regulator is turned on and the digital reading on the control module is zeroed before testing. The reaction plate is threaded onto the pull-stub until light contact is made with the piston. Then the pressure is applied by pressing the RUN button until piston assembly with attached pull-stub detaches from the test surface. The burst pressure reading on control module, the type of piston used and the mode of failure are noted. Figure 8 is a schematic representation of the PATTI piston assembly.

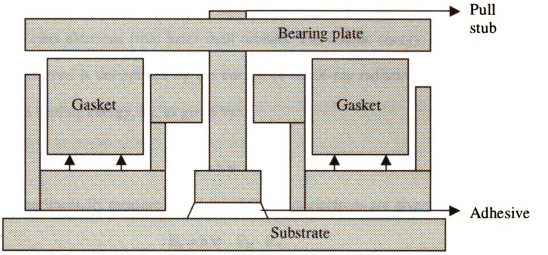


Figure 3.5: Schematic Representation of the PATTI System

3.6) X-Ray Photoelectron Spectroscopy

X-Ray Photoelectron spectroscopy is used to determine the chemical composition of the sample surfaces.

X-ray photoelectron spectroscopy (XPS, also called electron spectroscopy for chemical analysis, ESCA) is an electron spectroscopic method that uses X-rays to eject electrons from inner-shell orbitals. The kinetic energy, E_k, of these photoelectrons is determined by the energy of the X-ray radiation, $h\nu$, and the electron binding energy, E_b, as given by:

$$E_k = h\nu - E_b$$

The experimentally measured energies of the photoelectrons are given by:

$$E_k = h\nu - E_b - E_w$$

Where E_w is the work function of the spectrometer.

The electron binding energies are dependent on the chemical environment of the atom, making XPS useful to identify the oxidation state and ligands of an atom.

XPS instruments consist of an X-ray source, an energy analyzer for the photoelectrons, and an electron detector. The analysis and detection of photoelectrons requires that the sample be placed in a high-vacuum chamber. Since the photoelectron energy depends on X-ray energy, the excitation source must be monochromatic. An electrostatic analyzer analyzes the energy of the photoelectrons, and an electron multiplier tube or a multichannel detector such as a microchannel plate detects the photoelectrons.

XPS surface analysis is performed using a Perkin-Elmer Physical Electronics PHI5400 ESCA Spectrometer equipped with a standard magnesium X-ray source operated at 300 W (15 kV and 20 mA). Data is collected in the Fixed Analyzer Transmission mode utilizing a position sensitive detector and hemispherical analyzer. The elemental composition of the surface is determined from survey spectra collected using a pass energy of 89.45 eV. High-resolution spectra of the elements are obtained using a pass energy of 17.9 eV and a step size of 0.1 eV. Binding energies are referenced to adventitious carbon (C 1s = 284.6 eV) and were measured with a precision of $\pm$ 0.1 eV.

Chemical information indicating changes in the surface treated polymers is elucidated by curve fitting the carbon 1s (C1s) spectra. Curve fitting defines and interprets the carbon chemistry as detected at the sample surface by allowing the user to distinguish overlapping features within the C1s spectral envelope. The C1s spectra are fit with a Lorentzian-Gaussian mix Voigt profile function using a nonlinear least squares curve-fitting program. The model used is based on the assumption that there is an approximate 1.5 eV chemical shift per bond to oxygen. The resulting curve fits have levels of experimental error around 5-10%.

3.7) Environmental Scanning Electron Microscopy

Environmental Scanning Electron Microscopy is used to look at the surface of the samples to see whether the UV treatment has caused any topographical changes on the surface. The ESEM retains all the performance advantages of a conventional scanning electron microscopy, but replaces the high vacuum sample environment with one that contains ~2-3 torr of water vapor. It allows the examination of any specimen, wet or dry, insulating or conducting. The depth of field, resolution and microanalysis are superior to that of a light microscope. This technique does not require the samples to be vacuum tolerant and electrically conductive like in the SEM.

The ESEM used for this work is manufactured by Electroscan Corporation (model number – 2020). It is equipped with a Lanthium Hexaboride filament. Water vapor is used as the imaging gas. The samples to be examined are placed on the sample holder located in the sample chamber. The imaging pressure (chamber pressure) is set between 2 and 3 Torr. The working distance between the detector and the sample is set between 8 and 10 mm. The accelerating voltage is set at 20 kV. The sample is focused at different points on its area and micrograph pictures are taken.

Chapter Four

Results and Discussions

This chapter discusses the adhesion test results, surface chemistry and surface topography changes for the RC-500 UV lamp and the Excimer Laser treated Ticona at different conditions.

4.1) Adhesion Tests:

The RC-500 UV treated Ticona materials are tested using the PATTI tester for enhanced adhesive performance. The samples are exposed continuously to the UV light for the time of treatment. Ciba-Geigy Araldite 2015 adhesive, which is a two part epoxy based is used for making the PATTI samples. This adhesive has a curing time of 24 hours.

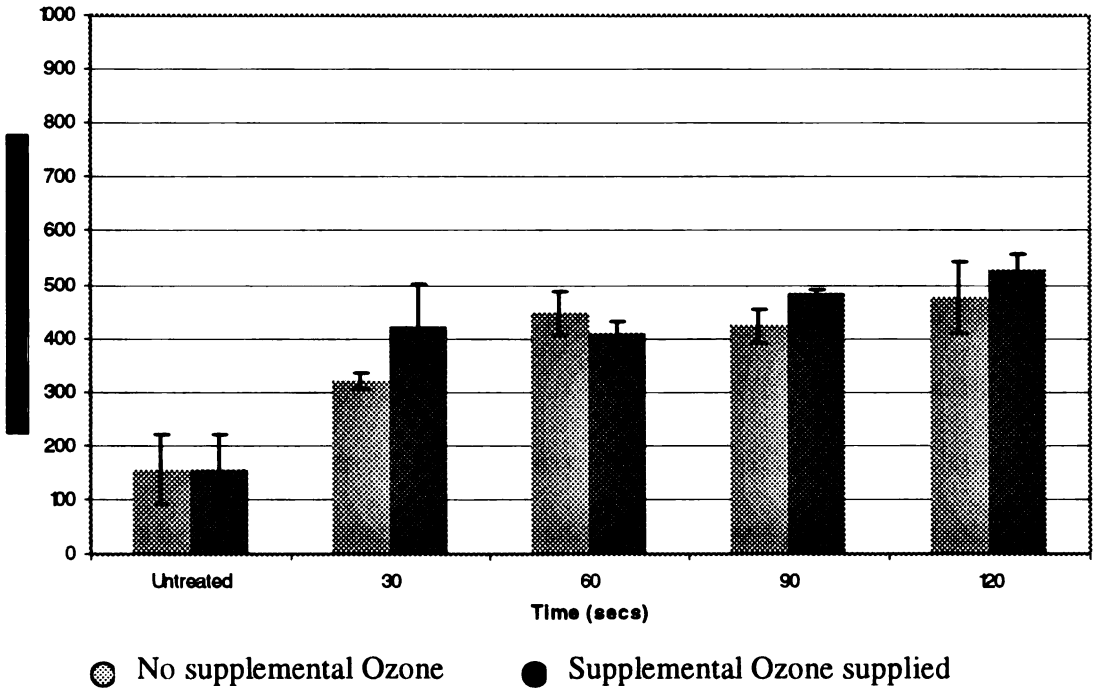


Figure 4.1: PATTI Results for UV Treated Ticona

The PATTI test results for the UV treated Ticona without using any supplemental ozone and using supplemental ozone are provided in Figure 4.1.

For the treatment in air maximum adhesive strength is obtained when the samples were treated for 180 seconds and for the treatment in ozone maximum adhesive strength is obtained when the samples were treated for 90 seconds. All the failures in both the treatment conditions (without ozone and with ozone) are adhesive.

In order to further improve the adhesive performance of Ticona, the UV treated samples are post-treated with a silane. The silanes are grafted to the surface of the Ticona by immersing the samples in hydrolyzed silane solution for 5 minutes. They are then dried and bonded to the PATTI stubs and tested after the adhesive is cured. Dow Corning Z-6020 Silane is used. The chemical name of the Z-6020 silane is N- (β-aminoethyl)- γ –aminopropyltrimethoxysilane. The silanes have methoxy groups that hydrolyze in water or a solvent. Once they hydrolyze, the methoxy groups are converted to hydroxyl groups, which are very reactive. Z-6020 silane has 3 methoxy groups, which on hydrolysis get converted to hydroxyl groups. These hydroxyls can undergo a condensation reaction, with hydroxyl groups on both the polymer substrate and the adhesive, thereby enabling the substrate to be receptive to the adhesive. Thus, the silanes act as connector molecules between the substrate and the adhesive. The end group of the silane can be selected depending on the adhesive used for bonding. The hydrolysis of the Z-6020 silane can be shown as follows.

$$(CH_3O)_3SiCH_2CH_2CH_2NHCH_2CH_2NH_2 \xrightarrow{\text{Hydrolysis}} (HO)_3SiCH_2CH_2CH_2NHCH_2CH_2NH_2$$

Figure 4.2 is a schematic of the grafting of the Z-6020 Silane onto the surface of UV treated polymer. 'R' in figure 4.2 represents the end group of the silane, which is '$CH_2CH_2CH_2NHCH_2CH_2NH_2$' in this case.

