Optimisation of Process Parameters

Important Factors for high Performance of Composites

For a high performance composite, incorporation of a coupling agent on the fibre has proved extremely helpful in minimizing delamination hazards. It is imperative that the fibre-surface is controlled by advanced techniques like XPS and TOFSIMS. Analytical tools like MDSC, DMA and DEA have proved very helpful in optimising the processing parameters after fibre-impregnation and hence ensuring the durability of the composite.

Polymeric composites 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 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. The energy required to separate the adhesive 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 resin is applied on a fiber-substrate, a chemical reaction takes place when each material 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 a composite, surface analysis of the substrate (chemical as well as topographic) and thermal analysis of cured polymeric 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.

»While characterizing various composites during the last decade, we have found the substrate surface to be the cause of trouble in the vast majority of failure of composites.«

Dr. Amir Hussain & Christa Pflugbeil, Comtech (Labor für Kunststoffe) GmbH, Munich

FIGURE 1

The regimes of bulk (≥ µm) & surface (≤ nm)analysis

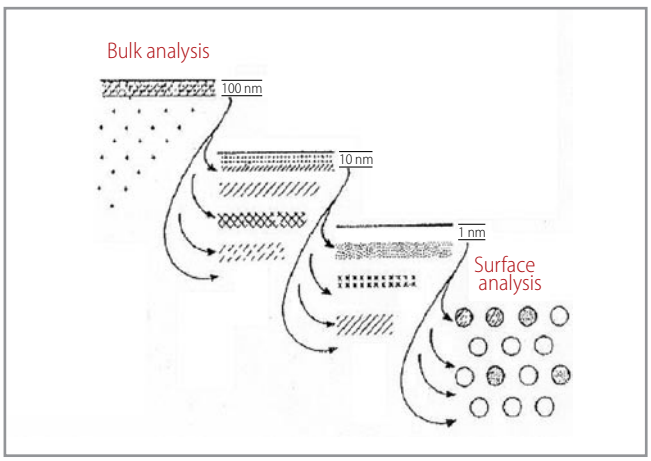


FIGURE 2

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	≤ 1 nm	indirect	very good

FIGURE 3

Fingerprints of epoxy- and amino coupling agent

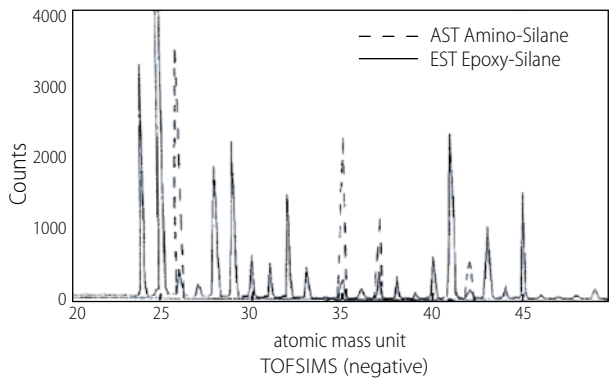
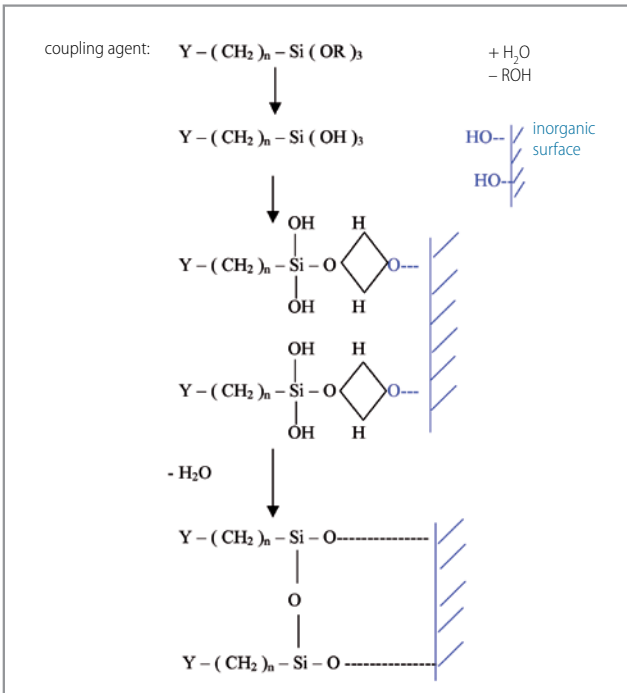


FIGURE 4

Silane Coupling Mechanism on an Inorganic Surface (Y can be an amino-, epoxy-, etc. group that is chemically incorporated into the adhesive.)



