Synopsis

The drive to improve performance of coatings and composites in automotive, electronics and aerospace applications is a never-ending story. This implies an extremely accurate and reliable characterisation of the substrate-surface and the polymeric coating materials . In order to have a durable adhesive bonding between the polymeric coating materials and the substrate, a pre-treatment of the substrate is required in many cases. Corona /plasma pre-treatment of the substrate and the use of coupling agents like organosilanes are well accepted recent methods. Advanced surface analytical techniques like ESCA and TOFSIMS are proving to be extremely helpful in the chemical characterisation of the substrate surface. Contamination on the substrate is one of the most serious enemies of adhesive bonding and the above mentioned techniques are playing a vital role in combating the enemy.

Modern thermal analytical methods have made tremendous contribution to the development and quality control of high-performance polymeric coatings / composites. MDSC, DMA and DETA are proving to be very useful tools for the characterisation of high-performance coating materials. An in-depth understanding of the structure-property relationship of these materials, predominantly epoxy and polyurethane coating systems, is a pre-requisite for their successful application and subsequent quality control.

Introduction

Polymeric coatings are the result of an arranged marriage between two different materials – an organic or an inorganic substrate and a polymeric resin - which form adhesive bonds with each other. The quality and durability of a coating is directly related to the nature of adhesion. Chemists tend to associate adhesion with the energy liberated when two surfaces meet to form an intimate contact termed as an interface. In other words, adhesion may be defined as the energy required to dismantle the interface between two materials. Physicists and engineers usually describe adhesion in terms of forces, with the force of adhesion being the maximum force exerted when two adhered materials are separated. There are many theories regarding the mechanism of adhesion – such as adsorption (van der Waals forces), electrostatic, diffusion (entanglement of polymers with a substrate), chemical bonding , mechanical interlocking etc. – all of which may play a significant role in interfacial bonding. The energy required to separate the adhesive (coating) and the substrate is a function of the adhesion level i.e. interactions at the interface, but it also depends on the mechanical and viscoelastic properties of the materials.