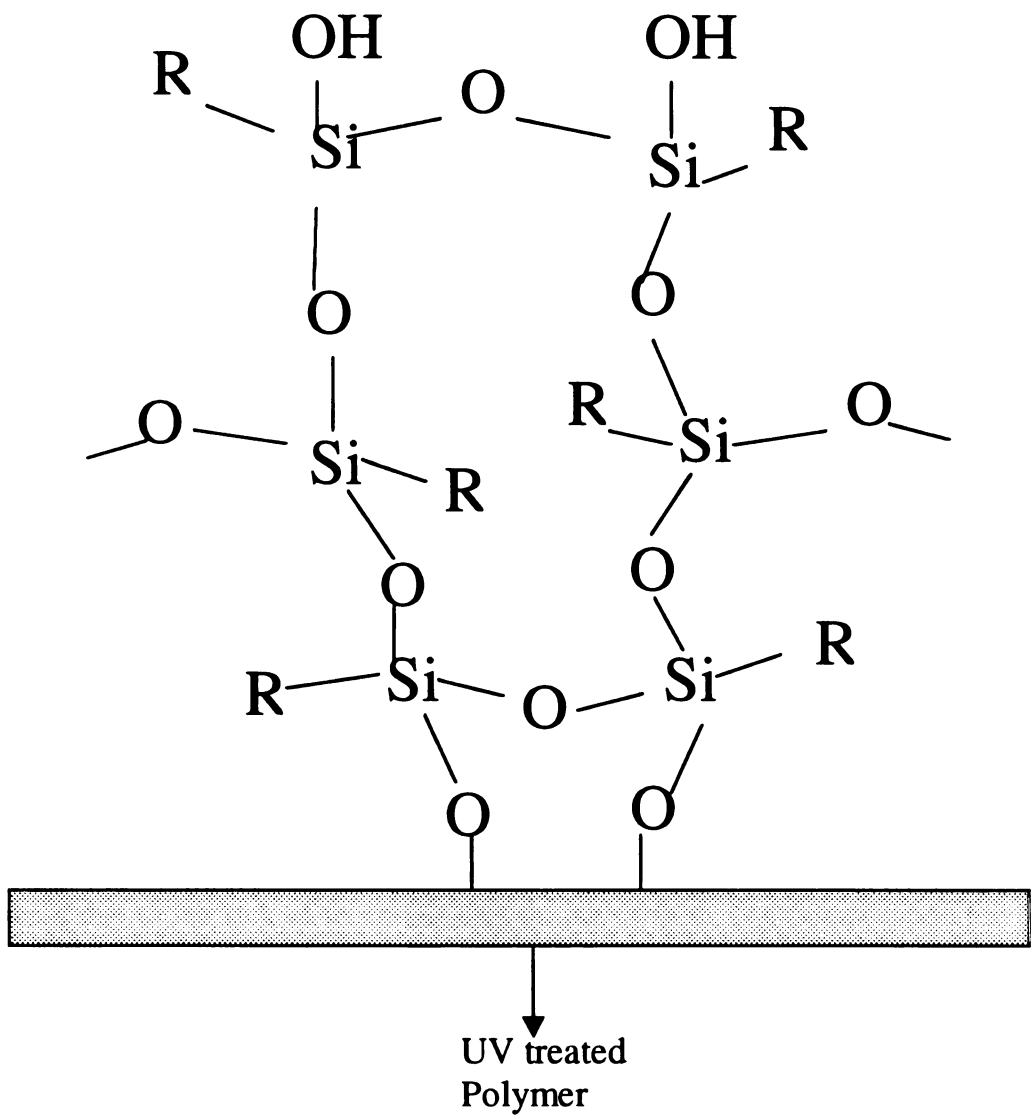


Figure 4.2 Schematic Representation of the Silane Reaction on the Polymer Surface

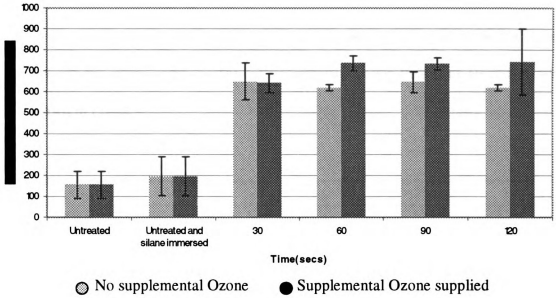


Figure 4.3: PATTI Results for UV/Silane Treated Ticona

The PATTI results for RC-500 UV treated and then silane immersed Ticona are shown in Figure 4.3. The surface grafted samples are tested for pre-UV treatments both with and without supplemental ozone.

The tensile strength required to detach the PATTI stub increased considerably for the UV treated silane grafted Ticona surfaces. The untreated samples showed low adhesive performance because silane could not be grafted onto them due to the lack of receptive sites on the surface. The failure mode for the UV treated samples is a cohesive failure. By using the silane treatment technique, the failure mode for the UV treated Ticona samples changed from adhesive to cohesive.

Another set of experiments were conducted in which the Ticona samples are first immersed in silane solution and then treated by exposure to the UV light through the silane solution. The PATTI results for this treatment procedure are shown in Figure 4.4.

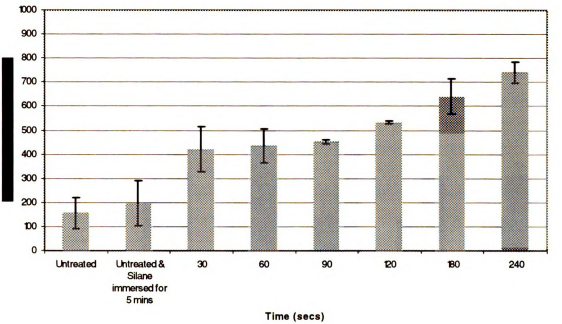


Figure 4.4: PATTI Results for UV Treated Ticona through Silane

Longer UV treatment times are required in this case in order to reach the same values of tensile strength as in the earlier silane treatment procedure. The failures are adhesive upto the 120 seconds treatment condition and the failure mode changed to cohesive for the 180 and 240 seconds treatment conditions.

The Ticona samples were also treated with the Excimer Laser for enhanced adhesive performance. The samples are treated using the 248 nm wavelength KrF Excimer Laser with increasing pulse rates keeping the energy

fluence constant at 100 mJ/sq.cm. The treated samples were tested using the PATTI tester. Some of the Laser treated samples are post-treated with silane following the same procedure like the UV-silane treatment. Figure 4.5 compares the PATTI test results between the laser treated Ticona and the laser treated and silane immersed Ticona samples.

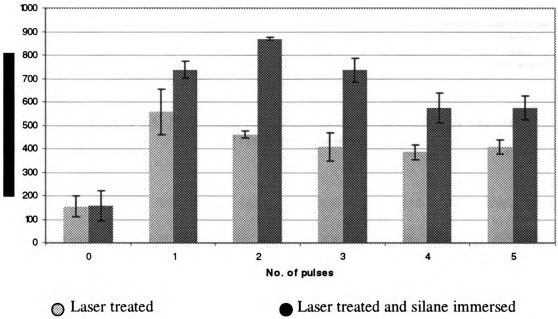


Figure 4.5 PATTI Results for Laser Treated Ticona

Maximum adhesive strength is obtained when the Ticona samples are treated with just for 1 pass of the Laser. The adhesive strength decreases thereafter as the pulse rate increases. When silane is used along with the laser treatment maximum adhesive strength is obtained at a pulse rate of 2 and decreases thereafter.

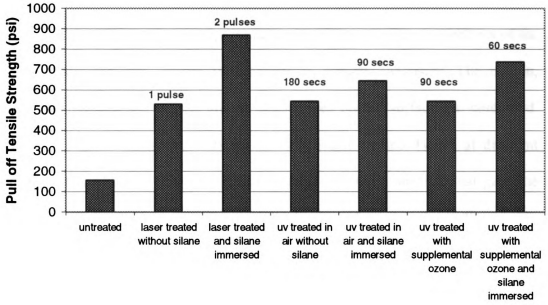


Figure 4.6: Maximum values of Adhesive Strengths for various Treatment Conditions

The PATTI test results using different experimental procedures are summarized in Figure 4.6 which displays the maximum adhesive strength obtained using various treatment techniques.

4.2) Surface Chemistry Characterization:

X-Ray Photo Electron Spectroscopy is used to examine the surfaces of the treated samples and analyze the changes in surface chemistry. The carbon, oxygen, nitrogen and silicon atomic percentages on the surface are compared. Table 4.1 gives the XPS results for UV and silane treated Ticona at different treatment conditions. Ticona samples treated for the optimum time that gave the maximum adhesive strength for a particular set of treatment conditions was investigated.

Table 4.1: XPS Results for UV Treated Ticona

	Control (%atomic conc)	60 secs UV treated and silane immersed (% atomic conc)	240 secs UV treated through silane (% atomic conc)
C	71.2	61.8	73.4
O	18.7	21.7	16.5
Si	10.2	12.6	4.9
N	0.0	3.8	5.1

By comparing the atomic concentrations of the the control sample with the UV/silane treated ones, it is obvious that silane is grafted onto the surface of Ticona. Also the increase in oxygen atomic concentration in the case of UV treated first and then silane treated Ticona suggests that the surface has been oxidized by the UV/Ozone treatment. The decrease in oxygen concentration in the case of UV treated Ticona through the silane must have been the result of the increased concentration of the grafted silane on the surface. In order to better understand the results, nitrogen atomic concentration can be compared. There is no nitrogen present on the surface of the control sample. Whereas, the UV/silane treated samples have nitrogen present on their surface. This nitrogen on the surface results from the silane that is grafted on the surface. The amino groups in the end group of the silane are responsible for the Nitrogen atomic concentration on the UV/silane treated samples.

Table 4.2 gives the XPS results for the Excimer Laser treated Ticona at various conditions.

