Surface Treatment and Adhesion of APTIV® Film

Introduction

Untreated Victrex APTIV® films, made with VICTREX® PEEK polymer, have a low surface free energy, as with most polymer surfaces. The untreated film surface may therefore exhibit low bond strength with adhesives, printing inks etc. Surface treatment increases the surface energy of the non-polar PEEK surface. The optimum adhesion is obtained when the surface energy of the solid is greater than the surface tension of the liquid (adhesive/ink etc.) to enable the surface energy of the substrate to overcome the surface tension of the liquid in contact with it to enable good 'wetting' onto the substrate.

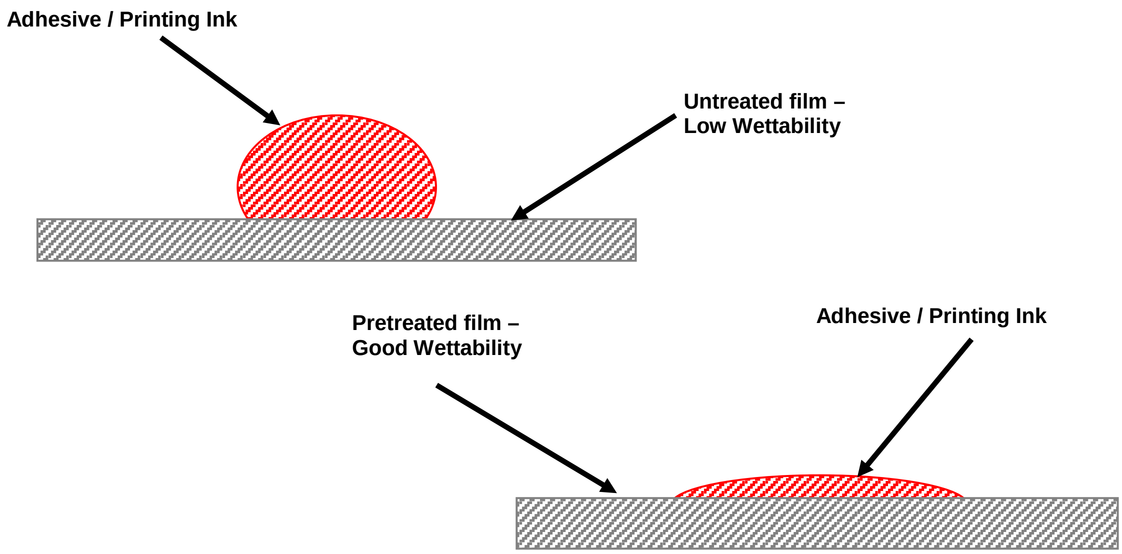


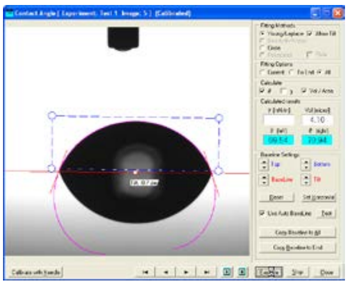
Figure 1 - Shows the Wettability of APTIV Film Surface.

The surface energy of untreated PEEK lies between 34–38 Dynes/cm^2 (mN/m), with surface treatments (plasma, corona etc.), this can be increased to ~60 Dynes/cm^2. The critical effect of most surface treatments is to increase the polar portion of the surface free energy, to provide active species on the film surface. These active species can act as sites for bonding to take place between the film and the adhesive/ink.

The surface energy required on the film surface should be the highest for adhesive bonding, with laminating and printing requiring lower activation levels. A surface energy of 55 Dynes/cm^2 should be high enough for all finishing processes encountered.

Verification of the presence of an activated surface can be made using Dyne test inks or Dyne test pens to ISO 8296 / DIN 53364 / ASTM D-2578 or by contact angle measurement (all methods are available from Dyne Technology Ltd., www.dynetechnology.co.uk). Dyne test pens are also available from Enercon Industries in the USA. The ink/pen method of determining surface energy is the most widely used, especially for production control and is simply applied. It has the advantage that the full width of a web can be tested in one application either using Dyne Test Pens or Dyne Test Fluids applied with cotton swabs. The surface to be examined is wetted with liquids of graduated surface tensions. The surface tension of the liquid that just adequately wets the film surface (uniformly distributed, not retracting into individual droplets) corresponds to the surface energy of the film. This method of surface energy determination should not be considered as a method for defining the (dispersive and polar functions of) energy of the surface and only gives the total. It is also possible to use the contact angle method to measure the surface energy, and has the advantage that it can be resolved into dispersive and polar components of the total surface energy.