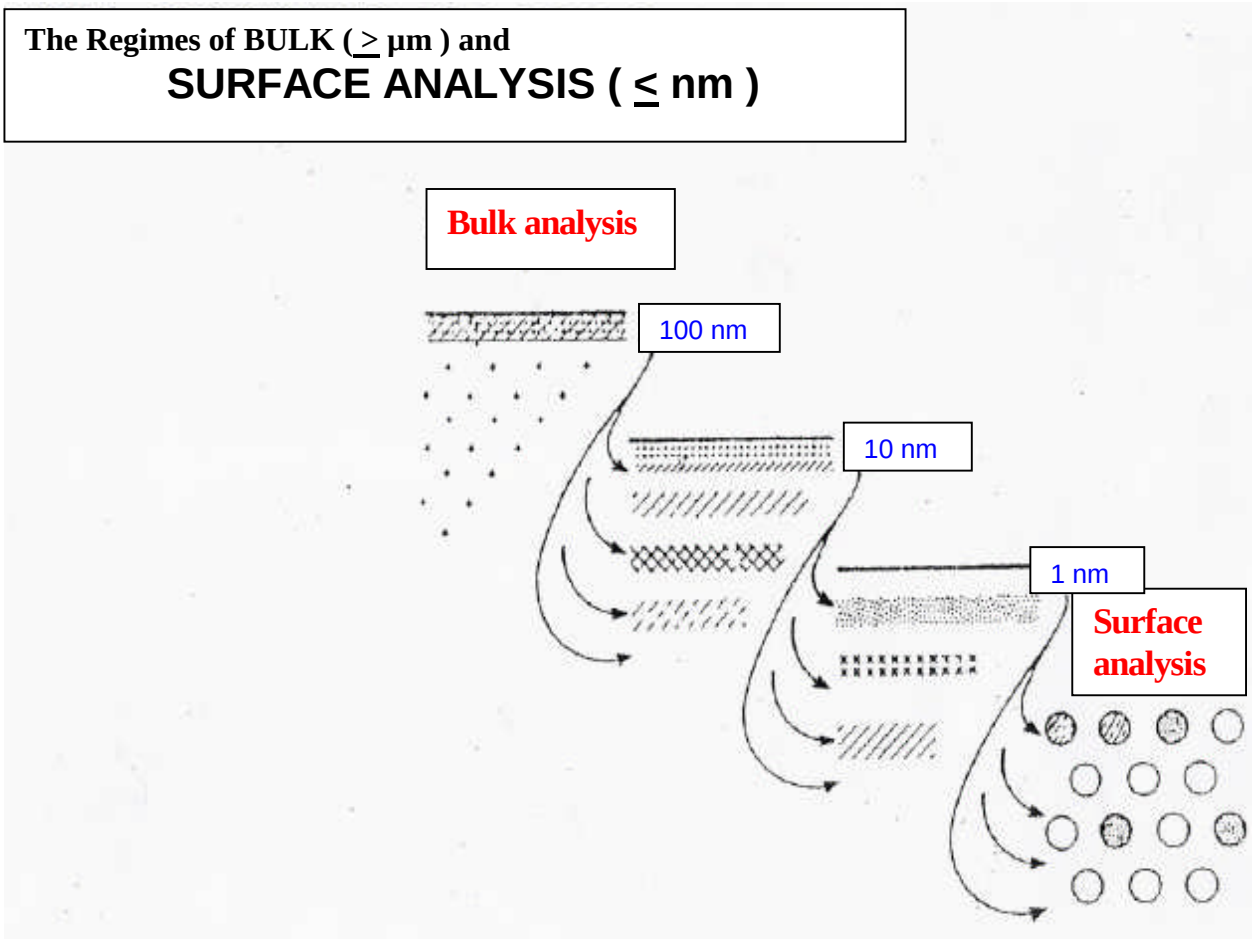
When a polymeric coating is applied on a substrate, a chemical reaction takes place when each surface contains functional groups. It is often desirable to modify the substrate to ensure the reactivity at the interface by removing contamination and / or introducing functional groups. This simplified view of the interfacial or interphase bonding neglects physical forces between two materials which are influenced by e.g. surface roughness. For a comprehensive characterisation of coatings, surface analysis of the substrate (chemical as well as topographic) and thermal analysis of cured polymeric coating materials is of great importance.

According to the famous scientist Pauli, **GOD** made the MATERIALS - but SURFACES were the work of the **DEVIL**. The surface, therefore, deserves special attention.
Today's surface, where the DEVIL has enormous influence towards adhesion, measures a few nm only *(Fig. 1)***.**

Surface analysis

The concept regarding the dimension of surface has changed dramatically in the last decade or so as shown in the *fig. 1*.

Fig. 1: The regimes of bulk & surface analysis



What was considered to be surface over a decade ago is now termed as 'bulk'.
Today's surface, where the DEVIL has enormous influence towards adhesion, measures a few nm only *(Fig. 1)***.**

It is almost impossible to list all the factors that may affect adhesion because of the broad range of substrates that can be involved , or a variety of organic / polymeric materials utilized in a bond. Some aspects / contributions of FTIR (Fourier Transformed 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 [1]:

Fig 2: Scope and limits of surface analytical techniques

Technique	Sensitivity	Depth	Quantification	Molecular Structure
FT-IR	> 1000 ppm	>100 nm	indirect	very good
ESCA	1000 ppm	1-5 nm	direct	good
TOFSIMS	< 0.1 ppm	$\leq$ 1 nm	indirect	very good

FTIR:

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.
Generally, the FTIR surface techniques can be classified in two categories: reflection (e.g. ATR: attenuated total reflection) and non-reflection techniques (e.g. PAS: photoacoustic spectroscopy). PAS utilizes the detection by a sensitive microphone of an acoustic signal emitted from a sample after absorption of a modulated radiation. This technique is proving increasingly useful for oxidation depth profiling of polymeric surface after corona or plasma treatment.
FTIR has its limits when < 100 nm depth of surface penetration is involved for the analysis.