Table 4.2: XPS Results for Laser Treated Ticona

	Control (% at conc)	1 pulse (% at conc)	2pulses (% at conc)	1 pulse and silane immersed(% at conc)	2 pulses and silane immersed(% at conc)
C	71.2	90.7	89.7	86.9	85.5
O	18.7	8.8	9.8	11.1	11.7
Si	10.2	0.5	0.4	1.2	1.6
N	0.0	0.0	0.0	0.8	1.2

It can be observed that there is a decrease in Oxygen content as well as the Silicon content on the surface of the Laser treated samples. This could be the result of the Laser degrading away the surface and the evolving products from the Laser degradation settling down back on the surface. This degradation can be responsible for creating surface roughness, which in turn improves adhesive performance.

4.3) Microscopy:

Environmental Scanning Electron Microscopy is used to look at the surfaces of the UV and Laser treated Ticona samples. The following figures are the ESEM pictures of the Ticona samples, untreated as well as treated.

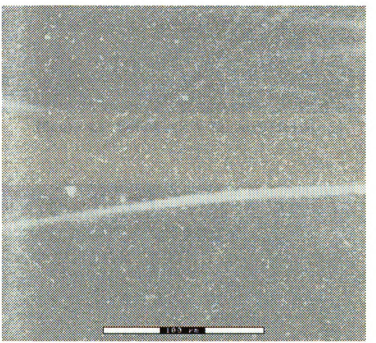


Figure 4.7: ESEM of Control Ticona Sample

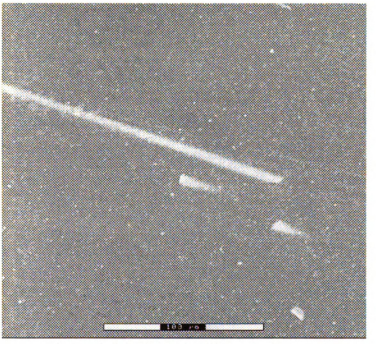


Figure 4.8: ESEM of UV Treated Ticona

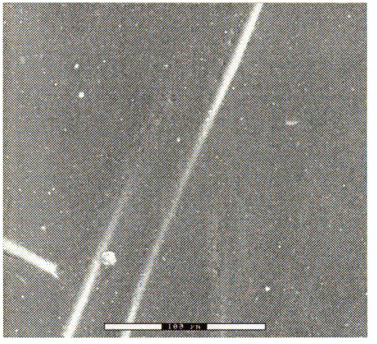


Figure 4.9: ESEM of Excimer Laser Treated Ticona

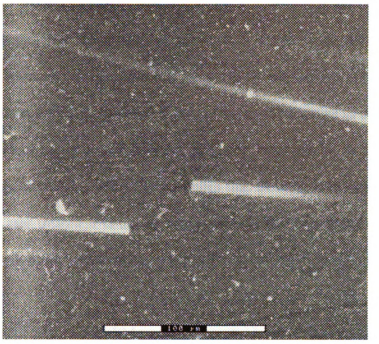


Figure 4.10: ESEM of UV and Silane Treated Ticona

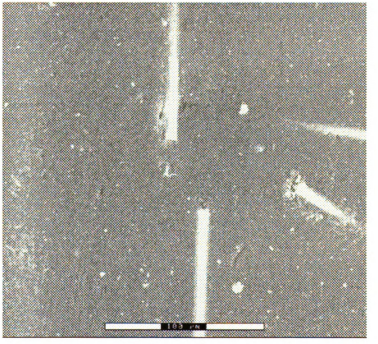


Figure 4.11: ESEM of Excimer Laser and Silane Treated Ticona

The ESEM pictures show that neither the UV treatment nor the UV/silane treatment changed the topography of the surface at the level detected by the scanning electrion microscope. This means, that the UV treatment did not alter the surface of Ticona i.e. the UV treatment did not cause any damage to the surface of the material. The Laser treated samples however, have cracks on their surface located mainly around the fibers. This implies that the adhesion improvement in case of the Laser treatment could be due to the mechanical interlocking coming about as a result of the adhesive penetrating into the surface cracks created on the surface.

From the XPS and ESEM results, it can be inferred that the improvement in surface adhesion in case of the UV treatment is due the surface oxidation whereas the improvement in surface adhesion in case of the Laser treatment is mainly due to mechanical interlocking.

Chapter Five

UV Treatment of Polymer Composite Valve Covers

5.1) Valve Covers

The valve cover in an engine covers the valve train. The valve train consists of rocker arms, valve springs, push rods, lifters and cam. Oil is pumped up through the pushrods and dispersed underneath the valve cover, which keeps the rocker arms lubricated. Holes are located in various places in the engine head so that the oil re-circulates back down to the oil pan. For this reason, the valve cover must be oil-tight. The valve covers are usually made out of metals or alloys

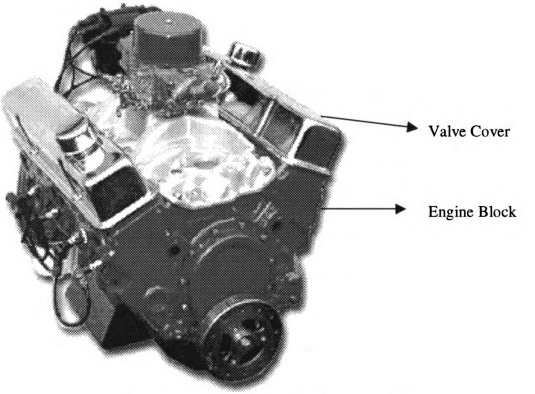


Figure 5.1: Valve Cover location in an Engine

like aluminum, steel or iron. Since there is always lubricating oil circulating in the interior of the valve covers, the valve covers have to be oil-tight and for this purpose gaskets are used. These gaskets are sealants which prevent oil leakage. Figure 5.1 is a picture showing the location of the engine valve covers and their structure.

Reducing the overall weight of an automobile is much sought after way to increase its fuel efficiency. Hence, plastics and composites are finding increasing importance in the manufacture of automotive structural components. Fiber reinforced plastic composites are desirable in this respect as they have structural mechanical properties comparable to that of metals and are of low weight. The automotive structural systems made up of these fiber reinforced plastics satisfy the needs of safety, strength and durability in addition to being affordable, manufacturable with desired fit and finish and recyclable. The composite components made from fiber-reinforced plastics are capable of carrying structural loads under static and dynamic conditions. A recent development in the use of polymer composites is the Daimler Chrysler program to replace the metallic valve covers of an engine with plastic and composite valve covers. These valve covers are made out of Hivalloy X83-21-5 composite. Hivalloy X83-21-5 is a 35% glass fiber reinforced polypropylene/polystyrene composite. Along with the use of composite valve covers adhesive bonding is being evaluated as an efficient technique to join these valve covers to the engine block. Adhesive joining of the valve covers eliminates the use of gaskets, distributes the load more uniformly and eliminates the need for alternative joining methods.

The valve covers made from fiber reinforced plastic are selected for their structural and environmental performance (thermal stability, oil exposure stability and mechanical properties) but have a surface with qualities or contaminants that make it difficult to adhere paints of adhesives. Hence, if adhesive joining is to be used, the bonding surfaces of these valve covers require surface preparation or pre-treatment before they are bonded. The MSU UV surface treatment method has been used to prepare these surfaces for a satisfactory adhesive bond. The valve covers are treated by the UV light, bonded together using an adhesive after treatment with a RC-747 UV lamp manufactured by Xenon Corporation and then tested. Figure 10 is a picture of the Daimler Chrysler valve cover.

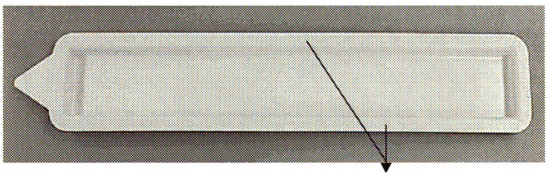


Figure 5.2: Daimler Chrysler Valve Cover

5.2) UV Treatment of Flat Valve Cover Specimens

The first experiments were done initially done on flat sample plaques of the valve cover materials as the screening experiments. These screening tests are used to establish the process parameters for the valve cover treatment. Flat 1 in x 1 in samples are cut using the band saw. The 1 sq. in flat samples were treated in the UV treatment chamber both in air and in ozone under various treatment conditions in order to optimize the process parameters. For treatment in air, supplemental air at a flow rate of 30 scfh was supplied to the chamber. For treatment in ozone, supplemental ozone at a flow rate of 30 scfh was supplied to the chamber while maintaining the voltage to the ozone generator at 50% V and using oxygen as the input gas to the ozone generator. For a particular set of experiments all other parameters such as the type of lamp, gas flow rate, ozone concentration and lamp to sample distance were kept constant and only the treatment time was varied. PATTI samples are made using the Ashland Pliogrip 7779 adhesive and the samples are tested. The increase in bond strength of the treated samples can be determined using the PATTI system. Figure 5.3 shown below gives the PATTI results of Ticona at various treatment conditions.

