ADHERIA®

Knowledge in bonding

Part 3

Characterization

November 2003

SUMMARY

1 - CHARACTERIZATION OF ADHEREND SURFACE

It is almost impossible to list all the factors that may affect adhesion of composite materials because of the broad spectrum of substrates that can be involved with adhesive bonds. Outlines of some contributions of FTIR (Fourier Transform Infrared Spectroscopy), ESCA (Electron Scanning Chemical Analysis), TOFSIMS (Time of Flight Secondary Ion Mass Spectroscopy), AFM (Atomic Force Microscopy) and contact angle techniques are mentioned here. With regard to an adhesively bonded joint wetting is a necessary condition, but only wetting isn't sufficient enough.

- FTIR (Fourier Transform Infrared Spectroscopy):

FTIR is based on the absorption of infrared light as it passes through the sample. The IR spectrum, i.e. the amount of transmitted energy as a function of wave number, is obtained.

- ESCA (Electron Scanning Chemical Analysis):

In ESCA (also know as XPS), the sample is bombarded with soft X-rays and the photoelectrons emitted are analyzed in terms of kinetic energy. For elemental surface analysis in the range of 1 to 5 nm, ESCA has proved to be very useful.

- TOFSIMS (Time of Flight Secondary Ion Mass Spectroscopy):

The sample is bombarded with primary ions of 15 to 25 KV; the generated secondary ions are extracted perpendicular to the sample surface before being deflected to the detector. Whereas ESCA involves characterization of a 1 to 5 nm surface depth and is mainly helpful in quantitave elemental analysis, TOFSIMS is suitable for surfaces <1 nm and gives information about the molecular structure of monolayers at the surface.
These two techniques complement each other quite well.

- AFM (Atomic Force Microscopy):

Surface roughness contributes to the adhesion of paints/coatings by way of interlocking. The level of surface roughness needs, therefore, to be controlled accurately. Atomic Force Microscopy is being increasingly employed for characterization in submicron range.

Characterization

- Wettability and contact angle

Wettability can be quantified in several ways. Methods include contact angle, goniometer, wettability pens, dyne fluids, droplet area measurement, etc.

Contact angle is a simple, rapid and widely used method to measure the wettability of a solid surface.

Contact angle meters are used to measure adhesion of liquids to solid or liquid surfaces, and to calculate surface energies or adhesion tension. The measurement of the contact angle formed at the point where a liquid contacts a substrate (liquid or solid) is called the "contact angle". The contact (tangent) angle formed between a "sessile" drop and its supporting surface is relative to the forces at the liquid/solid or liquid/liquid interface and can be used as a direct test specification or as a quality characteristic. Both direct (protractor measurement) and indirect (dimensional measurements and formulation) methods can be employed to obtain highly accurate and repeatable contact angle measurements.

2 - CHARACTERIZATION OF ADHESIVES CURE MODE

The strength and durability of bonded structures is a combined effect of interfacial and cohesive factors. Besides the interface, cohesive properties of adhesive bulk are very important.

The cohesive energy is determined largely by the molecular structure arising from careful curing of adhesives; cure reactions can be controlled by advanced techniques of thermal analysis.

- MDSC

DSC has been employed for more than two decades for investigating cure kinetics of various adhesives and coatings. With rising demands of high-performance adhesives, the resolution and sensitivity of this technique became inadequate.

MDSC (Modulated Differential Scanning Calorimetry), a recent modification of a conventional DSC, has gained importance by overcoming the limitations of the latter.

- DMTA

DMTA (Dynamic Mechanical Thermal Analysis) defines the state of cure and hence the molecular architecture by measuring modulus and mechanical damping or loss with respect to temperature and frequency.

- DETA/DEA

In the presence of polar groups in the adhesive materials (e.g. epoxy end PU), this technique has proved to be the most sensitive of the three techniques mentioned here.
A sinusoidal electric field is applied to the sample and the electric displacement followed.
DETA (Dielectric Thermal Analysis) is very sensitive for detecting moisture absorption at the interface and in the polymeric bulk material.

3 - CHARACTERIZATION OF THE ASSEMBLY

3 - 1 Stresses of adhesively bonded joints and long-term resistance (durability)

3-1-1 Stresses of adhesively bonded joints

Adhesively bonded joints are mostly subjected to (b) peel-, (d) tension-, (a) or (c) shear-, torsion- or pressures stresses (figure 1.1)