Typical Contact
Angle Meter



Contact Angle
Meter Screenshot

Dyne Test Pen Method.
(material is at least 38 Dynes
but less than 44 Dynes)

Surface Treatment Methods:

Plasma, corona, flame and chemical etching methods work by implanting reactive species into the surface of the polymer film. Mechanical etching would appear to work by purely providing a mechanical key, however one theory suggests that part of the mechanism is due to the removal of weak boundary layers.

Victrex offers the option of Atmospheric Plasma Treatment on its APTIV film.

1. Atmospheric Plasma (APT)

Plasma is formed in a chamber by the application of a high voltage at a frequency in the radio/microwave region to a carefully controlled gas mixture. The use of inert carrier gases allows plasma processing to be done under atmospheric conditions. This plasma is then directed onto the moving film surface to give the required level of activation. The plasma consists of a mixture of highly energetic species – electrons, ionic species and ozone. Glow discharges produced by this method have a charged particle density approximately 100x greater than that of corona discharges. This gives the advantage of higher treatment levels and increased surface etching. Both of which will lead to an improved bond to the surface.

It is not possible to go into any great detail of the particular species formed on the film surface in this guide but plasma produces surface functionality (acid, ester, ketone groups), ablation (removal of portions of polymer chains) and cleaning of the surface.

Advantages of plasma vs. corona are:

- High treatment energy levels
- No reverse side treatment
- No pin holing in thin films
- Longer lasting treatment (see Figure 2 below). A plasma treated film was tested by Victrex over 120 days. Peel Strength (Adhesion of film to aluminium plate using epoxy adhesive) and Polar Component of film surface (Contact angle determination)

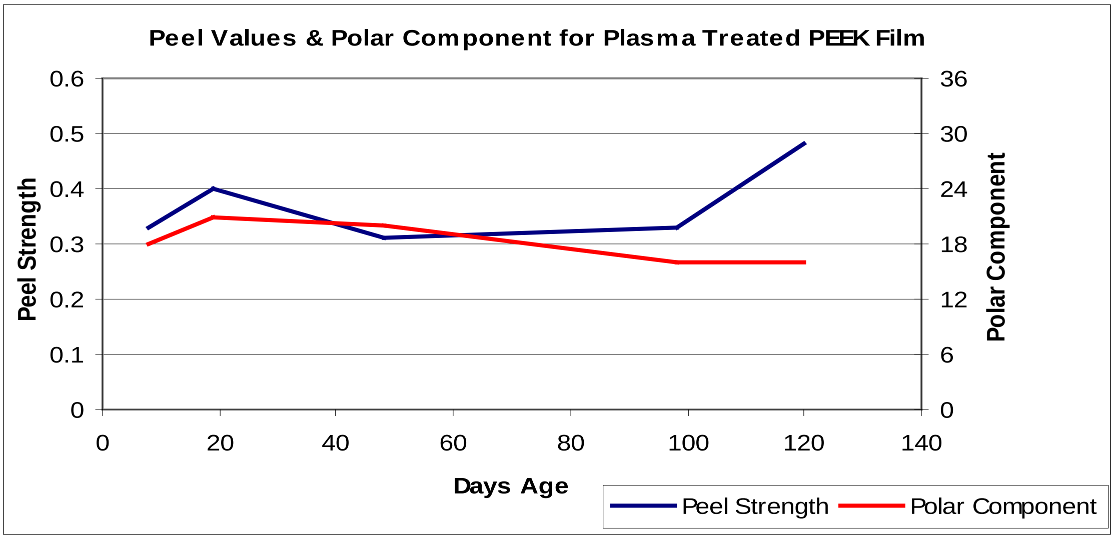


Figure 2 – Peel Strength (N mm^{-1}) and Polar Component (mJ m^{-2}) Ageing Over 120 Day Time Period

APTIV film can be treated with atmospheric plasma in a helium/oxygen gas mixture to greater than 55 dynes/cm.

