Surface Treatment & Adhesion of APTIV™ Film

Introduction

Untreated Victrex APTIV™ films, made with VICTREX® PEEK™ polymer, have a low Surface Free Energy (surface tension), 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 tension of the non-polar PEEK surface. The optimum adhesion is obtained when the surface tensions of the contact partners are the same or as similar as possible.

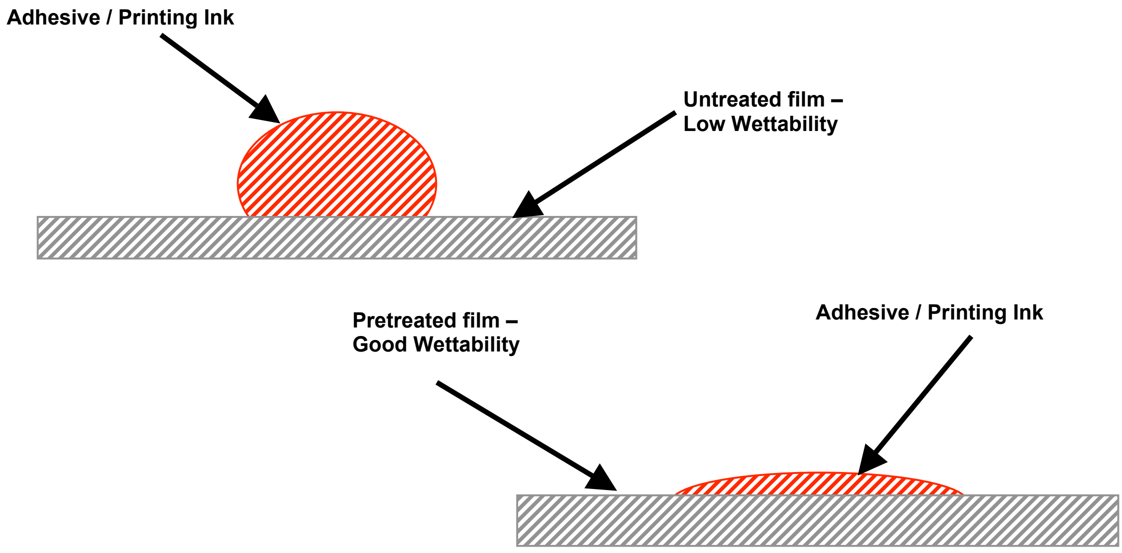


Figure 1 _ Shows the Wetability of APTIV film surface.

The surface tension of untreated PEEK lies between 34 – 36 dynes/cm, with surface treatments (plasma corona etc.), this can be increased to ~ 60 dynes/cm. 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 tension (surface energy) required on the film surface should be the highest for adhesive bonding, with laminating and printing requiring lower activation levels. A surface tension of 55 dynes/cm should be high enough for all finishing processes encountered.

Verification of the presence of an activated surface can be made using the ink test to ISO 8296 / DIN 53364 / ASTM D-2578 or contact angle measurement. The ink method of determining surface tension 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. 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 tension of the film. This method of surface tension 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 tension, and has the advantage that it can be resolved into dispersive and polar components of the total surface energy.

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 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 100 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 paper 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)

