Surface Modification of PEEK™ Polymer

Adhesive bonding of many polymers often results in joints with poor joint strength. Reasons for this are low surface energy, poor spreading of the adhesive and high chemical resistance of some polymers; all of this applies to PEEK. Thus, adhesive bonding of polymers has been subject to numerous studies. Some of these are related to bonding of PEEK and will be shown here.

A basic requirement for successful bonding is spreading of the adhesive on the adherent or substrate (PEEK) which however is not necessarily sufficient. Spreading will occur if surface free energy of adhesive is lower than surface free energy of the adherent – this is not so for the combination adhesive / untreated PEEK: typical values of surface energy are 30 to 50 mJ/m for adhesives and 20 mJ/m for plastics of poor bonding properties. Since the surface energy of the adhesive can hardly be changed attempts are made to increase surface energy of adherent by employing different surface modification techniques.

1. Surface treatments and mechanical properties: a literature survey

Ian Griffiths has shown[1] that there a number of chemical reactions which change the surface chemistry of PEEK presumably enhancing adhesive bonding. All take place in vessels under very strict time-temperature-pressure conditions which are according to our opinion difficult to handle and not feasible to be used on an industrial scale. Therefore they will not be discussed any further and will not be considered for our experimental work.

Aside from these chemical reactions experimental results after surface roughening and surface etching, plasma, laser and corona treatment are reported in literature. The following summary gives results determined on VICTREX PEEK and compounds thereof as well as results determined with samples made of PEEK as supplied by other processors.

One has to be aware that these results have been gained using different experimental methods such as lap shear test, peel test, fracture mechanics etc., as well as different adhesives. The experiments also differ with respect to sample preparation: some samples have been injection moulded, others have been machined, sometimes the process has not been stated at all.

Consequently, *the results from the literature survey merely show that each technique has been found to improve adhesive bonding of PEEK; a conclusion as to what technique or adhesive would be superior can not be drawn*.

1.1 Mechanical surface roughening

Surface roughening is probably the most easy and inexpensive modification technique since costs for equipment are low. Plain roughening may be accomplished using a silica carbide paper or by sand or grit blasting. Either way, PEEK™ should first be degreased with MEK or acetone, roughened and then cleaned again in order to remove debris and grease. To enhance the cleaning action the use of a ultrasonic bath containing the solvent would be advisable. Induced surface irregularities should not be too severe since low viscosity adhesives cannot penetrate and wet extremely rough surfaces properly.

Surface roughening of PEEK 450G increased bond strength to values 4.6 times as high as without roughening. The maximum shear strength reported is 3.88MPa using an epoxy Araldite 2005 from Ciba. Other epoxies as well as cyanoacrylat, anaerobic and a silicon sealer showed lower bond strengths [2].

Surface roughening of a PEEK compound in combination with epoxy adhesives resulted in increased bond strengths with values between 9MPa and 30MPa [3] [4] [5]. Urethane and acrylic adhesives did not improve adhesion quite as well with this technique.

1.2 Surface etching

Etching by wet chemistry is something not everybody is keen of doing because it requires disposal of chemicals used.

Etching of carbon fibre filled PEEK has been done by Davies et.al. [5] who used a composition of 7g $K_2Cr_2O_7$ + 12g H_2O + 150g H_2SO_4 . Already after treatment times of 5s the failure locus moved from interfacial failure which is failure at the interface between adhesive and adherent to failure within the adhesive. A maximum lap shear strength of 30MPa was reached after treatment times of 120s or longer.

1.3 Plasma treatment

A cold gas plasma treatment is an important technology for surface modification which alters the surface chemistry of a polymer and, if held upright long enough, will also have an effect of surface roughening.

A plasma is simply spoken a gas which is excited by applying an alternating electrical field at radio or microwave frequencies to electrodes in a chamber under low pressure. These excited molecules will decay and excite other species. This 'soup' of excited species in a chamber – the plasma – interacts with the polymer surface in a dry chemical way forming a new surface layer. Typical gases used for treatment of polymers are air, oxygen, nitrogen, helium, argon and ammonia. It may be advisable to degrease samples prior to plasma treatment.