Considerations for the use of plasma treated APTIV film:

- Optimum storage conditions are in a cool, dry environment away from strong light sources
- Do not handle with bare hands – moisture and oils/greases can compromise the treatment
- Victrex advises discarding the first few layers of film from the roll since additives from packaging materials can leech onto the film surface and compromise the treatment.
- Victrex place a shelf life of six months for plasma treated APTIV film but could be used beyond this, especially if stored in the recommended conditions. If using plasma treated film beyond the shelf life it is advisable to check the surface energy level by contact angle or dyne pen/ink methods.

2. Corona Discharge

Corona is a glow discharge, directed on to the film from an electrode placed in close proximity to the film surface. The frequency used is in the kilohertz region and the voltage is usually between 10 – 15 kV. The discharge takes place in atmosphere and the reactive species formed are similar to plasma treatment. It is the most widely used treatment in the plastic films industry.

Corona treatment gives good bonding for printing inks, for laminates and adhesives, however there are some disadvantages with corona. The treatment is not as robust as plasma and the surface energy value tends to fall off more rapidly than with plasma (see Figure 3). If the surface tension value falls below the demanded value, due to prolonged storage, the treatment can be repeated. In practice however, too many treatments and too strong a level of treatment can damage the film surface. High treatment levels tend to “break up” the surface producing low molecular weight material on the surface giving poor adhesion values to the adherent.

A secondary problem can be reverse side treatment, occurring if there is air trapped between the film and the roller acting as the second electrode. This results in undesired surface treatment, usually in patches, to the opposite side of the film being treated. This can cause on the reel blocking before and after printing with polyolefin films. This possible side effect can easily be eliminated by implementing simple maintenance and good cleaning procedures. Victrex does not have any experience of this effect with APTIV film but it could theoretically occur.

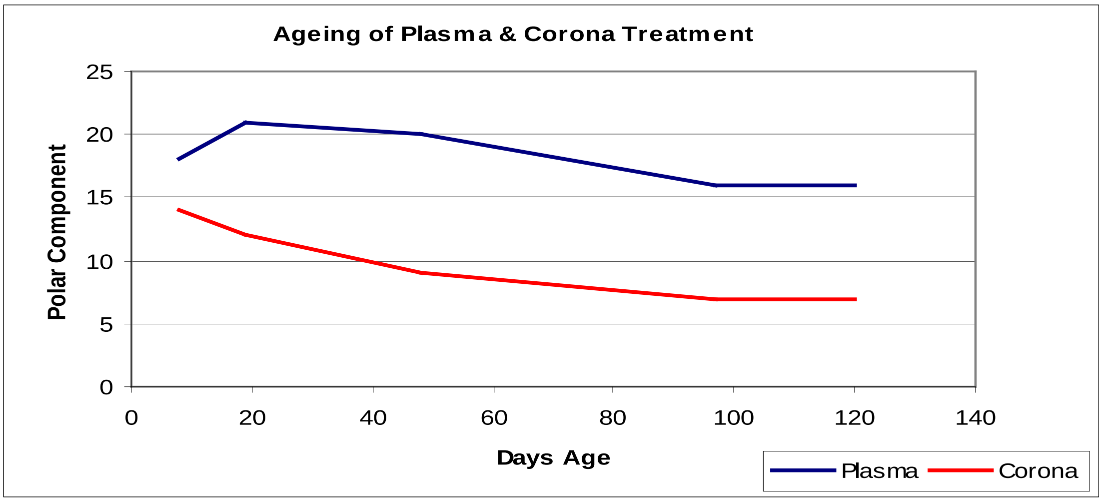


Figure 3 – Comparison of Plasma & Corona Treatment Ageing

Victrex has limited experience of corona treatment of APTIV film; however it is known to give acceptable levels of treatment for finishing processes.

3. Flame

This process is not often used in the film industry, except for specialist applications. The process is more suited to objects that have an irregular shape – it has been used extensively by the automotive industry for plastic mouldings e.g. bumpers.

It consists of running the film over an oxidising flame with a metal chill roll behind the film to prevent "burn through". The ambient flame temperature is approximately 1800^0C. This has the effect of oxidising and cleaning the film surface. The treatment is not as energetic as plasma or corona; hence the density of active species on the surface is not as great.

Victrex does not currently have any experience of flame treatment being used on APTIV film.

