CHARACTERISATION OF THE SUBSTRATE SURFACE FOR HIGH PERFORMANCE ADHESION

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SUMMARY: For high performance adhesive bonding in aerospace, automotive, biomedical and electronics applications, a precise knowledge of the adherend surface is of immense importance. Inorganic as well as organic substrates are often pretreated – corona, plasma, silane coupling agent etc. – before an adhesive is applied for bonding. Topography, wettability, chemical functionality and surface cleanliness play a very important role in the quality of adhesion. Each of these factors plays a significant role and the contribution of these factors to the quality of the bonded product is additive.

For accurate characterization of the surface, advanced analytical techniques like AFM, ESCA and TOFSIMS have proved to be of great benefit. These techniques have gone a long way in providing an insight into the surface / interface of the bonded materials and the main cause of adhesion failure. Contamination is one of the main enemies in industrial bonding; ESCA and TOFSIMS have proved to be very effective to identify and combat the enemy.

KEYWORDS: Surface analysis, substrate, adhesion, contamination, quality control ESCA, TOFSIMS

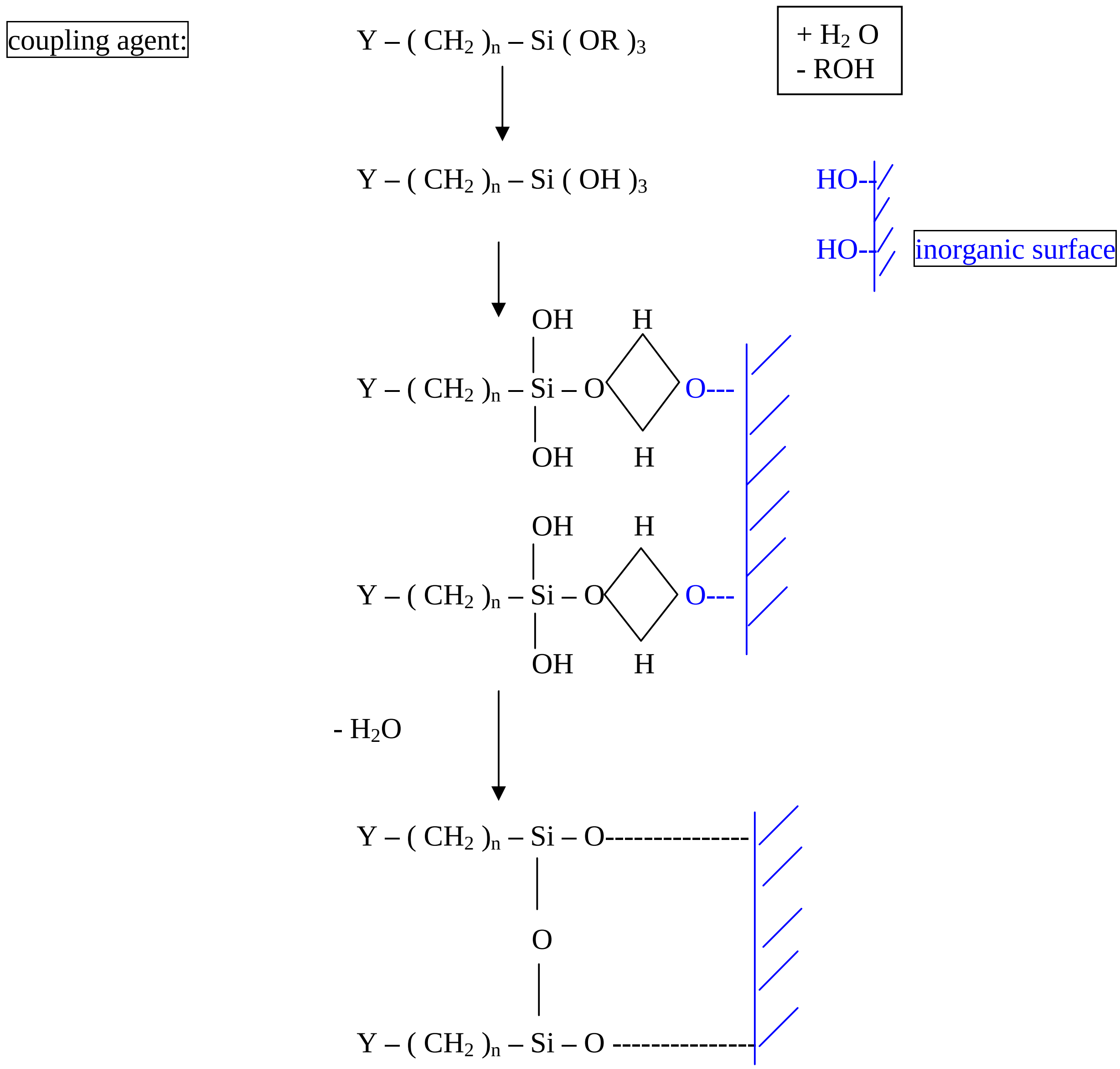
INTRODUCTION

Composites / coatings are the result of the 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 composite 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.

According to the famous scientist Pauli, **GOD** made the MATERIALS - but SURFACES were the work of the **DEVIL**. The surface, therefore, deserves special attention.

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. 1* is a proven method of strengthening chemical bond between an adherend and an adhesive.

fig. 1: Silane Coupling Mechanism on an Inorganic Surface



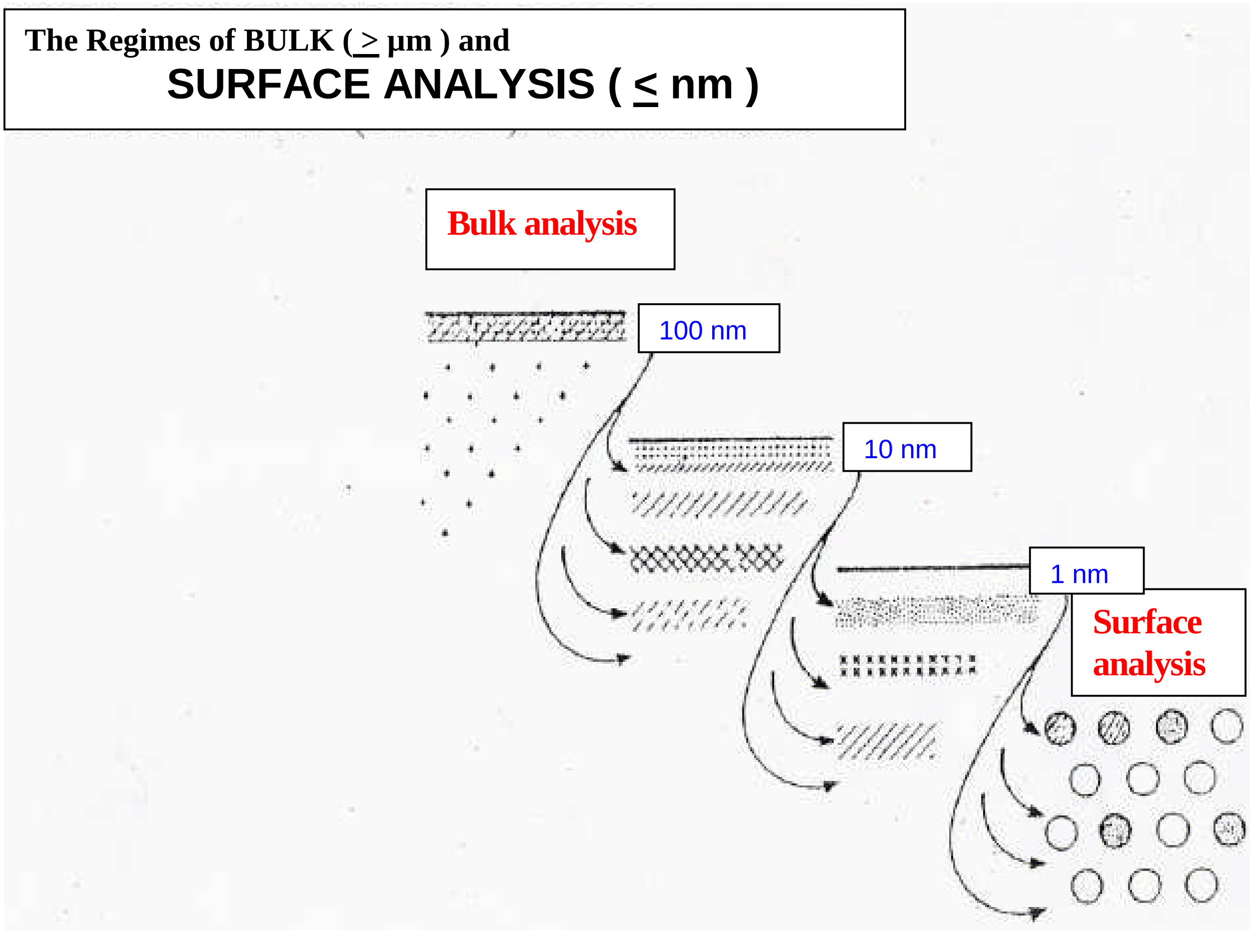
Y can be an amino-, epoxy-, etc. group that is chemically incorporated into the adhesive.