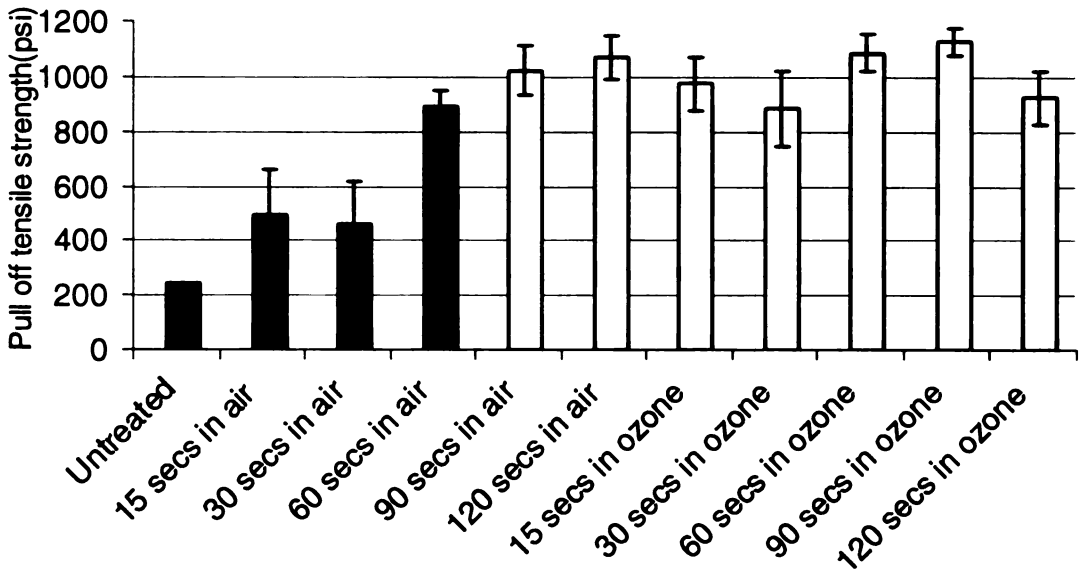


Figure 5.3: PATTI Results for UV Treated Ticona

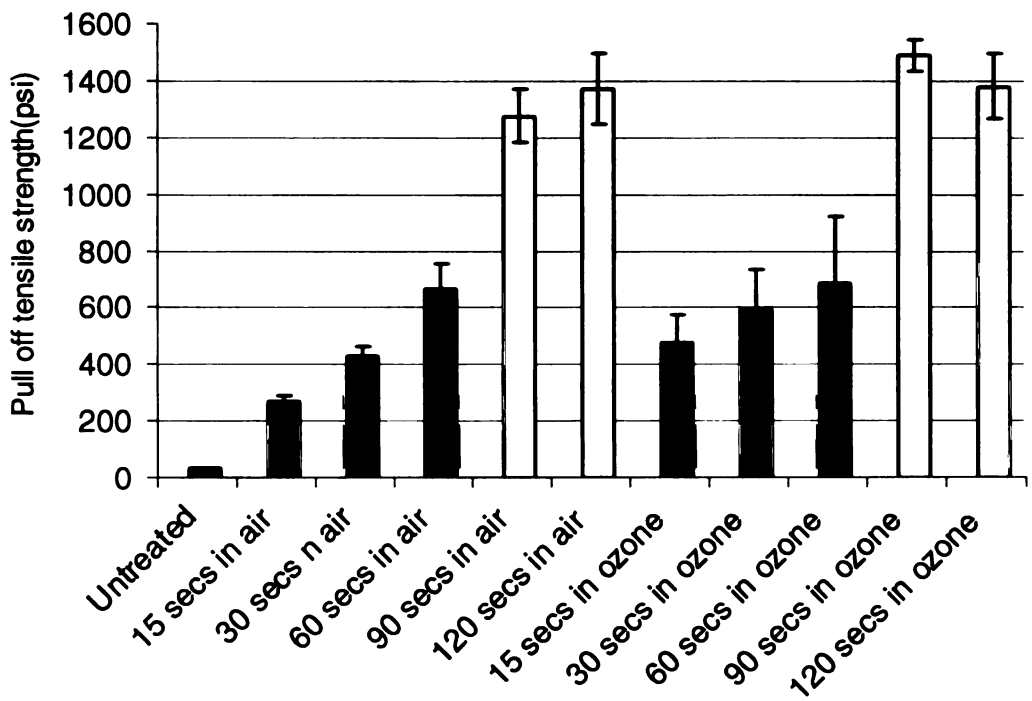
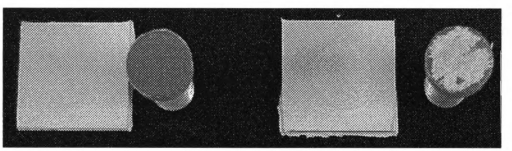


Figure 5.4: PATTI Results for UV Treated Hivalloy

The black bars in the above figure represent an adhesive failure and the white bars represent a cohesive failure. The untreated samples failed at very low adhesive strengths. Maximum adhesive strength was achieved using the 120 second UV treatment condition in air and alternatively using the 90 second treatment in ozone. The failures at these conditions are completely cohesive.

Figure 5.4 gives the PATTI results for Hivalloy at various treatment conditions. The black bars represent an adhesive failure and the white bars represent a cohesive failure. The untreated samples failed at very low values of bond strengths. Maximum adhesive strength is also obtained after the 120 second UV treatment in air and after the 90 second treatment in ozone. The failures at these treatment conditions are also completely cohesive.



Untreated **UV Treated**

Figure 5.5: Tested PATTI stubs and substrates

PATTI tests show that UV treatment increases the bond strength to both Ticona and Hivalloy to a point of generating a failure completely in the substrate. Figure 5.5 shows the failure mode difference between an untreated sample (adhesive failure) and a UV treated sample (cohesive failure). Treatments in air

and ozone gave comparable results. But treatment in air requires a longer time to reach the same strength as in ozone. Even though supplemental ozone is not supplied, the UV lamp can generate ozone by interacting with the oxygen in air. Longer treatments are required in air as it takes some time for the creation of sufficient ozone to interact with the surface. This transient effect would not be present if this method was used in a manufacturing environment since the lamps would be on all of the time.

5.3) Design of a Conveyor System for Treating the Valve Covers:

In order to simulate a manufacturing operation in which the UV treatment was used to modify the valve cover surface, a simple conveyor system was made to treat the valve cover parts. The valve covers are 35 inches long and the distance between the two lips of the valve cover, that are to be treated is 7 inches. The RC-747 UV lamp is 16 inches long and 3.5 inches wide (3.5 inches is the width of the quartz glass plate covering the lamp). In order to treat the entire valve cover, a long lamp would have to be manufactured to provide sufficient exposure to the entire valve cover. The valve cover could be treated in parts under the lamp but the treatment will be non-uniform with some areas being over treated and some areas untreated at all. Hence a conveyor system, which can transport the valve cover under the lamp in a direction perpendicular to the length of the lamp (along the width of the lamp) and can carry the valve cover on it was designed. In this way the entire length of the valve cover could be treated uniformly by passing the

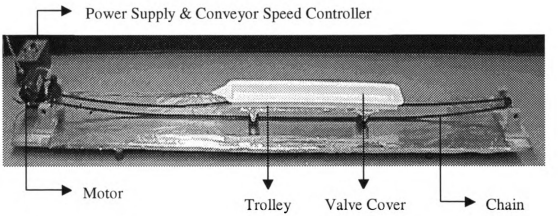


Figure 5.6: Conveyor System for UV treating the DC valve covers

cover under the fized lamp. The UV treatment time can also be varied by varying the speed of the conveyor. The conveyor system designed for treating the valve covers is as shown in the figure 5.6.

In order that the entire valve cover is UV treated for the required time, the conveyor was powered by a motor and chain arrangement to move it at a very low speed. A rheostat controls the rotational speed of the motor shaft to vary the speed of the trolley. A combination of a worm and a worm gear was added to obtain the desired speed reduction. A 30 tooth worm gear was used to produce a speed reduction ratio of 30:1 can be obtained. The worm gear drives a shaft and the other spur gear sitting on the same shaft drives the chain, which passes over another spur gear that moves on another shaft at the other end reducing the speed appropriately enabling the entire valve cover to be treated by UV in the required time. The rheostat, which varies the speed of the motor shaft, can be used to vary the speed of the trolley. Variation in the speed of the trolley results in variation of the UV treatment time. In order to supply supplemental ozone a glass delivery system with diffusers has been designed. This gas delivery system sits on the lamp , and is positioned so that the gas is delivered to the lips of the valve cover. The pictures below show the mounting of the worm and the worm gear and the ozone delivery system.

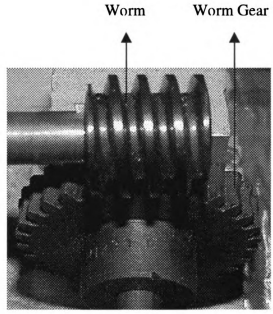


Figure 5.7: Worm and Worm Gear

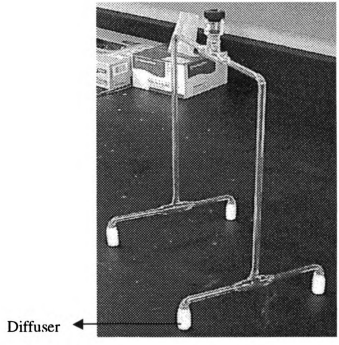


Figure 5.8: Ozone Delivery System

The efficacy of the UV treatment conditions was tested using the PATTI system on 1 sq. in samples of valve cover material. The samples were placed on the trolley and passed under the lamp for various times (at various speeds) to develop a new set of treatment conditions different from the previous static treatment conditions. The following chart (figure 5.9) is a calibration curve for setting up the desired time of treatment with a reading on the power supply.