4. Mechanical Surface Roughening/Etching

In theory this is the easiest and most inexpensive surface modification available, however it can be time consuming and expensive due to the manual labour requirements. There are numerous options for mechanical roughening ranging from silicon carbide paper to sand/grit blasting. A good working practice is to degrease the film first (MEK/Acetone), apply the abrasive treatment and finally degrease to remove abraded material/abrasive. If sand/grit blasting, care has to be taken not to make any severe irregularities in the surface or leave any abrasive on, or in the surface. Both of these would prevent wetting by adhesives or inks etc.

5. Chemical Etching

PEEK is resistant to most chemicals, so the etchant has to be particularly aggressive. Classically oxidising mixtures are used. The most common and one that is known to be effective with APTIV film is a mixture of potassium chromate and concentrated sulphuric acid. (7g $K_2Cr_2O_7$ + 12g H_2O + 150g H_2SO_4). It is highly oxidising and corrosive and great care should be taken. Additionally there is the problem of disposal – chromium compounds are very toxic and there is strict legislation regards disposal of them. This method does require good control of the chemicals being used and management of the associated risks. Unless you are familiar and capable of dealing with such hazardous chemicals it may be best to refer to a specialist company for such treatments.

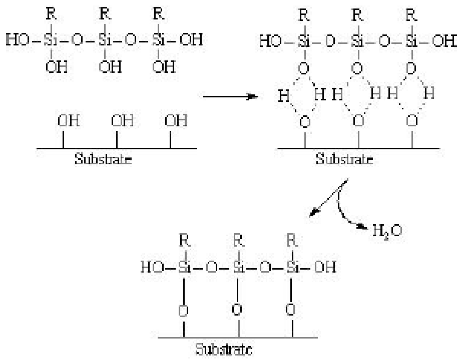
This method of surface activation gives a good surface activation to promote adhesive processes and has the advantage of the treatment not being constrained by shape.

6. Primers

Silane primers in particular may be used to promote adhesion between two non-bonding surfaces or to create a stronger bond than using adhesive alone. Whilst these primers are intended for use with silicone adhesives, they may also be used with other adhesive types, such as epoxies. The primers generally consist of one or more reactive silanes, a condensation catalyst and some type of solvent carrier. The reactive silane(s) typically have two different reative groups, one compatible with the substrate and the other with the adhesive. Some reactive groups may be hydrophilic like a silanol (Si-OH) group or hydrophobic like a 1-octenyl group. These different groups form a compatible interface between the substrates in order to promote adhesion. The reactive silanes are usually added as moisture sensitive alkoxy silanes and, in the presence of water and a condensation catalyst, form the priming surface by forming a very thin polymeric film on the substrate surface; the silanes begin to hydrolise with atmospheric moisture and the condensation catalyst begins to join all the hydrolised groups into a primer film on the substrate.

aptiv.

VICTREX® PEEK FILM TECHNOLOGY



In theory, the best primer film is a mono-molecular layer with the compatible groups facing the substrate and the organic groups facing the silicone adhesives surface. In reality, these mono-layers do not exist, but compatible bi or tri-layers do. This illustrates the importance of thin primer films and the necessity of solvent carriers in the primer formulation. Thick, overly primed surfaces tend to build chalky primer films that can be points of adhesive failure. Victrex has limited experience with primer/adhesive systems but in one particular case has seen a marked increase in bond shear strength by application of a primer in combination with a silicone adhesive.

Treatment of 3D Parts

In some cases customers may wish to bond parts made from APTIV film or indeed moulded PEEK components onto other substrates (e.g. thermoformed speaker diaphragm bonded to a voice coil). In such cases Victrex can supply treated film but the level of treatment could be compromised with exposure to elevated temperatures and other processing conditions such as moisture, release agents etc. Temperatures of around 100^{o}C with exposure time as short as one minute have been shown to have a significant effect on the surface free energy. To ensure the best results Victrex advises post treatment of 3D parts prior to any further bonding/printing etc. Generally lower power corona discharge equipment is recommended for treatment, especially for thin parts, as high power equipment (standard in many industries) can deform the part shape and, ideally, equipment with variable power control should be used in order to establish the optimum conditions. Victrex have proven this technology in conjunction with 'Dyne Technology Ltd'. who have performed corona treatment on intricate 3D parts which gave good results at the end user when compared with parts formed from APTIV film without post treatment. Post treatment of such parts can be arranged upon request. Contact Mr Chris Lines at Dyne Technology Ltd. for more information on available lab and industrial scale equipment at sales@dynetechnology.co.uk or Tel. +44 (0) 1543 411460 www.dynetechnology.co.uk .