ESCA:

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

In *fig 3* below, O/C ratio of a PP surface is analysed with the help of ESCA and correlated with advancing and receding contact angle findings:

Fig. 3: Surface Characteristics after Various Pretreatments

Surface Treatment	time/s	O/C	Θa/°	Θr/°
No Treatment	----	0	117	95
Corona (1.7 J/cm²) (0.17 J/cm²)	0.5 0.05	0.12 0.07	71 74	52 50
Flame	0.04	0.12	73	24
Plasma	0.10	0.12	82	33

O/C ratio of at least 0.12 was found to be desirable for PP after surface treatment. ESCA has proved to be a very useful analytical tool for surface elemental analysis and also for establishing a correlation between the elemental composition and contact angle observations.
ESCA has been very helpful in monitoring the Aluminium surface after plasma etching [2].

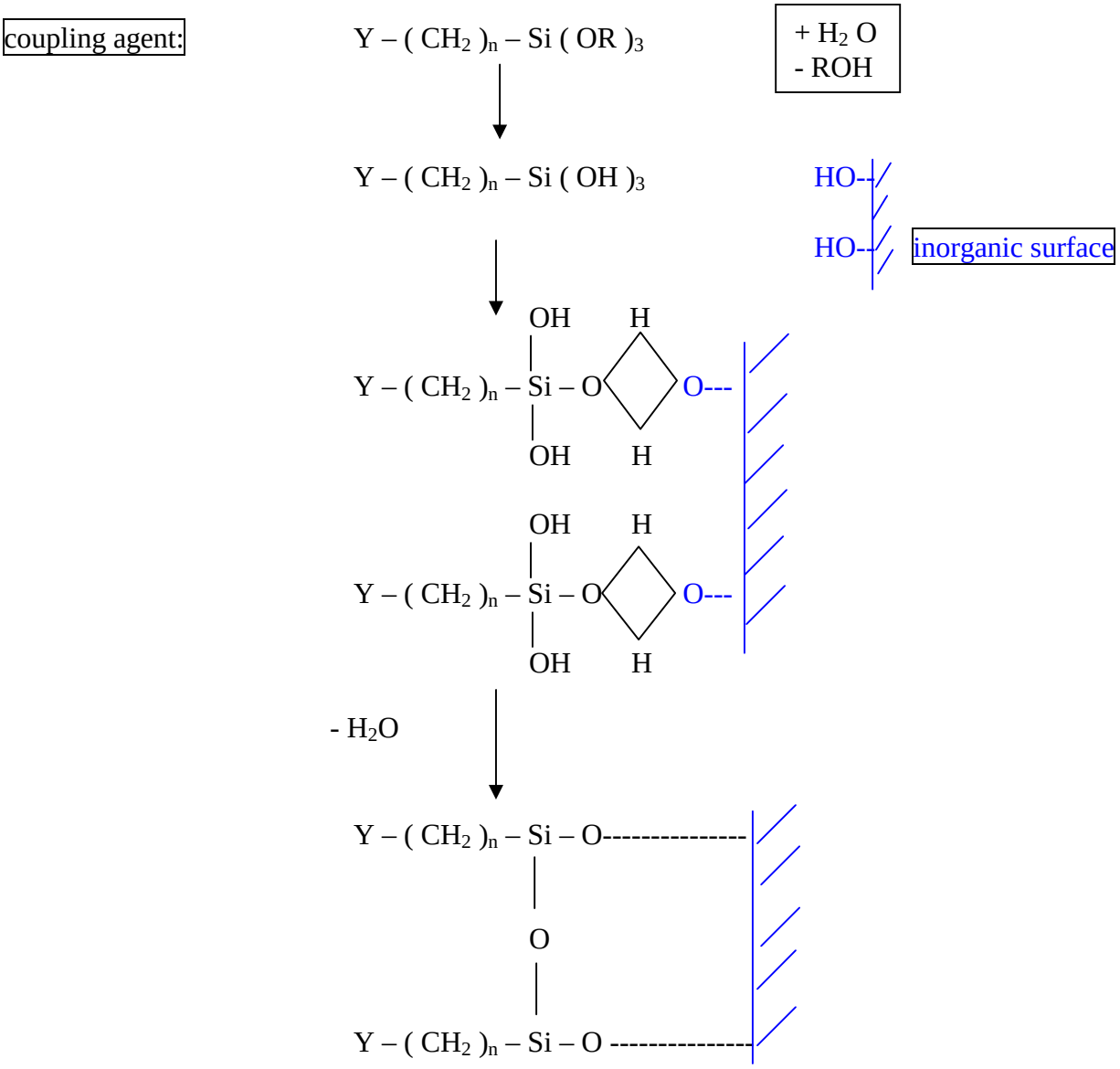
TOFSIMS:

The sample is bombarded with primary ions of 15-25 KV and the secondary ions are extracted perpendicular to the sample surface before being deflected to the detector. Whereas ESCA involves characterisation of 1- 5nm surface depth and is mainly helpful in quantitative elemental analysis, TOFSIMS is suitable for surfaces $\leq$ 1nm and gives information about molecular structure of monolayers at the surface. These two techniques complement each other quite often.

TOFSIMS is a very effective method of detecting silicone (PDMS: Polydimethylsiloxane) and other release agents / surfactants encountered as contamination on metallic and polymeric substrates. Surface contamination is the most important enemy of surface engineering. What is more important is not a clean surface, but a CONTROLLED one. Surface analysis is the most effective weapon against the enemy. ESCA helps in quantifying silicone by measuring Si-content as a complementary technique to TOFSIMS, which is an excellent technique for detecting minute traces of contaminations/ surfactants and release agent residues: Silicones, Stearates, Bis-Stearamides, fluorinated hydrocarbons, anionic- cationic and nonionic surfactants represent typical examples.

Most substrate surfaces need to be pretreated for physical and / or chemical modification for good wettability and bonding. A silane coupling agent, as shown in the *fig. 4* is a proven method of strengthening chemical bond between an adherend and an adhesive.

fig. 4: Silane Coupling Mechanism on an Inorganic Surface

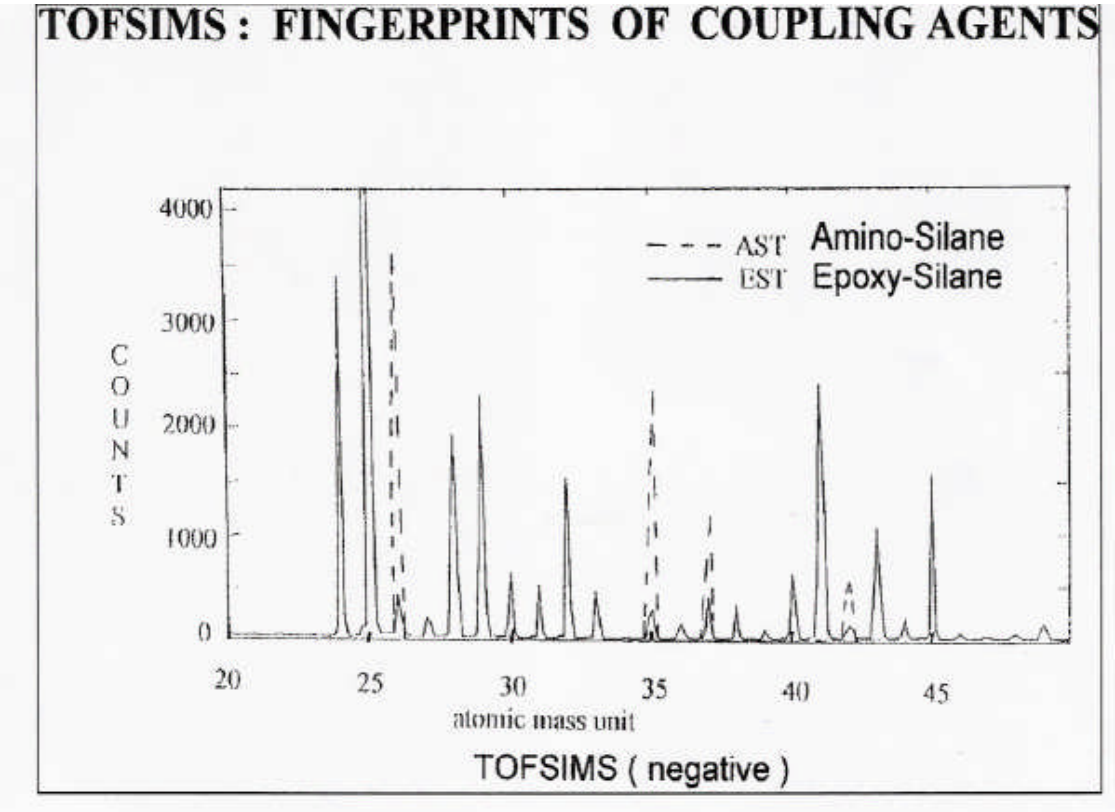


Y can be an amino-, epoxy-, etc. group that is chemically incorporated into the adhesive.

Coupling agents like epoxy- and amino silanes are often applied as very thin layers on substrates like steel / aluminium before an adhesive is applied. In many cases, only TOFSIMS is able to characterise the very thin layer of the coupling agent on the substrate (*Fig. 5*)

ESCA and TOFSIMS analyses have to be carried out at high vacuum (disadvantage!).

Fig. 5: fingerprints of epoxy- and amino coupling agent)



Surface contamination

In bonding technology, contamination is one of the most serious enemies. It is not absolutely necessary to have a perfectly clean surface; what is more important is to have a controlled surface. Silicone (PDMS), tensides – cationic, anionic and nonionic – and various types of lubricants, which are encoutered frequently on the surfaces, should be kept at the lowest level and controlled strictly.

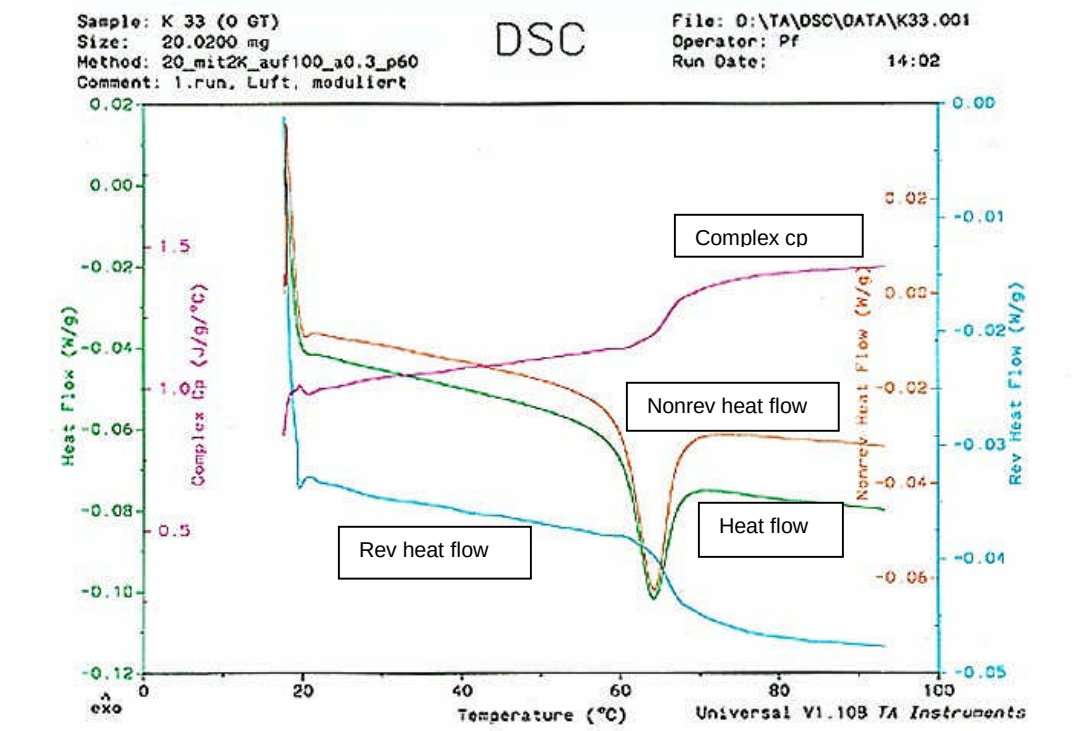
Chacterisation of cure mode of polymeric coatings