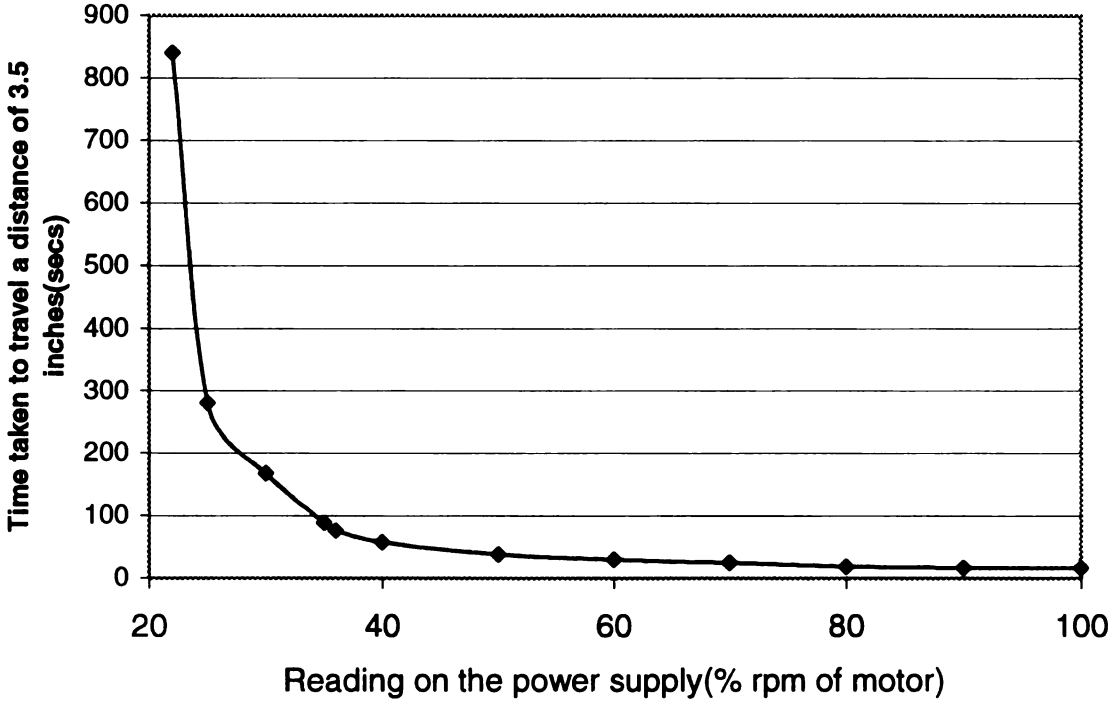


Figure 5.9: Calibration Graph of the Conveyor System

The ozone concentration used with the static treatment (1 sq. in. sample treatment in the closed chamber) was measured. The same concentration was maintained under the lamp for the dynamic treatment and the ozone concentration was kept constant for all the treatments. shroud of thin aluminum sheets was built

around the lamp in order to maintain the desired ozone concentration under the lamp during this dynamic treatment.

In order to measure ozone concentration, a Perkin Elmer Lamda 900 Spectrometer was used. Ozone has a very strong absorption at 254 nm. This property of UV light absorption by ozone at 254 nm was used to calculate the ozone concentration. The spectrometer measures the absorbance of ozone at 254 nm and from the Beer's law absorbance is directly proportional to concentration. The ozone from under the lamp is drawn into the spectroscopy cell using suction through teflon tubing. The flow rate of oxygen to the ozone generator is kept constant at 30 scfh in both the static and dynamic experiments. In static experiments a voltage of 50% V is used. At these conditions the absorbance of ozone is measured to be 0.0239. In the dynamic case, the voltage to the ozone generator is varied. Increasing the voltage increases the ozone concentration. It is found from the absorbance measurements that at 30 scfh oxygen flow rate and 75% V the ozone absorbance is approximately 0.0239 as in the static case.

Figure 5.10 gives the PATTI results for UV treated Hivalloy treated using the conveyor system. Three different adhesives are used. The black (dark) colored bars represent the PATTI results when Essex Betamate 73005 adhesive is used. The slate colored bars represent the PATTI results when Dow AH5643A (LESA) adhesive is used and the gray (light) colored bars represent the PATTI results when Ashland Pliogrip 7779 adhesive is used. The curing times of the adhesives are listed in the results section.

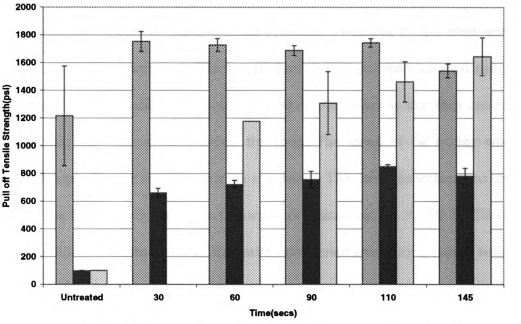


Figure 5.10: PATTI Results for UV treated Hivalloy using the conveyor system

Based on the above PATTI results, the 30-second treatment condition is chosen when Dow LESA adhesive is used to bond the valve covers. The 110-second treatment condition is used when Essex Betamate adhesive is used to bond the valve covers and the 145-second treatment condition is used when the Ashland Pliogrip adhesive is used to bond the valve covers.

5.4) Treatment of Valve Covers

Based on the PATTI test results, the optimum conditions for UV treatment of valve covers was determined. The lips of the valve covers were cleaned using isopropanol before the valve covers were placed on the trolley so that they can be passed through the shroud surrounding the lamp. The speed of the trolley was controlled depending on the treatment time required. The ozone generator was set at 30scfh gas flow and the setting on the ozone generator was set at 75% V. These conditions allowed the treatment of the entire valve cover emerging from the lamp area that was shrouded in aluminum foil.

Figure 5.11 shows the set up for UV treatment of valve cover.

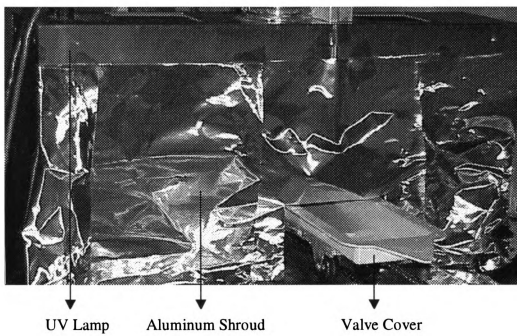


Figure 5.11: Set up for the UV treatment of valve cover

5.5) Bonding the Valve Covers

The UV treated valve covers are adhesively bonded together to so that they can be tested for enhanced adhesive performance. However there are certain problems in bonding them due to their shape. The valve covers have a bow shape that results from their mold. The bow shape is convex upwards i.e. the lips to be bonded bulge outward like a bow. Apart from poor surface adhesion, their bow shape makes it more difficult to bond the valve covers.

In order to fabricate specimens for adhesive testing, two UV treated valve covers treated at the same set of conditions were bonded to each other. Adhesive was applied to the bottom valve cover along its lip and was spread uniformly using a thin Teflon sheet. The lips of the top valve cover were aligned with the lips of the bottom valve cover and then clamped together. Small spacers were used to insure a uniform adhesive thickness. Uniform clamping force is maintained along the length of the valve covers during bonding by using aluminum bars as shown in the figure below. The aluminum bars are placed so that they align with the lips on the non-bonded side (reverse side) along the length and clamped. They are clamped at the location of each spacer. Figure 5.12 shows adhesively bonded and clamped valve covers.

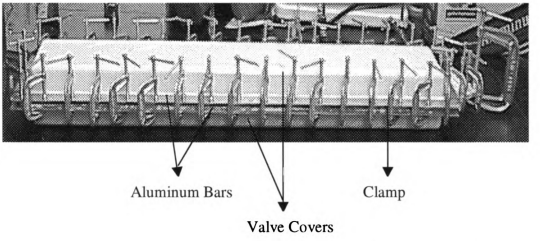


Figure 5.12: Valve covers adhesively bonded and clamped together

5.6) Testing the Valve Covers

The bonded valve covers are kept clamped for the curing time of the adhesive. The clamps are then unclamped and the aluminum bars are removed. The extra adhesive is trimmed off. The bonded pair of valve covers was cut into 2 inch sections transverse to its length resulting in 14 coupons for adhesive testing. These samples are numbered 1 to 14 starting from one end of the bonded pair of valve covers for all of the valve cover assemblies. These samples were tested in tension using the United SFM-20 testing machine manufactured by the United Calibration Corporation.

This machine is composed of two components – the load frame, where the actual testing of the specimen takes place and the console, which contains the computer to process and store data and control the load frame. The rate at which the load is applied can be controlled. The position of the crosshead is measured by an optical encoder. The crosshead speed and its position can be monitored. The load applied to the specimen is measured by a strain-gage type load cell. The strain imposed on the specimen may also be measured by an extensometer. These various measurements are collected by the computer and displayed graphically and tabulated numerically.

For testing the valve covers 1k (1000 lbs) load cell is hooked to the machine with its position under the crosshead. The crosshead speed is set at 1 inch/min. The bonded area is measured using calipers and entered in the computer. Numerical values of the maximum tensile load and maximum tensile

strength appear on the computer for each run. The computer also displays a graph between force and position for each specimen.