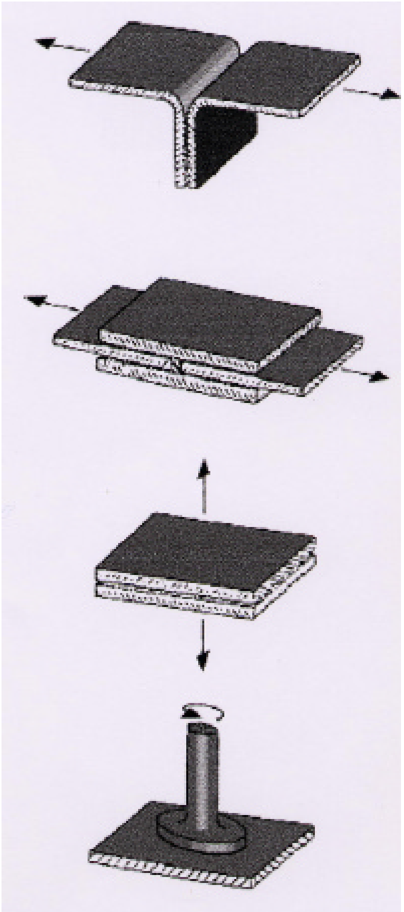

Figure 1.1: Kinds of stresses an adhesively bonded joint may essentially be subjected to

Peel stresses because a high stress of the adhesive in the joint that nearly has got the form of a line. They exceed the inherent strength of the adhesive several times. Therefore peel stresses within an adhesively bonded joint have to be avoided by all means.

The tension stresses take place vertically to the surface that is bonded. Such stresses aren't as important as peel stresses that were mentioned above but because of the shear strength of the materials to be bonded normally being higher it is impossible to exploit the strength of the adherends with butt adhesive bonding because of constructive reasons.

Adhesive bonding represents an extensive joining method. Therefore adhesively bonded joints must be designed to shear. The disadvantage of the relatively low shear forces that can be transferred is constructively compensated by an appropriate increase of the surface to be bonded.

The torsion stress of rotationally symmetrical surfaces to be bonded can be compared with shear stresses. Adhesives are insensitive towards pressure stresses (loads).

3-1-2 Long-term resistance

The resistance of connections that were conventionally joined is nearly exclusively designed by mechanical aspects. These aspects may not be neglected with adhesively bonded joints. Besides this there are also environmental conditions influencing the adhesively bonded joint.

Long-term influence will change the strength properties of these material compounds over the years. They are normally caused by exterior influences such as e.g. temperature, humidity or even stresses (loads). The following kinds of influences have to be observed more closely:

- Water absorption and strength,
- Water absorption and adhesion,
- Corrosion of the material of the adherend,
- Mechanical load.

- Water absorption and strength

The penetration of humidity into the adhesive represents that kind of influence that is mostly known. This behaviour is known of other plastics. The water diffuses into the material (in this case: adhesive) and is absorbed there. Because of this it is easier to deform the plastics. The adhesive is rendered flexible favourably influencing the strength behaviour. This is a disadvantage concerning long-term, static stresses. The penetration speed of the water into the joint, however, is low. Nevertheless, this effect mustn't be neglected.

- Water absorption adhesion

The humidity often has damaging effects on the adhesion in the interface between adherend and adhesive. Therefore it is absolutely necessary when testing adhesively bonded joints not only to consider the strength behaviour but also to analyse the appearances of fracture (adhesion fracture, cohesion fracture, corrosion, adherend fracture). In this way an adhesion fracture indicates that the adhesion between adhesive and adherend must be improved.

The reduction of adhesive forces normally represents a process also taking place slowly. This process is run by the slow penetration of water into the adhesive.

- Corrosion

The corrosion of the adherends is closely connected with water absorption of a metal bonding. Corrosion causes a quick failure of the adhesively bonded joint. Therefore it is very critical. It often takes place very quickly, especially in cases when not only water but also other materials supporting corrosion can attack the adherend or if those materials are part of the adhesive itself. In many cases, however, this influence can be controlled by protecting the complete adherend, especially the surfaces to be bonded of these adherends.

- Mechanical load

Adhesively bonded joints can also be influenced by mechanical loads. But they can only be influenced in this way if a certain load level is exceeded. Such an exceeding, however, can constructively be avoided. Then the adhesive creeps, that means it leaves the admissible limit. By doing so, micro-crackings are formed within the bond line.
These micro-crackings are irreversible. The same is true with dynamic loads.

Mechanical, static and dynamic loads also influence the absorption of humidity. If a certain load level has been exceeded a higher diffusion speed has to be assumed. This has already been proved by tests carried out with epoxy resins.
The maximal concentration of absorbed water also increases considerably. This fact can be put down to the formation of micro-cracking. Therefore ageing processes take place more quickly in adhesively bonded joints that aren’t loaded.
By all means the influences caused by properties of the coating materials also have to be taken into consideration at this place.

3-1-3 Summary

The research of adhesive interactions is an essential part of the application of the adhesive bonding technology in the future. The comprehension of interactions between adhesive and surface of the material make specific optimisations possible. Therefore the basic examinations have to be judged as being orientated to application because they serve as specific improvements as described above.