Tantec Lab Scale Equipment for Treatment of 3D Parts Supplied by Dyne Technology Ltd.

Adhesives and Their General Properties

Listed below are the most common classes of adhesives and their general properties. Victrex is actively developing more knowledge on appropriate adhesive systems for APTIV film. It should be stated however that applications for PEEK film are varied and diverse; hence any adhesive application should be qualified by the customer for the unique conditions required by that application.

1. Epoxy

- Epoxies have a good gap filling capability, high strength, good temperature and solvent resistance.
- They are available in 1K (1 part) or 2K (2 part - resin + hardener) formulations: 1K must be heat cured, typically at temperatures between 150°C and 200°C; 2K system cures at room temperature but may be heat cured to increase strength and to speed up handling.
- 1K epoxy has higher cross link density than 2K epoxy, thus higher temperature and water resistance. The drawback may be increased brittleness unless rubber toughened.
- 2K epoxy needs proper measuring and mixing for desired properties; thus, 1K is easier to apply.

2. Acrylics

- Acrylics are flexible at ambient and elevated temperatures, but become very brittle at low temperatures.
- They have good impact, peel and shear strength.
- Their strength decreases rapidly at elevated temperatures.
- Their environmental durability is not as good as that of epoxies.
- Acrylics have a fast cure and a great tolerance with respect to proper surface preparation (degreasing, surface roughness)

3. Cyanoacrylates

These types of adhesives require a weak base chemical environment. In general ambient relative humidity is sufficient to initiate curing reaction. Use of a plasma/corona treatment can be problematic due to the fact that the slightly acidic surface of the treated film can retard the cure of cyanoacrylates. However, it is not thought that the final strength of cure is affected.

The extremely rapid cure of these types of adhesives ensures efficient production. Cyanoacrylates are manufactured in various systems and may be differentiated into subcategories:

- Methyl Cyanoacrylates – These are short molecular chained adhesives with nearly instant cure and a fairly high temperature resistance.
- Butyl Cyanoacrylates – These are adhesives with long molecular chains. They are suitable for bonding plastics which are likely to suffer from stress crazing.
- Ethyl Cyanoacrylates - This type of adhesive is temperature resistant to 100°C. Its inherent inner elasticity ensures durability and good ageing characteristics. Ethyl Cyanoacrylates are good for bonding adherents of different thermal expansion coefficients.
- Allylester based Cyanoacrylates can withstand a temporary temperature loading of up to 200°C

4. Urethanes

- The elasticity of urethanes is higher than that of epoxies or acrylics.
- Urethanes are of good toughness and flexibility which also remains at low temperatures.
- Their adhesion to polymers is generally better than that of other adhesives.
- The drawback of urethanes are poor environmental and temperature resistance, in particular their sensitivity to moisture.

5. **Silicones**

- Silicones possess good sealing properties for low stress applications.
- They have very high flexibility and water resistance.
- Show good heat resistance and are best suited to higher temperature applications with continuous use possible at ~200^{o}C and short term exposure up to ~250^{o}C.
- The solvent resistance is poor and some silicones can cure very slowly.
- Some silicones which are able cure rapidly at elevated temperatures can exhibit bubbling formed by outgassing during the curing stage. In such cases this can be prevented by application of pressure to the bond area or performing the curing under vacuum.

6. **Anaerobics**

- Anaerobic adhesives cure rapidly and enable easy automation.
- Although usually somewhat brittle there are flexible formulations for tough bonds available.
- High strength on some substrates may be achieved.
- Their chemical resistance is good, their temperature resistance poor.
- Anaerobic adhesives have a limited gap cure.

7. **UV Curing Adhesives**

UV curing adhesives have become increasingly popular in the manufacturing sector due to their rapid cure times and high bond strengths. They can bond dissimilar substrates and withstand high temperatures. They can also find uses in sealing and coating applications.