Lap shear tests on natural PEEK were performed on plasma treated samples using epoxy film adhesive AF-163-2K from 3-M [6], epoxy adhesive AV118 from Ciba [5] and epoxy adhesive Endfest 300 from UHU [7].

- Maximum lap shear strength obtained was 34MPa using oxygen as process gas.
- Strength increases with increasing exposure time.
- Using air, argon and ammonia as process gas were not quite as efficient.
- Effect of power and gas pressure were tested in peel tests. Tendencies may not be clearly stated for interaction of the parameters was found.
- Changing the adhesives mentioned above resulted in 34MPa, 34MPa and 14MPa maximum shear strength respectively. This must be considered with care since the parameters used in plasma treatment by different test houses are not identical.
- Storage of plasma treated samples for 10 days in air prior to bonding reduced the peel strength by 60%.
    ⇒ *plasma induced effects decay with time*

Plasma treatment seems to be an effective way to improve adhesive bonding of PEEK. Using air as process gas seems to result in slightly lower bond strengths as compared to other process gases. However, air is always available and thus easy to use.

One disadvantage of using plasma technique could be the low pressure condition which requires a chamber for treatment making plasma treatment a discontinuous process.

1.4 Corona treatment

The corona treatment is a glow discharge very similar to plasma treatment. Except for laboratory conditions it is usually operated in air at atmospheric pressure. In this case air between two electrodes is being excited by a high voltage power supply while the sample to be treated is placed between the electrodes.

PEEK was corona treated and bonded with UHU Endfest 300 [7] and epoxy AF-163-2K from 3M [8]. In both cases lap shear strength nearly doubled: from 3MPa to 5.6MPa and from 17MPa to 30MPa respectively.

Ageing air-corona treated samples for 30 days decreases strength slightly; using an ammonia gas the bond strength is unaltered even after 90 days of storage.
    ⇒ *corona induced effects decay* [9]

1.5 Laser Treatment

With laser treatments either a gas or a solid is excited to emit light of a particular wavelength. Typical gases and corresponding wavelengths are:

    XeF (351nm), XeCl (308nm), KrF (248nm), ArF (193nm), ArCl (175nm) and F_2 (157nm).

Wavelengths smaller than 175nm produce ozone so that closed chambers with extractors are necessary. Samples may be treated in air or in various gaseous atmospheres if a chamber is used. Usually lasers work at ambient conditions: air and atmospheric pressure.

PEEK was tested in lap shear experiments using an excimer laser with XeCl (308nm) [7]. The energy density used was above the ablation threshold (AS) meaning that the chemical modification of the surface was accompanied by surface roughening or ablation. In this case lap shear strength increased from approximately 3MPa to 18MPa.

Effects of Excimer laser treatments using ArF radiation (193nm) and KrF radiation (248nm) were investigated using a double cantilever beam specimen which has been tested in cleavage. In this case the result is a rupture energy [10] [11].

- Untreated samples showed poor rupture energies of 4mJ/m^2 (Ciba 2016: epoxy or polyurethane) and 200mJ/m^2 (AF 163 epoxy from 3-M). In this case, since test conditions were identical, the difference in values is indicative for the effectiveness of both adhesives. In both cases failure was interfacial – the bond was of poor quality.
- At both wavelengths and at energy densities below AS the surface becomes smooth due to a possible amorphization. This is ascribed to local heat up and quick cool down during laser pulses of short duration at high energy.
- Laser treatment below the ablation threshold (AS) always induced a strong increase in rupture energy. Interfacial failure gave way to cohesive failure (failure within the adhesive).
- Increasing number of pulses increased failure energy slightly.
- Using argon instead of ambient air resulted in a slight increase of failure energy.
- At energy densities above ablation threshold the failure energy increased only by a few percent as compared to working below AS.
- The ablation threshold (AS) is independent of the surrounding gas (oxygen, argon, air).

These results on laser treatment are based on modifications using an Excimer Laser. This is the type commonly used to enhance bonding and coating of polymers since solid state lasers allegedly don't have the same effect. This statement has been confirmed by many test houses we were talking to.