The same is true with long-term influences of an adhesively bonded joint. The mechanisms that have been demonstrated cause the necessary comprehension and make it possible for the applicant to use certain measures so that he can design the service life of an adhesively bonded joint in an appropriate way.

3 – 2 Testing of adhesively bonded joints

Several standard test methods exist for characterizing adhesives and bonded joints:

- American (ASTM)
- British (BS)
- French (AFNOR)
- International (ISO)
- German (DIN)
- European (EN)
- Other specifications from industry
- Military Industry
- Aerospace
- Automotive
- Electronic
- Other

3-2-1 Destructive tests

- Lap shear tests

The lap shear tests defines the bond strength of single-cut overlapped adhesively bonded joints when the adherends are loaded by tensile forces that are directed to the bonded area.

- The floating roller peel test

The floating roller peel test determines the resistance of adhesively bonded joints against peeling forces. The test is mostly used when adhesives and adhesively bonded joints have to be evaluated in a comparable way or when methods of surface pre-treatment shall be controlled.

- The angular peel test

The angular peel test also determines the resistance of adhesively bonded joints against peeling forces. The test is mostly used for a comparable evaluation of adhesives and adhesively bonded joints as well as for the control of surface pre-treatments.

The 90° offset, adhesively bonded sample having the form of a “T” is loaded at its arms that haven’t been bonded until the bond line breaks and both halves of the sample are separated of each other. The force that is necessary for doing so is recorded in a peel diagram. At the same time the change of length between the fixing heads is measured.

- The wedge (penetration) test

In order to carry out a wedge (penetration) test two sheets with a specified thickness that have been pre-treated at manufacturing conditions are adhesively bonded. A wedge is driven into the adhesively bonded joint. The crack peak is marked and measured.

- The bending peel test

When using the modified bending peel test for plastic-metal-compounds the surface of a plastic sample is adhesively bonded with the surface of a steel sample. Partly, a folio that isn't bonding is put between the adherends in one direction. Samples without a folio can also be adhesively bonded if the bulge of the adhesive is removed of the front edge of the steel sample.

- Compression shear test

The compression shear test is used in order to determine the shear strength of mostly an aerobically cured adhesive and in order to carry out a comparable evaluation of their shear load.

3-2-2 Non-destructive test methods

The manufacturing control isn't always sufficient because the tests are carried out with control samples and not with the real product. This fact inevitably causes the incompleteness of this test method because the strength of the samples doesn't reflect the strength of the adhesively bonded element by all means. Therefore non-destructive test methods for adhesively bonded joints have been developed.

The main techniques used include:

- ❑ Ultrasonics:
    - C-Scan widely used to locate disbonds. More sophisticated techniques include data from A and B-scans, and signal processing.
    - Lamb waves (leaky) for interfacial investigation.
    - Acousto-ultrasonic, a relatively new technique which shows some promise for qualitative assessments of bond strength

- X-Radiography,
- Holography,
- Thermography,
- Acoustic Emission.

- Visual control

For initial assessments, visual inspection and coin tapping are used. These can provide subjective evidence, particularity in detecting the presence of gross defects such as delaminations, debonds, and severe core damage in sandwich panels.

- Ultrasonics

C-SCAN

The technique is particularity suited for identifying delaminations, debonds and cracks. Voids and porosity are also detectable.

LEAKY LAMB WAVES (LLW)

This technique uses two transducers in a “pitch-and-catch” arrangement placed at an angle. The probes and test piece are immersed in water, or a water column is maintained between the probes and the part surface.

ACOUSTO-ULTRASONIC

This is a relatively new technique which combines ultrasonic and acoustic emission probes. Repetitive ultrasonic pulses are injected into the test piece by a broadband ultrasonic transducer. A receiving acoustic emission sensor is placed on the same side of the specimen to intercept propagating stress waves.

- X Radiography

X-Radiography is used for the volumetric NDT of components. An image is formed on a photographic film or electronic detector following differential absorption of X-ray energy by elements present in the component. Low energy or “soft” X-rays (a few tens of keV) are used for composites, compared with 50-150 keV for metallic sections.

Characterization

- Acoustic emission

Acoustic emission is a technique which may indicate the significance of a defect without identifying its nature. AE may be regarded as not truly non-destructive, in that emissions are generated by failure mechanisms within a structure. However, proof and qualification tests are carried out on structures before they are put into service.

- Holography

The monochromaticity and coherence of laser light allow holograms to be produced, storing reflected intensity and phase information from the sample.
In testing, a hologram of the component or structure is produced. This is then used to project a holographic image onto the subject in exactly the same position in space.

- Thermography

Thermographic techniques can be appropriate for inspecting entire structures provided the facilitities and experience are available. All types of thermography require some means of creating a surface temperature distribution which correlates in some way with the integrity of the structure or the defect population.