- UV curing adhesives exhibit rapid cure times in a matter of seconds or minutes compared to hours for some other adhesive types
- Less waste is produced since these are one component systems. The user only applies enough material to do the job.
- Extended work times are achievable with this type of adhesive as, unlike two component systems which have a set pot life, UV curing formulations can be used without time constraints.
- UV formulations do not contain hazardous solvents

Whilst PEEK based APTIV films do not generally show good long term resistance to UV radiation, some processors have had success using UV curing adhesives in their processes. Consideration must be taken with regards to the wavelengths of UV being used for the curing process as PEEK absorbs UVB & UVC but only partially absorbs UVA and UVV (UV Visible). Therefore Victrex would recommend using a UV cure source with wavelengths in the UVA/UVV region. Sources with lower wavelength UV (especially UVB & UVC) are higher energy and have the potential to damage/degrade Aptiv film. Please note that most photo initiators absorb in the UVA and UVB region so it is important to ensure the photo initiator in the formula matches the spectral output of the UV source lamp.

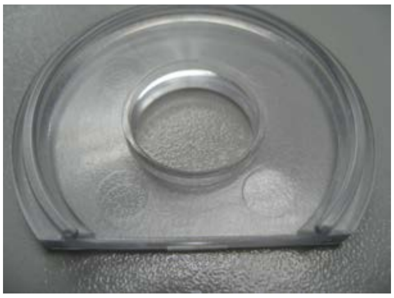
(UV absorption data for APTIV films can be provided upon request.)

The adhesives mentioned are listed according to their chemistry. Their properties are only to be viewed as being typical. For each system one can easily find adhesives with increased toughness, strength, elasticity, temperature resistance, etc. Adhesives may also be sorted according to their curing mechanism which may be anaerobic, heat cured, using relative humidity, activators or UV-light.

General information for UV curing adhesives processing with APTIV film:

- For best performance bond surfaces should be clean and free from grease or, ideally surface treated.
- Cure rate is dependent on:
    - Lamp intensity
    - Spectral distribution of the light source
    - Distance from light source
    - Depth of cure needed or bondline gap
    - UV transmittance of the substrate (or jig/fixture) through which the radiation must pass
- APTIV film should be checked for risk of distortion and yellowing when exposed to UV light. The minimum light intensity should be determined to avoid potential damage caused by UV.
- Consideration must be given to the fact that APTIV films absorb UV in the curing region of some adhesives and this will influence the choice of adhesive.
- If the UV light intensity is not sufficient to cure the adhesive, the recommended minimum intensity for cure (identified in the adhesive's datasheet & measured at the bondline) combined with an exposure time 2-3 times the fixture time should yield good results.
- To obtain full cure on a surface exposed to air, radiation at 220 to 260 nm is also required.
- Some situations may need a jig/fixture for positioning and locating the components. If the material of the jig (for example, metal) has no or poor UV transmittance, the UV light would be blocked. Therefore, a two stage cure process may be necessary for full cure. Alternatively a UV transparent material may be used to make the jig (e.g. Evonik PLEXIGLAS® GS or PLEXIGLAS® SUNACTIVE or, alternatively, PVF which exhibits greater UV transparency than PLEXIGLAS® SUNACTIVE).
- The curing machine is flexible i.e. changeable bulb positions, number of bulbs and cure time.

Metal jig



Transparent jig

Adhesive Systems Currently Used with APTIV Film

The list below shows just a small selection of adhesives that have been proven to work in applications utilising APTIV film. There are many more in used applications as diverse as electronics, acoustics, aerospace, automotive, industrial, oil & gas, chemical processing and others:

Grade Name	Adhesive Type	Supplier	Application
Araldite® F305 (Previously named Agomet F305)	Fast curing methacrylate	Huntsman	Acoustics
Med1-4013 & Med-161 primer	Silicone	NuSil	Food
Loctite 3106	UV curing acrylic	Henkel Locktite	Acoustics
Loctite 3108	UV curing acrylic	Henkel Locktite	Acoustics
Loctite 3321	UV curing acrylic	Henkel Locktite	Acoustics

Adhesive Systems Supplier Contact Information:

Company	Country	Contact	Phone	email
Huntsman Advanced Materials	UK	Stuart Thompson (Technical Support & Sales)	+44 (0)7747 476433	stuart_j_thompson@huntsman.com
Polymer Systems Technology	UK	Derek Williams Wynn (Technical Support)	+44 (0)1494 446610	dww@silicone-polymers.co.uk
Henkel Loctite	Hong Kong	Alex Siu (Sales Supervisor)	+852 (0) 9300 9487	alex.siu@hk.henkel.com
Henkel Loctite	UK	Ray Pateman	+44 (0) 7803 799 749	ray.pateman@henkel.com

It is important to note that there is no single adhesive system that will meet all KER's so choosing an adhesive system will strongly depend on the application. For example, if high strength is required one generally would choose an epoxy, however it has the disadvantage of lower flexibility. It is worth mentioning that some applications require adhesives which meet various specifications for military, automotive, aeronautical and medical applications. Choosing the proper adhesive requires precisely listing all requirements for the adhesive joint and then sourcing and engaging in dialogue with an adhesive supplier who can recommend the most appropriate products to meet these requirements.

PSA (Pressure Sensitive Adhesive) Tapes

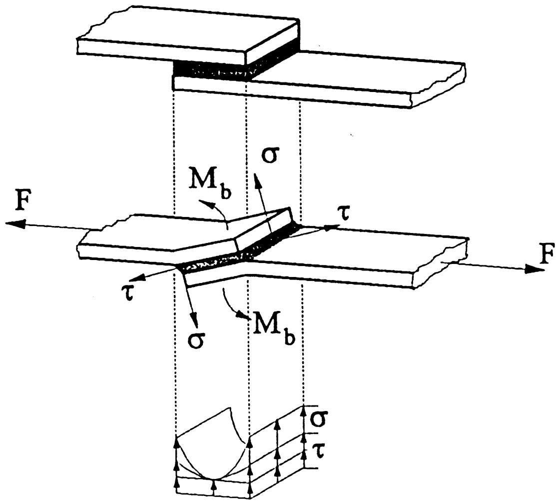
APTIV films are also available in an adhesive backed PSA tape format in a range of thicknesses (from 8 to 125µm) with either acrylic or silicone based adhesives. Several regional partners produce PSA tapes based on APTIV film.

APTIV PSA tapes compare to other high performance materials such as PTFE and polyimides but with added benefits. APTIV film possesses greater abrasion resistance, lower smoke and toxicity release, higher mechanical and dielectric strength, less permeability and lower density than PTFE. APTIV film also possesses improved chemical resistance, hydrolysis and barrier properties over polyimides. APTIV film can also be produced in a greater range of thickness, particularly <25µm. As such APTIV PSA tapes are ideally positioned for use in a wide variety of applications including wrapping, insulation, shielding and masking. Please contact Victrex to request samples of APTIV PSA tapes.

Adhesive Testing

Lap Joint - A Consideration for Testing

The geometry of a single lap shear joint is illustrated in the following figure which also shows the complex state of stress within the joint.



The upper picture shows two specimens which are bonded with an overlap. Applying a force F on either end of the shear joint will bend the sample as shown in the central part of the figure. Bending occurs since the point of application of F is not in line with the joint. Therefore we find a bending moment M_b leading to a tensile stress σ. The tensile stress by itself may be viewed as acting like a peel stress.

Further, the joint will show two components of shear stress τ. One part is due to sliding of two surfaces in shear, the other arises from straining the sample.

The sum of all these stresses gives a hyperbolic stress distribution as indicated in the bottom of the figure – it is not uniform

The tensile tester will show a force F which, divided by the overlap area, will result in a lap joint shear strength. The observed value includes effects of cohesive strength of the adhesive as well as the effectiveness of surface modification. Thus, this value is characteristic for the joint and not solely for the effect of surface modification. This may be a draw back for a fundamental study. However, we are not aware of a single test which allows testing the adhesion by itself.

The magnitude of lap joint shear stress depends on

- Joint length
- Joint width
- Thickness of adhesive
- Shape of fillet at end of overlap

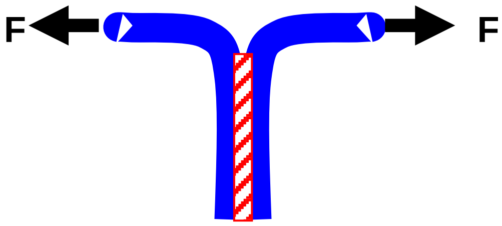
As well as on adhesive and polymer properties themselves, temperature, pull rate and grip length of tensile tester.