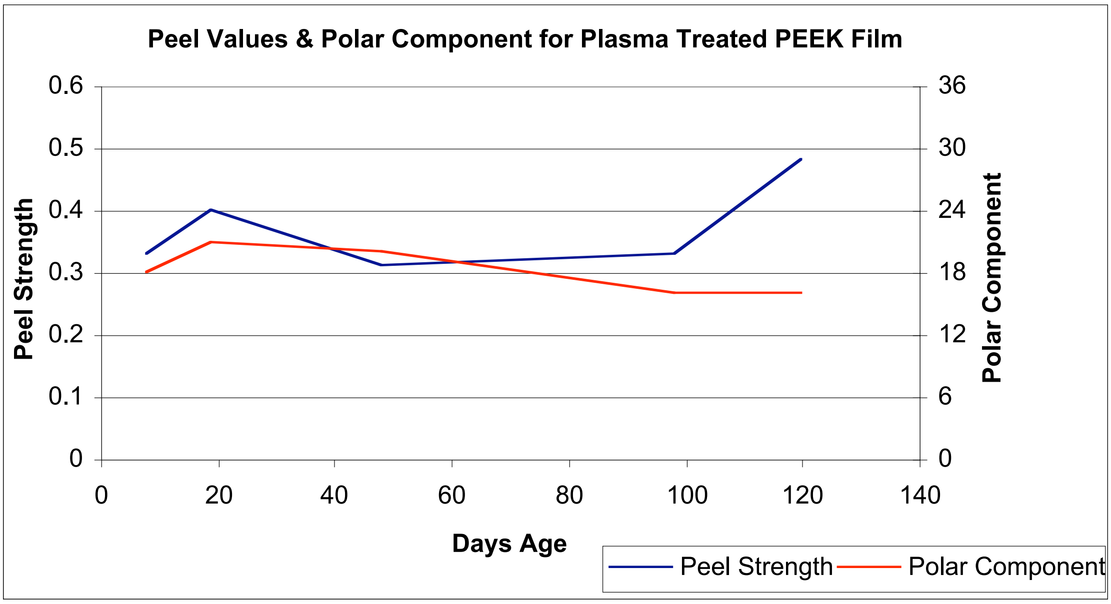


Figure 2 – Peel Strength ($N\ m^{-1}$) & Polar Component ($mJ\ m^{-2}$) ageing over 120 day time period

APTIV film supplied by Victrex is treated with Atmospheric Plasma in a Helium/Oxygen gas mixture to approximately 55 dynes/cm.

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 a 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 tension 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. Victrex does not have any experience of this effect with APTIV film but it could theoretically occur.