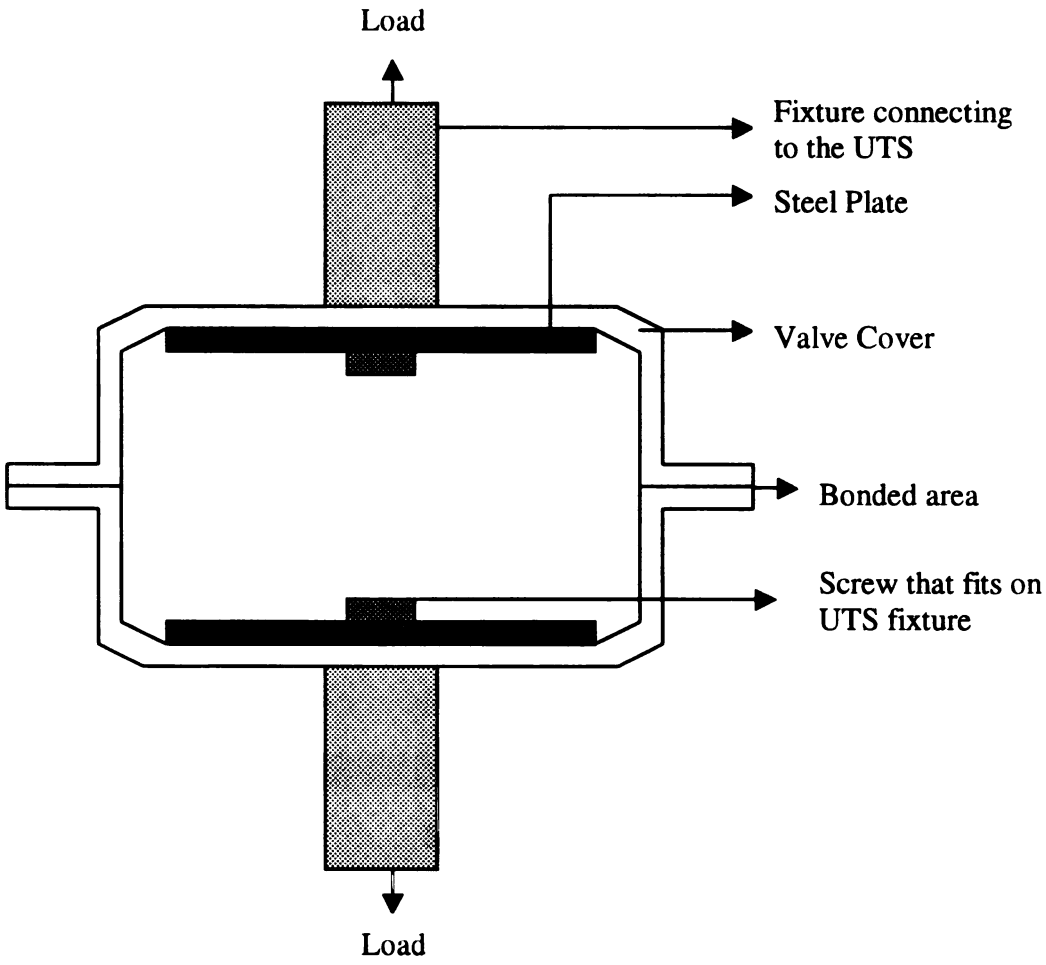


Figure 5.13: Schematic Representation of the UTS valve cover Specimen

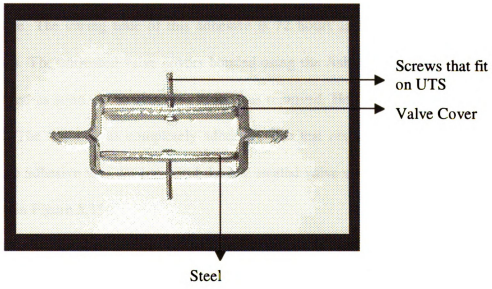


Figure 5.14: Picture showing the cut section of valve cover and the testing fixtures

5.7) Results and Discussion

The three different adhesives mentioned earlier, Ashland Pliogrip 7779, Dow AH5643A (LESA) and Essex Betamate 73005 were used to bond the valve covers and test their adhesive performance. The UTS test results when each of the above adhesives is used to bond the valve covers are provided in the following figures.

5.7.1) Ashland Pliogrip Adhesive: This is a two part Polyurethane based adhesive. The curing time of this adhesive is 72 hours and its work time is 15 minutes. The untreated valve covers bonded using the Ashland Pliogrip adhesive debonded as soon as the clamping force was removed. Hence, they could not be tested. The failure was completely adhesive. The test results when the Ashland Pliogrip adhesive was used to bond the UV treated valve covers valve covers are shown in Figure 5.15.

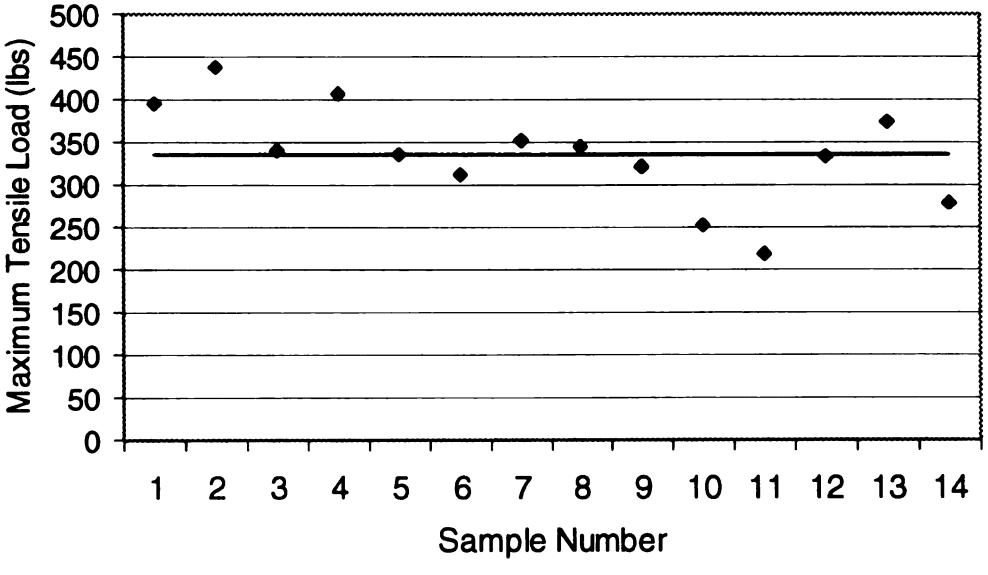


Figure 5.15: UV treated and adhesively bonded Valve cover test results; Adhesive used: Ashland Pliogrip

The average tensile load for the failure is about 335 lbs. All the failures are completely cohesive in the valve cover material. In order to confirm the results, the tests were repeated. The results of the repetition experiment are displayed in Figure 5.16.

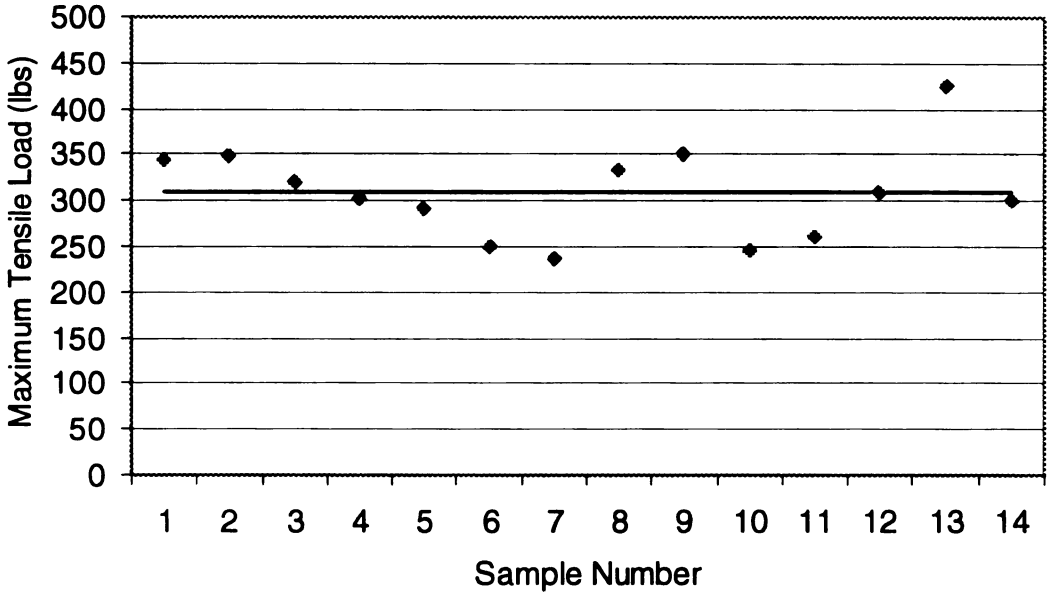


Figure 5.16: UV treated and adhesively bonded Valve cover *repetition* test results; Adhesive used: Ashland Pliogrip

The average maximum load for the repetition experiment is 308 lbs. All the failures again were cohesive and similar to the ones in the previous experiment. The confirmation results matched well with the previous results.

Upon visual inspection, the UV treated valve covers, bonded using the Ashland Pliogrip adhesive appeared to have failed cohesively in the valve cover material. To confirm this, the valve cover lip surfaces were examined using the ESEM. The lip surfaces of untreated and non-bonded valve cover, untreated and

bonded valve cover, UV treated and bonded valve cover and the adhesive were examined in the ESEM shown below.