Yet, screening tests on PEEK with a Nd-YAG [12] laser which works above the ablation threshold at 532nm showed an increase in lap shear strength from 1.9MPa to 9.2MPa. This is an increase of nearly a factor 5. One of 3 values was even at 13MPa. Here the reference sample was roughened and acetone wiped.
A promising process using this Nd-YAG type laser for pretreatment has been developed by Ciba and is referred to as CLP-process (**C**iba **L**aser **P**re treatment). It involves the additional step of priming the surface prior to laser treatment; the nature of the primer is company secret.

1.6 UV-light
It has been shown[13] that UV treatment is an effective way to enhance adhesive bonding of PEEK. UV treatment employs 'light bulbs' emitting light at wavelengths between 172nm and 308nm. No mechanical testing has been reported. However, the study shows increasing oxygen content and decreasing contact angle which both are indicative for improved bonding properties.

Conclusions:
- All surface treatments improve adhesive bonding of PEEK
- It is not clear which modification technique would be superior to others
- It is not clear which adhesive is superior
- it seems like dry chemical modifications (plasma, corona, laser) are most promising.

2. Techniques to measure changes in surface properties

2.1 contact angle θ
As mentioned above one aim of surface modification is to enhance spreading of the adhesive which may be correlated to changes in surface tension. A common way to monitor changes in surface tension is to measured the contact angle θ of a droplet of i.e. water. Other liquids may also be used and should be specified since θ depends on the liquid used (and on other parameters).
In case of successful surface modification θ will decrease indicating better spreading of the liquid (adhesive) on the substrate (PEEK). This in turn is related to an increase in the surface tension or better bonding properties.

The contact angle of a droplet of water on untreated PEEK is typically 70°. Values of θ after surface treatment are reported to be in the order of 30° to 45° in case of corona treatment, between 10° and 40° for plasma modified samples and in the order of 60° for samples that had been treated by excimer lasers. Treatment by UV-light decrease the contact angle also.

2.2 XPS: X-ray photoelectron spectroscopy
Another effect of surface modification may be a change in surface chemistry by i.e. breaking chain bonds, introducing new elements or cross linking. These type of changes may be seen using XPS: here an X-ray beam hits the polymer and interacts with the innermost electrons of the atoms. This in turn will emit photoelectrons of an energy which is characteristic for the element. Measuring this

energy enables XPS to determine quantitatively the elements within the polymer's surface as well as their chemical state.

The chemical structure of PEEK depicts an O/C-ratio of 0.17 (17 oxygen atoms for every 100 carbon atoms). Measured O/C-values of untreated PEEK are between 0.16 and 0.2. After surface modification the O/C-ratio increases to values in the order of 0.3. The increased oxygen content increases the polarity which in turn is related to increased bond strengths. Depending on the gaseous environment other species like nitrogen may also be induced.

3. Adhesives and their general properties

The internet shows that there are several hundred suppliers world wide offering adhesives. Most of these suppliers offer various types and then again several modifications of each type. The most common types of adhesives and their general properties are listed below according to their underlying chemistry.

3.1 EPOXY
- Epoxies have a good gap filling capability, high strength, good temperature and solvent resistance.
- They are available in 1K or 2K (resin + hardener): 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.

3.2 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)

3.3 CYANOACRYLATES
These type of adhesives require a weak basic environment. In general ambient relative humidity is sufficient to initiate curing reaction. The extremely rapid cure of these type of adhesives ensures efficient production. Cyanoacrylates are manufactured in various systems and may be differentiated into subcategories:
- Methyl Cyanoacrylates
  are short molecular chained adhesives with nearly instant cure and a fairly high temperature resistance.
- Butyl Cyanoacrylates
  are adhesives with long molecular chains. They are suitable for bonding plastics which are likely to suffer from stress crazing.
- Ethyl Cyanoacrylates
  This type 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

3.4 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.

3.5 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.

3.6 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.
The Dymax corporation tested a series of UV-curing systems on PEEK [14]. These were urethane acrylates and urethane methacrylates as well as blends thereof (instant glues). A few of these showed good adhesion to PEEK as determined by the 'pick' test where the ease of picking a drop of adhesive off of PEEK was rated.