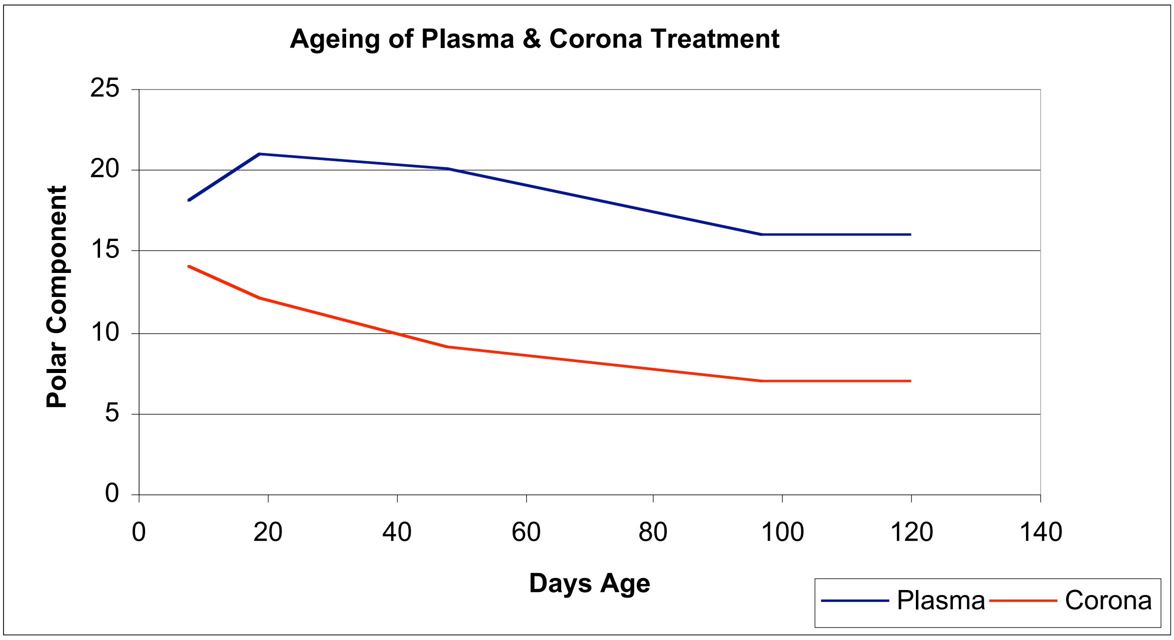


Figure 3 – Comparison of Plasma & Corona Treatment Ageing

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^{0}C. 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 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 (bonding?) key to further adhesive processes and has the advantage of the treatment not being constrained by shape.

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 basic 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.
- The solvent resistance is poor and silicones cure very slowly.

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.

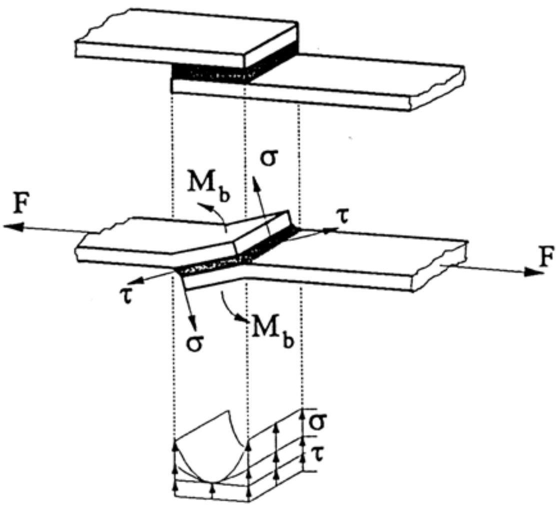
The adhesives mentioned are listed according to their chemistry. Their properties are only to be viewed as being typical. For each system one can easily find adhesives with increased toughness, strength, elasticity, temperature resistance, etc. Adhesives may also be sorted according to their curing mechanism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

It is important to note that there is no all purpose adhesive available so choosing an adhesive will strongly depend on its 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 an adhesive and supplier who can meet these requirements.

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

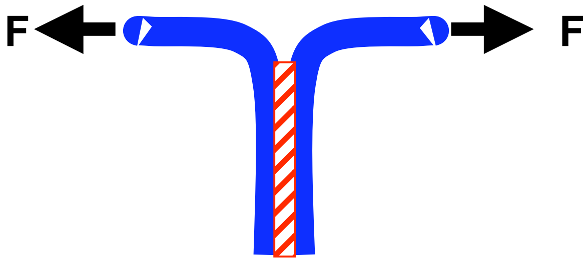
As well as on adhesive and polymer properties themselves, temperature, pull rate and grip length of tensile tester.

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.

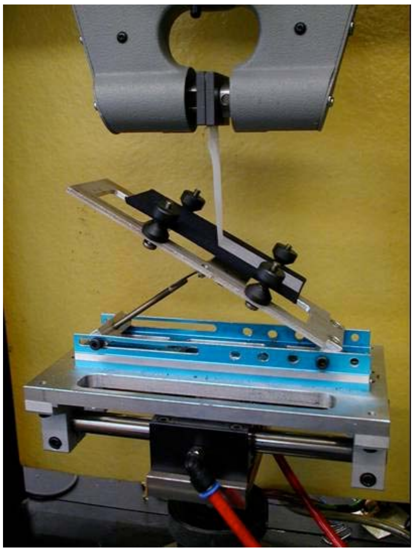


This is a very popular test used to evaluate the durability of adhesively bonded systems. The popularity of the method can be attributed to the ease of use. Sample preparation and testing are straight forward – the specimen can be loaded into standard tensile test equipment. Peel resistance is defined 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 ICI 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 93^0C 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
Victrex Technology Centre, Hillhouse International, Thornton Cleveleys, Lancashire FY5 4QD, England.