As illustrated the stress distribution shows peaks at either end of the bond length: the ends carry most of the load while the mid range carries only a fraction of it. Hence failure will occur at the ends of overlap first. If the bond width is increased the bond area at each end bearing the highest load is also increased with the result of a stronger joint. Increasing bond length does not have such a great impact.

The adhesive thickness is another variable. If the adhesive layer is too thin, e.g. <0.05mm, the bond area may not necessarily be wetted entirely which results in points acting as crack initiators. A thickness between 0.05mm and 0.3mm is commonly used since effects of shrinkage and inhomogeneous wetting are eliminated. If adhesive is much thicker than approximately 0.3mm the bond tends to fail cohesively.

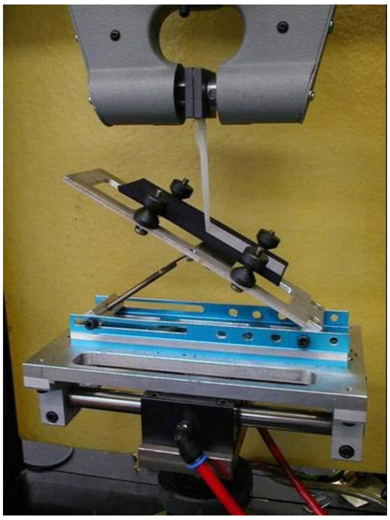
T-Peel Test

Another type of test is the "T" Peel.



This is a very popular test used to evaluate the durability of adhesively bonded systems. The popularity of the method can be attributed to the ease of use. Sample preparation and testing are straight forward – the specimen can be loaded into standard tensile test equipment. Peel resistance is defined as the average force per unit width, measured along the bond line that is required to separate the two adherend members of the bonded joint. The test has been shown to readily discriminate between various combinations of pre-treatments and adhesives, although coefficients of variation are typically about 30%.

A major disadvantage of the T-Peel test is that excessive extension of flexible adherends contributes to failure of the bond. This makes it a very severe test for polymer films.



Fixed Arm Peel Test Method

Detail of this test was developed and refined for Victrex by Intertek Measurement Science Group.

The basis of the test is the adherence of the PEEK film to an aluminium substrate, using an epoxy adhesive and peeling the joint formed using a tensile tester – see photograph below.

Initial tests showed that the epoxy-Al interface in some areas was weaker than the polymer adhesive interface. The adhesion between epoxy and aluminium was improved so that a consistent locus of failure between epoxy and the film was achieved. This was done by silane priming the aluminium surface.

Priming and bonding procedure is as follows:-

1. Aluminium is grit blasted, ultrasonically cleaned using acetone and allowed to dry.
2. Once dry, the aluminium was treated with a 1% 3-aminopropyltriethoxysilane solution that had been left to hydrolyse for 2 hours, using an almost dry brush. It is dried at 93^{0}C in a covered dish for 30 minutes.
3. Once cooled, the adhesive is applied in the required area, removing any excess. The film is then placed on the adhesive and the whole assembly is placed in a press. The press is bought up to pressure and the assembly is left overnight. Once removed the joint is allowed to condition for 3 hours at 23^{0}C and 50% RH before testing. Adhesive used was Araldite "Precision" Epoxy, which requires a room temperature cure.
4. The specimen was trimmed to 20mm width and the peel strength determined using an Instron 5565 with a 100N load cell and 5mm/min test speed.

About Victrex

Victrex is the world's leading manufacturer of VICTREX PEEK. The company is headquartered in the UK with dedicated sales, market development and technical specialists located around the world. These teams work hand-in-hand with processors and end users to provide assistance in new application development and prototyping together with product performance data and processing support.

Engineers and designers time and time again select VICTREX PEEK and the Victrex team to reduce system costs, improve part performance, exploit greater design freedom, and create a differentiated application.

By selecting VICTREX PEEK, customers gain not just one performance benefit, but a unique combination of chemical, wear, electrical, hydrolysis and high temperature resistance, as well as its excellent dimensional stability, fatigue, high purity, fire, smoke and toxicity performance. Victrex works with end users and processors in a variety of markets such as aerospace, automotive, electronics, food processing, industrial, defense, medical, and semiconductor.

Manufactured in the U.K. under a Quality System approved to ISO 9001 by Victrex plc,
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