It is important to note that there is no all purpose adhesive available so that choosing an adhesive will strongly depend on its application. If high strength is required for example one generally would choose an epoxy which however has lower flexibility.
It is worth mentioning that some adhesives offered meet various specifications for military, automotive, aeronautical and medical applications.
Choosing the proper adhesive means to precisely list all requirements for the adhesive joint and then to go on and look for a supplier who can meet these requirements.

4. Final remarks

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[7].
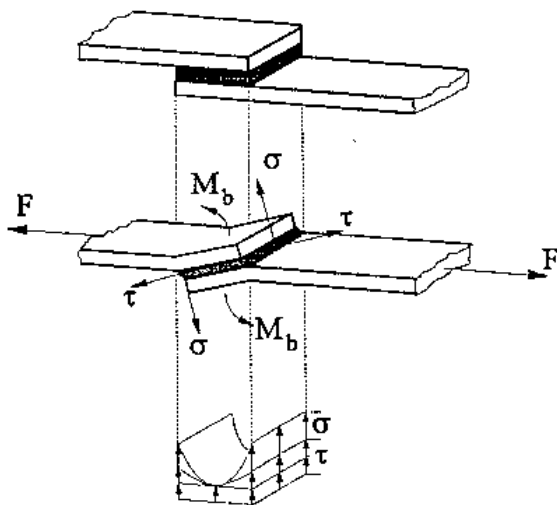
The upper picture shows two specimen which are bonded with an overlap. Applying a force F on either end of the shear joint will bend the sample as shown in the central part of the figure. Bending occurs since the point of application of F is not in line with the joint. Therefor we find a bending moment 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 has not such a great impact.

The adhesive thickness is another point of interest. 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.

There are no specifications pertaining to testing adhesive joints using polymeric substrates which would be useful for bonding injection moulded samples. All specifications deal either with adhesive bonding of metals or require machined samples. Machining polymeric specimen for bonding induces cracks which is the worst one can do for mechanical testing of polymers.

[1] Griffiths I.: internal report No VT0037, VICTREX.

[2] Provisional data sheet PK PD 11, ICI Petrochemicals and Plastics Division.

[3] Guha P.K., Epel J.N.: Adhesives for Bonding Graphite/Glass Composites; Adhesives Age (1979) 31-34.

[4] Stevens T.: Joining Advanced Thermoplastic Composites; ME, March 1990, 41-45.

[5] Davies P., Courty C. Xanthopoulos N., Mathieu H.-J.: Surface treatment for adhesive bonding on carbon fibre-poly(etherether ketone) composites; J. of Materials science letters 10 (1991) 335-338.

[6] Comyn J., Mascia L., Xiao G. Parker B.M.: Plasma-treatment of polyetheretherketone (PEEK) for adhesive bonding; Int. J. Adhesion and adhesives 16 (1996) 97-104.

[7] Zeiler T.: Oberflächenmodifizierung von thermoplastischen Polymerwerkstoffen in Hinblick auf die Verbesserung ihrer Verklebbarkeit; Thesis Erlangen (1997).

[8] Comyn J., Mascia L., Xiao G., Parker B.M.: Corona-discharge treatment of polyetheretherketone (PEEK) for adhesive bonding; Int. J. Adhesion and Adhesives 16/4 (1996) 301-304.

[9] Koleva, V.: verbal information; University of Elrangen.

[10] Laurens P., Sadras B., Decobert F., Arefi-Khonsari F., Amouroux J.: Enhancement of the adhesive bonding properties of PEEK by excimer laser treatment; Int. J. of Adhesion & Adhesives 18 (1998) 19-27.

[11] Sadras B., Decobert F., Arefi F., Amouroux J.: Enhancement of adhesion on polyether etherketone (PEEK) by excimer laser treatments; SPIE 2789 (1989) 305-313.

[12] Sandner P.: verbal information; Ciba Duxford.

[13] Mathieson I., Bradley R.H.: int. J. Adhes. Adhes., 16 Number 1 (1996) 29.

[14] DYMAX Corporation, Testing Report from Technical Service (1998)