The strength and durability of polymer coatings is a combined effect of interfacial and cohesive strength of the polymeric bulk. The cohesive energy is determined largely by the molecular structure arising from careful curing of coatings; cure reactions can be monitored accurately by advanced thermal analysis [3].

MDSC (Modulated Differential Scanning Calorimetry):

DSC has been employed for over 2 decades for investigating cure kinetics of adhesives / coatings. With rising demands of high performance coatings, the resolution and sensitivity of this technique became inadequate.
MDSC, a recent development of conventional DSC, has gained importance by overcoming the limitations of the latter. Specifically, a sinusoidal modulation of the heating profile is overlaid on the conventional linear heating. The net effect – i.e. increased resolution and sensitivity - is the same as if two experiments were run simultaneously. MDSC separates reversing and non-reversing components of the heat flow, so that the real glass transition temperature, tg, is determined from the reversing heat flow curve (*fig. 6*) .

Fig. 6: MDSC spectra of a typical epoxy coating

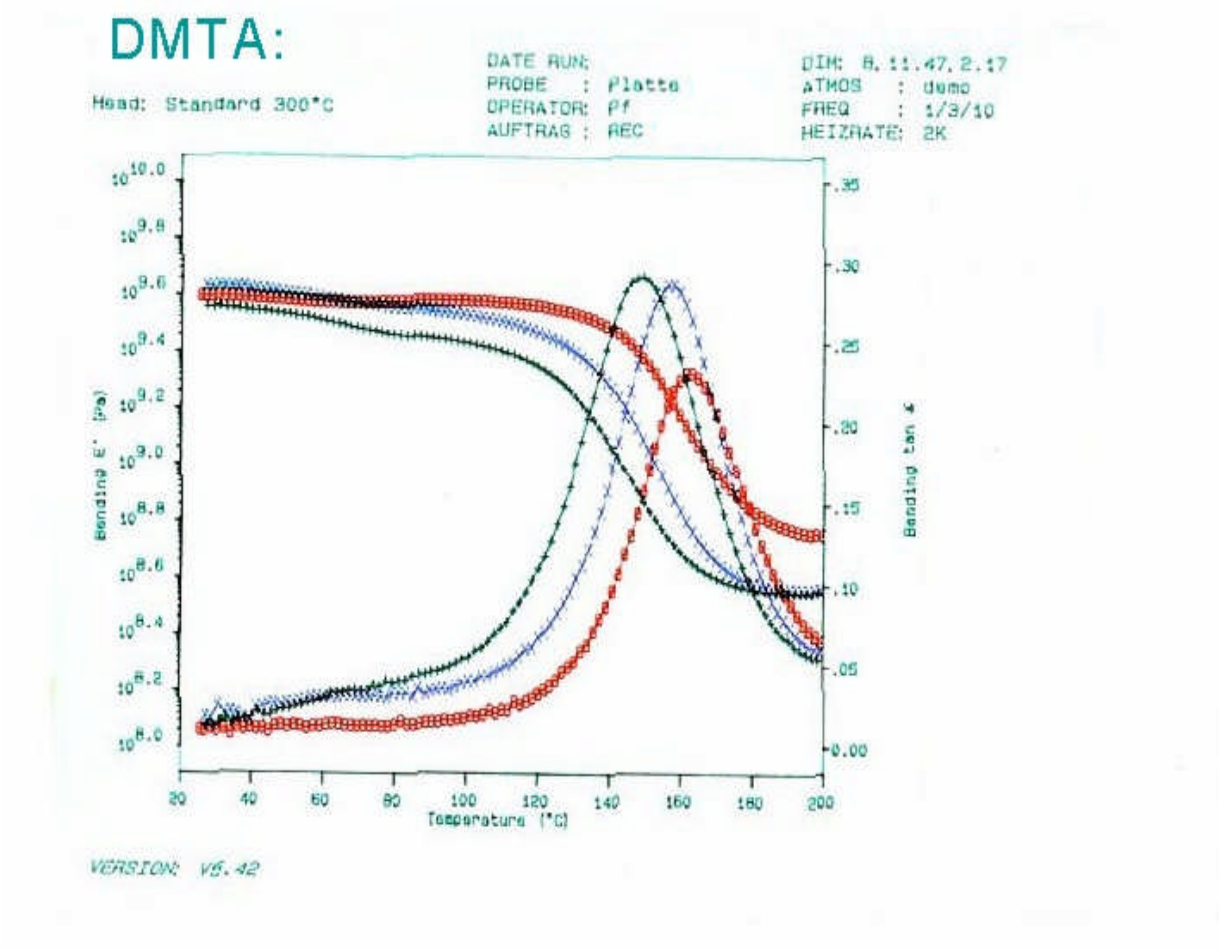


DMA (Dynamic Mechanical Thermal Analysis):

DMA (also known as DMTA) defines the extent of cure and hence the molecular architecture by measuring modulus and mechanical damping or loss with respect to temperature and frequency. When a sinusoidal stress is applied to the (visoelastic) sample, the strain response lags behind the stress applied. E* is then resolved into E' (elastic/storage) modulus and E'' (viscous / loss) modulus components.
The ratio E''/E' = tan δ, often referred to as mechanical loss or damping, is a very useful parameter.
The peak maximum of tan δ is defined as tg of the cured adhesive / coating (*Fig. 7*). DMA is an extremely sensitive and useful technique but has the obvious disadvantage of sample geometry and preparation.