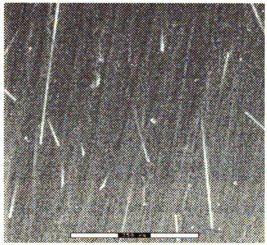


Figure 5.17: As Received (untreated and non-bonded) valve cover; Bar = 250μm

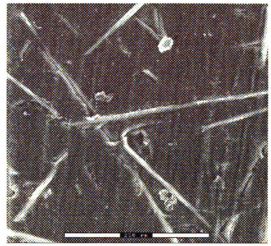


Figure5.18: Untreated and bonded valve cover; Bar = 250μm

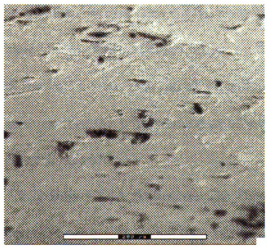


Figure 5.19: Cured Ashland Pliogrip Adhesive; Bar = 200μm

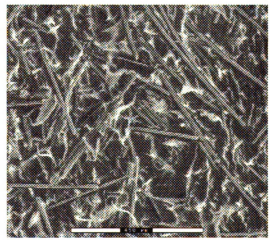


Figure 5.22: UV Treated and bonded valve cover; Bar = 450μm

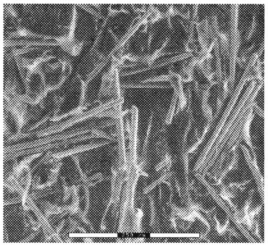


Figure 5.21:UV Treated and bonded valve cover; Bar = 250μm

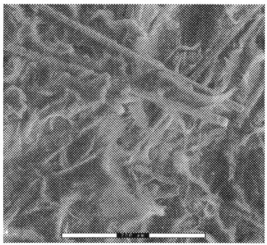


Figure 5.22: UV Treated and bonded valve cover; Bar = 200μm

It can be observed from the ESEM pictures that the UV treated and bonded samples have fibers pulled out to the surface from the bulk matrix. The cured adhesive also does not have any fibers in it. The as received samples do not have any evidence of fiber pullout on their surface. Since fibers are only present in the valve cover material, fiber pullout is taken as evidence of cohesive failure as a result of the improvement in adhesion following UV treatment of the valve cover samples.

5.7.2) Dow LESA Adhesive: The Dow LESA adhesive is an acrylic-based two parts adhesive. The curing time of this adhesive is 48 hours and the working time is 7 minutes. Untreated valve covers bonded with this adhesive failed before they were tested. The valve covers debonded as soon as the clamping force was removed. The failure mode was completely adhesive. The UTS test results for UV

treated and bonded valve covers using the Dow LESA adhesive are as shown in Figure 5.23.

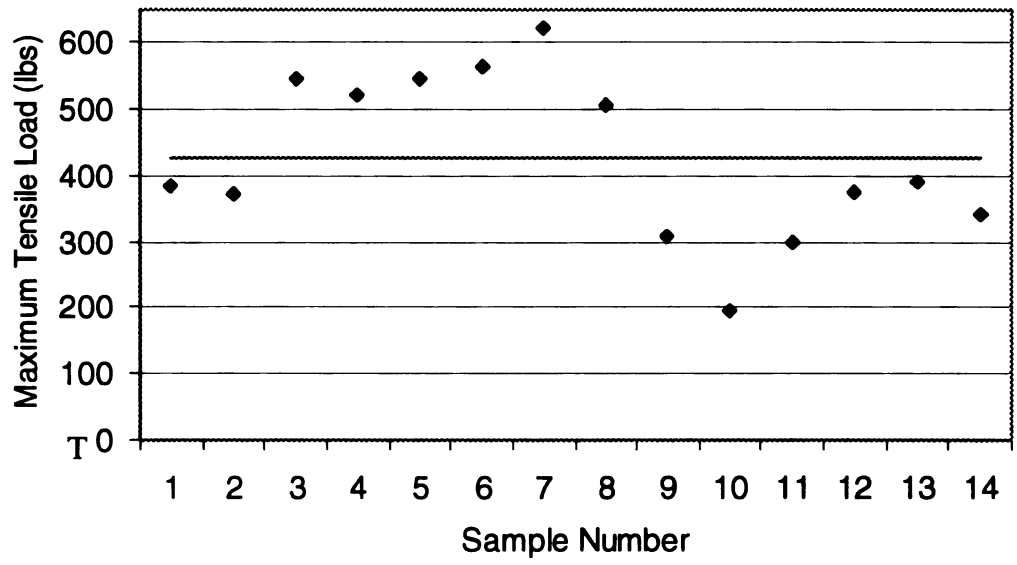


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Figure 5.23: UV treated and adhesively bonded Valve cover test results; Adhesive used: Dow LESA

average tensile failure load was 426 lbs. The failure in this case is not in the bonded area. The failure is completely within the material of the valve cover tearing either the top or bottom valve cover completely to failure. In order to confirm the results the experiment was repeated. The results are as shown in Figure 5.24.

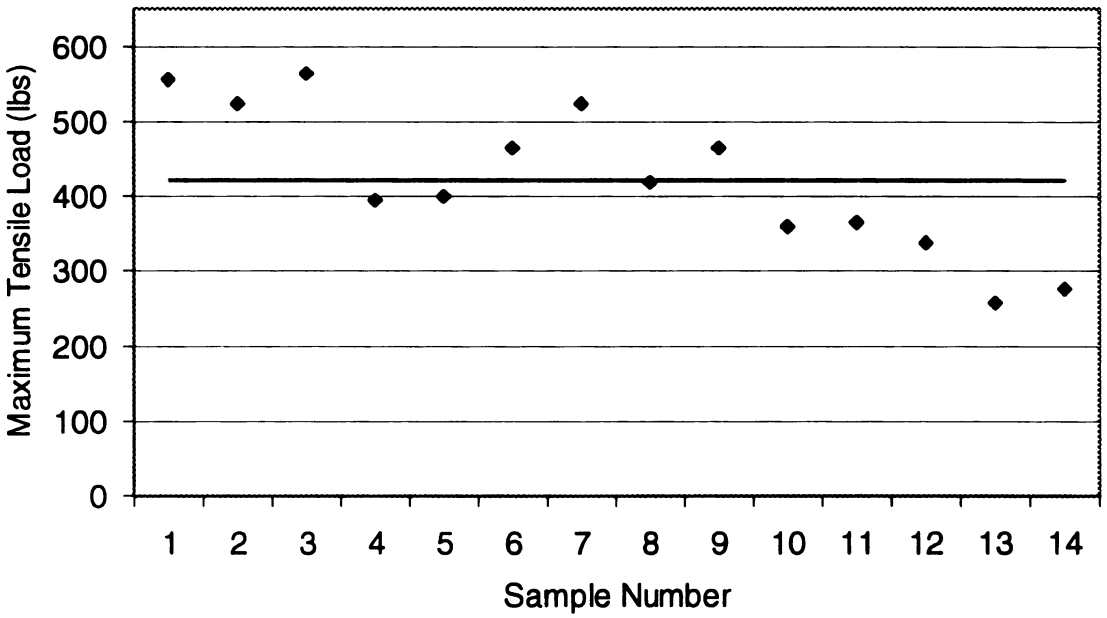


Figure 5.24: UV treated and adhesively bonded Valve cover *repetition* test results; Adhesive used: Dow LESA

The average tensile failure load for the repetition experiment was 421 lbs. The failure is exactly the same in both the experimental runs. The bonded area could not be disturbed and only a failure in the material of the valve cover could be generated.

5.7.3) Essex Betamate Adhesive: The Essex Betamate adhesive is a two part adhesive and has a curing time of 36 hours and a working time of 5 minutes.. Untreated valve covers could not be bonded with this adhesive since suffiecient adhesive was not available but from the PATTI results with this adhesive, it can be concluded that the untreated samples also have a very poor adhesion and that the untreated valve covers bonded with this adhesive would fall apart before

testing in the same manner as with the other 2 adhesives. The UTS results for UV treated and bonded valve covers using this adhesive are shown in Figure 5.25.

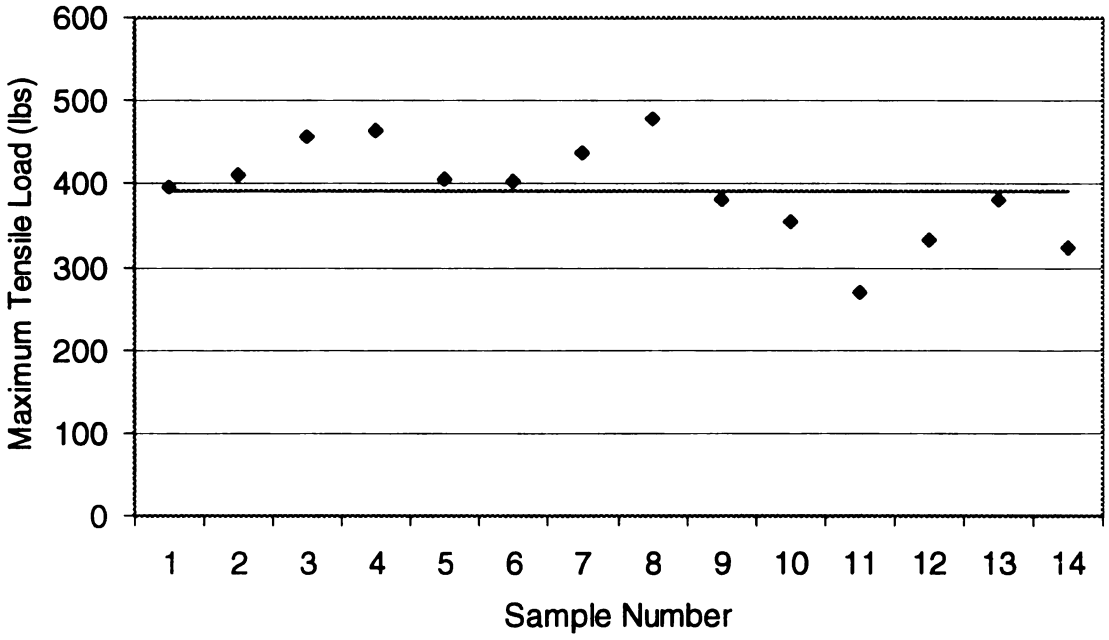
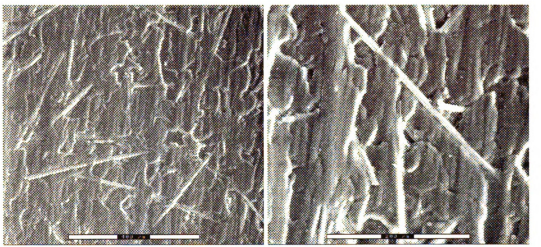