The purpose of this work is to underline the role of characterisation of the substrate surface for the quality and durability of adhesive bonding.

SURFACE ANALYSIS

The concept regarding the dimension of surface has changed dramatically in the last decade or so as shown in the *fig. 2* .

Fig. 2: 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. 3)*.

Fig 3: Scope and limits of surface analytical techniques

Technique	Sensitivity	Depth	Quantification	Molecular Structur
FT-IR	> 1000 ppm	>100 nm	indirect	very good
ESCA	1000 ppm	1-5 nm	direct	good
TOFSIMS	< 0.1 ppm	≤ 1 nm	indirect	very good

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]:

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 (ATR: attenuated total reflection) and non- reflection techniques (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 4* 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. 4: Surface Characteristics after Various Pretreatments

Surface Treatment	time/s	O/C	Θa/°	Θr/°
No Treatment	----	0	117	95
Corona (1.7 J/cm^2)	0.5	0.12	71	52
(0.17 J/cm^2)	0.05	0.07	74	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 desireable 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.

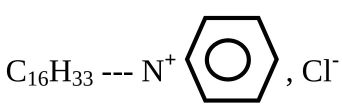
TOFSIMS is a very effective method of detecting silicone (PDMS: Polydimethylsiloxane) and other release agents / surfactants encountered as contamination on metallic and polymeric substrates. Surface contamination is the most important enemy of surface engineering. What is more important is not a clean 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, see *fig. 5/6.*

Fig. 5: some typical surfactants

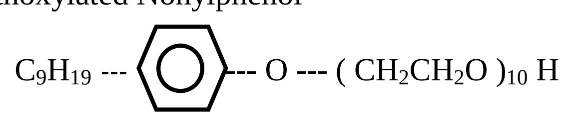
HTAB: **H**exadecyl – **T**rimethyl**a**mmonium**b**romide

CH_3
|
$C_{16}H_{33}$ --- N^+ --- CH_3, Br^-
|
CH_3

HPCl:**H**exadecyl-**p**yridin**chl**oride



Ethoxylated Nonylphenol



Sodium – Dodecylbenzene – sulphonate:

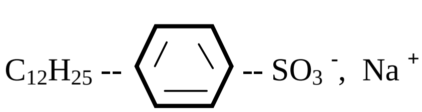
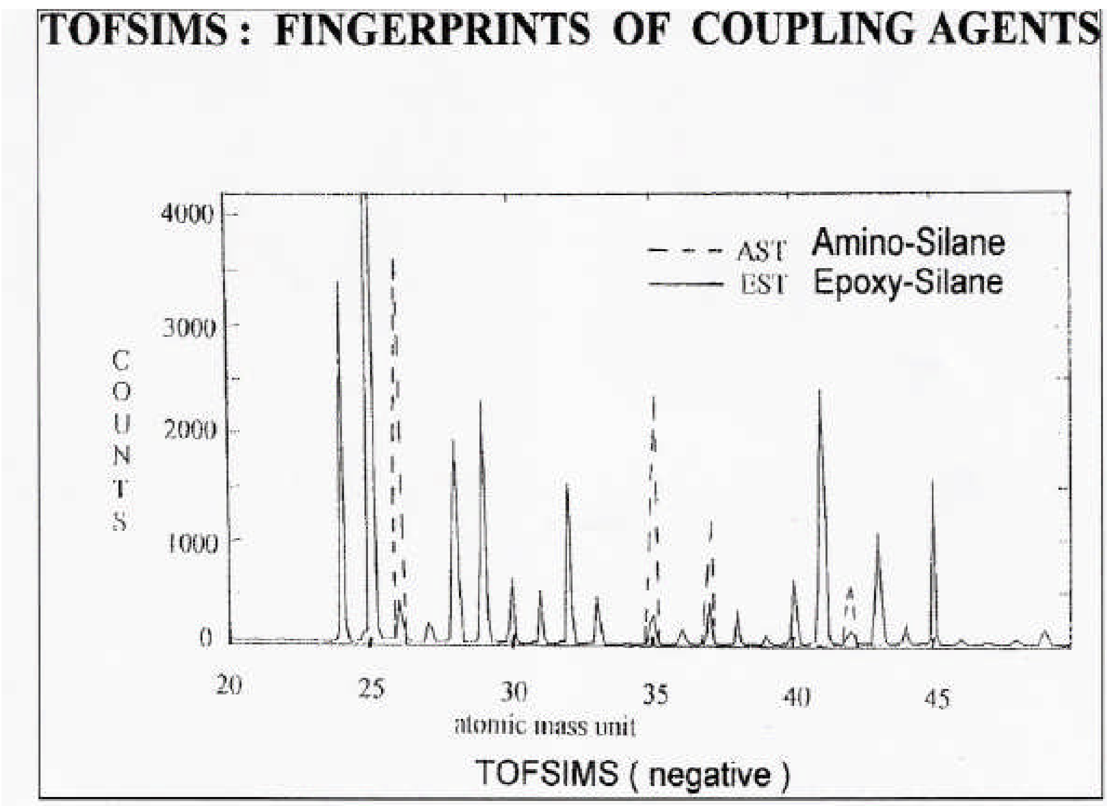


fig 6: some typical lubricants / release agents:

- Silicones (PDMS)
- Stearates (Ca / Zn)
- Bis-Amide (Ethylen-bis-stearamide)
- Inherent slip agents
- Plasticizers
- Fluorinated polymers (Teflon® - spray)

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. 7*)
ESCA and TOFSIMS analyses have to be carried out at high vacuum (disadvantage!).

Fig. 7: fingerprints of epoxy- and amino coupling agent)



AFM:

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

SURFACE CONTAMINATION

In bonding technology, contamination is one of the most serious enemies. It is not desirable 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.

CONCLUSIONS:

Strength and durability of a bond depend very much on the integrity of the interface and the dimensional stability of an adhesive after cure / cross-linking reactions. For reproducible high quality products, an accurate characterization of the substrate-surface and cure mode of adhesives is imperative. A combination of modern analytical techniques ESCA / 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 the properties profile of the bonding material. MDSC and DMA / DETA [3] have proved as powerful complementary techniques for quality assurance of cured adhesives.

Our experience while conducting failure analysis during the last 10 years has shown, that in over 70 % it was the surface / interface, that was the cause of adhesion failure.

ACKNOWLEDGEMENT

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