Fig. 7: DMA curves at various crosslinking densities of an epoxy system

ooo: after 3h/ 180°C; III: 1.run; xxx: 2.run

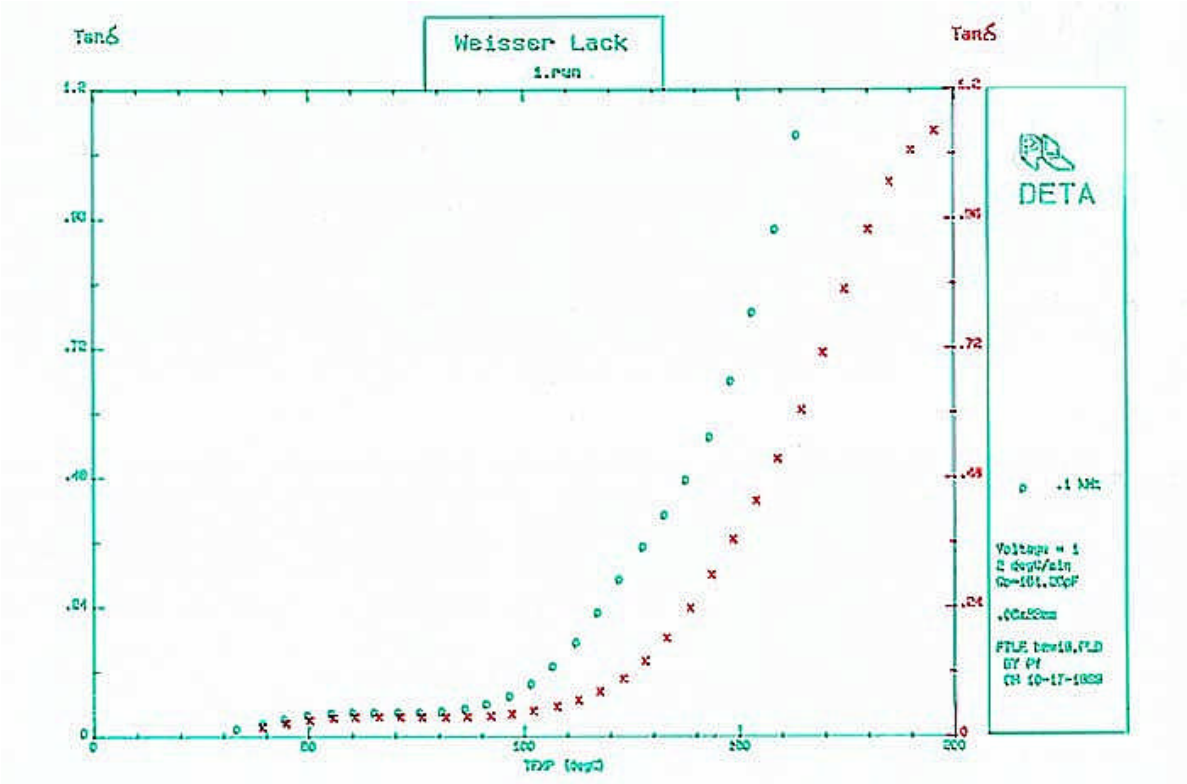


DETA (Dielectric Thermal Analysis):

In the presence of polar groups in the coating materials (e.g. epoxy and 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. The complex dielectric permitivity ε* obtained can be resolved into the storage component ε' and loss component ε''. The dielectric loss tan δ = ε''/ε' is determined with respect to temperature.

The higher degree of cure (165°C) is manifested in decreased dielectric loss (x x x)
The coating denoted by o o o was cured at 145 °C for the same period *(fig. 8)*.

Fig. 8: DETA of an automotive paint cured at different temperatures



DETA is very sensitive for detecting moisture absorption at the interface and in the polymeric bulk material.

This technique has also the disadvantage of sample geometry and preparation.

Conclusions:

Strength and durability of an adhesive bond in coatings depend very much on the integrity of the interface and the cohesive strength of the adhesive after adequate cure / cross-linking reactions. For reproducible high quality products, an accurate characterization of the substrate-surface and cure mode of adhesives is of immense importance. A combination of advanced analytical techniques like ESCA and TOFSIMS are becoming increasingly essential for understanding the role of the surface / interface. In addition to the surface, the other important factor we look at is the properties profile of the bonding material. MDSC, DMA and DETA [3] have proved as powerful techniques for quality assurance of cured adhesives.

While establishing the cause of adhesion failure in various cases of coatings during the last 7 years, we have found the substrate surface (DEVIL !) to be the cause of trouble in the vast majority.

Acknowledgement

ESCA and TOFSIMS analyses were conducted by our cooperation partners on contract basis.

References:

[1] A. Hussain, Haftungseigenschaften unter Kontrolle, Kleben & Dichten, Jahrgang 40, 9/96
[2] Turner R. H. and Boerio F. J. , J. Adhesion 78, 465-494 (2002)
[3] A. Hussain, Characterisation of the Cure of High-Performance Adhesives by Various Techniques, Structural Adhesives in Engineering V, Fifth Intern. Conf., Bristol, 1-3 April 1998.