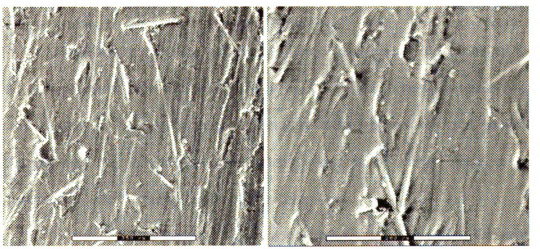
Figure 5.25: UV treated and adhesively bonded Valve cover test results; Adhesive used: ESSEX Betamate

The average load value was about 392 lbs. However the failure mode appeared to be adhesive to the naked eye. Inspection with the ESEM (as shown in Figure 5.27) does not suggest complete cohesive failure. For this kind of failure, the ~390 values of maximum load are very high and comparable to the maximum loads in the case where the failure was cohesive. This difference might be due to a difference in toughness of the adhesive itself. Therefore, as a qualitative comparison, the strain energies for all the three cases were computed for comparison. Strain energy values for each sample are obtained by calculating the area under the load-displacement curve. The area was determined from the

initiation of the loading cycle until the load reaches a maximum value in all the cases. The average strain energy values are shown in Figure 5.28.



Bar = 400μm Bar = 200μm



Bar = 350μm Bar = 200μm

Figure 5.26: ESEM pictures of failure surfaces when Essex Betamate adhesive is used for bonding

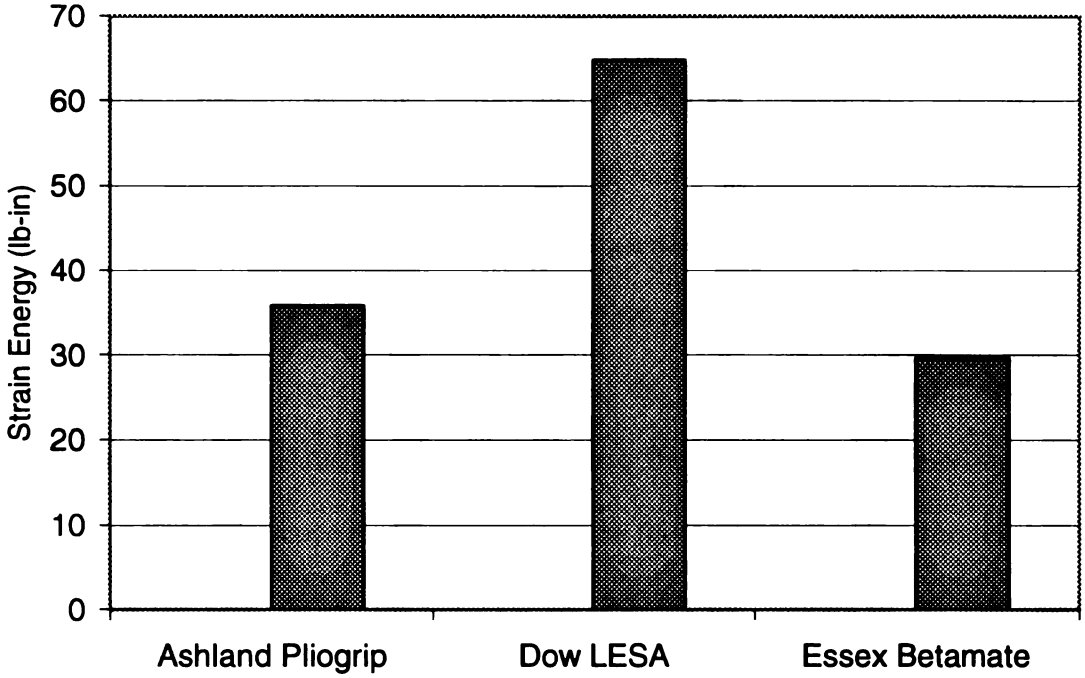


Figure 5.27: Strain Energy Comparisons of Valve cover test results using different adhesives

These results show that maximum average strain energy was produced for the case when the Dow LESA adhesive is used. Minimum average strain energy was obtained in the case when Essex Betamate adhesive was used and Ashland Pliogrip adhesive produced an intermediate average strain energy. These values are coincide with the failure modes of the three cases.

It was observed that at a particular position along the length of the valve cover, the adhesion is low in all the cases regardless of the adhesive used to fabricate the samples. The position is the location of samples numbered 10 and 11. To investigate this, the lips at the location of sample number 10 were examined using the optical microscope and compared with the sample located at position number 6. Sample number 6 is chosen because it required the maximum

load to debond in some cases. First the as received (referred to as non-polished surface hereafter) surfaces of the lips were observed under the microscope and then they were polished and looked under the microscope. The microscopy pictures are shown in the following page (Figures 5.29, 5.30, 5.31, 5.32).

It can be observed that non-polished sample number 10 has a more matrix rich surface i.e. it has a smaller amount of fibers on its surface when compared to the non-polished sample number 6. Whereas the polished samples numbered 10 and 6 appear to be the same and seem have the same amount fibers on their surface. This difference in the fiber content in this location could be the result of the how the valve cover was injection molded, i.e. the position of the gates and the resulting knit line producing a composite with different content and hence different properties than the rest of the valve cover, and could be the reason for the lower adhesion of the sample number 10 when compared to the other samples.

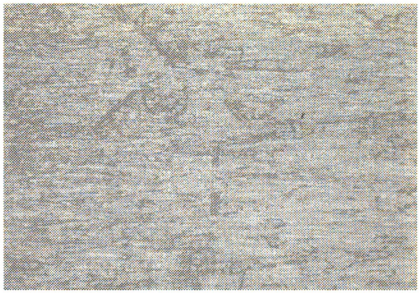


Figure 5.28: Sample Number 10 Non-Polished

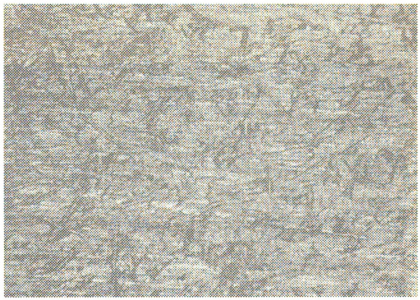


Figure 5.29: Sample Number 6 Non-Polished

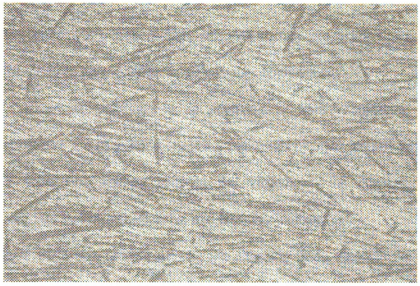


Figure 5.30: Sample Number 10 Polished

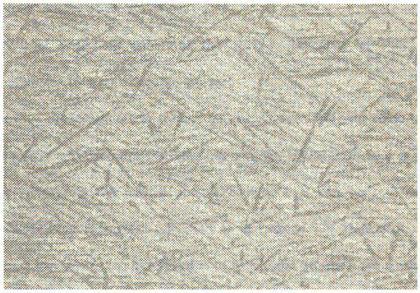


Figure 5.31: Sample Number 6 Polished

Chapter Six

Conclusions

1. Ultraviolet light treatment is an effective surface preparation technique for adhesively joining polymers and polymer composites.
2. UV treatment technique is an environment friendly method, with no emission or use of volatile organic compounds or other chemicals.
3. UV treatment method reduces the complexity of construction and operation, and is cost effective and less time consuming.
4. The PATTI results indicate that the adhesive bond strength between the polymer substrate and the aluminum stub is dependent on the UV light/laser treatment conditions.
5. The factors influencing the adhesive bond strength of the polymer are UV light intensity, treatment time, the environment surrounding the substrate and the nature of the substrate.
6. UV/laser treatment enhanced the surface adhesion of PET and PP composites by a considerable amount.
7. Further enhancements in surface adhesion were observed when the silane treatment was used in a combination with the UV/laser treatment.
8. On examining the ESEM and XPS results, it can be concluded that enhancement in surface adhesion a) in case of UV treatment using the lamps was due to the introduction of functional groups n the surface of the polymer and b) in case of laser treatment was due to the roughening of the surface by the laser.

9. UV treatment technique was successfully adopted to surface treat automobile valve cover panels, which have complex geometries in order to adhesively bond them.
10. UV treatment of the valve covers gave promising results indicating that this method is commercially viable. The failure modes changed from adhesive to cohesive after the UV treatment.
11. Though UV treatment is a very promising technique, there are certain challenges that need to be met before it can be used for commercial applications.
12. The process needs to be optimized for every material in terms of all the factors affecting the treatment. This at times could be a huge and time consuming task.
13. If a process window which can eliminate some of the treatment parameters basing on the physical properties of the polymer is developed, it can simplify the optimization process.
14. Industrial consumers, researchers and UV lamp manufacturers need to work together in order to design the lamps that suit a particular set of applications.
15. UV treatment has all potential to replace the existing surface treatment techniques.

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