»God made the Materials – but Surfaces were the work of the devil.«

SURFACE ANALYSIS

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

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/:

A few relevant surface analytical techniques with their characteristics can be seen in fig. 2.

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.

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, very often as a complementary technique.

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 – 5 nm surface depth and is mainly helpful in quantitative elemental analysis, TOFSIMS is suitable for surfaces < 1nm and gives information about molecular structure of mono-layers 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.

Coupling agents like epoxy- and amino silanes are often applied as very thin layers on glassfibre before an adhesive is applied. In many cases, only TOFSIMS is able to characterise the very thin layer of the coupling agent on the surface (Figure 3)

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 figure 4 is a proven method of strengthening chemical bond between an adherend and an adhesive.

PROCESS PARAMETER FOR APPLICATION OF SILANES

Depending upon the pH-value, temperature and time, silane can bring about coupling effect with varying degree of success: In the following SEM pictures of glass fibre reinforced epoxy systems, the increasing success of coupling effect corresponds to increasingly better coverage of the glass fibre. The last of SEM pictures in figure 5 represents the best set of process parameters.

CHACTERISATION OF CURE MODE OF POLYMERIC COMPOSITES

The strength and durability of polymer composites 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; cure reactions can be monitored accurately by advanced thermal analysis /3/.

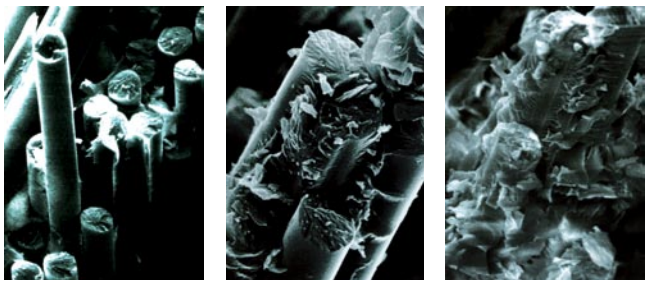
DSC has been employed for over 2 decades for investigating cure kinetics of adhesives. With rising demands of high performance coatings, the resolution and sensitivity of this technique became inadequate.

MDSC (Modulated Differential Scanning Calorimetry), 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 (figure 6).

DMA (Dynamic Mechanical Thermal Analysis) – 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,



FIGURES 5 SEM picture

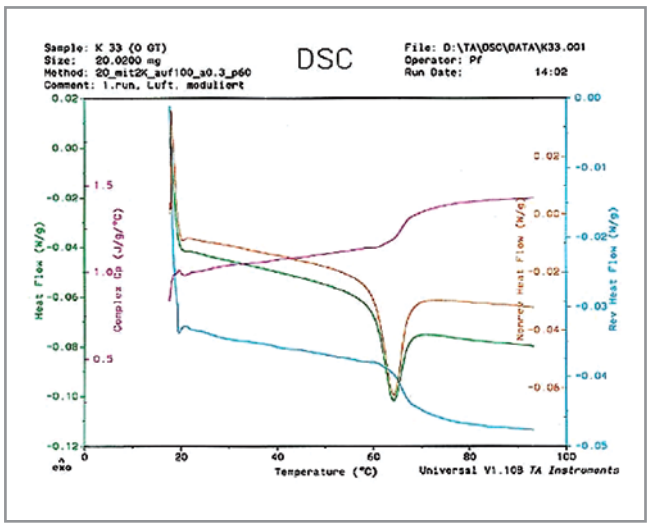
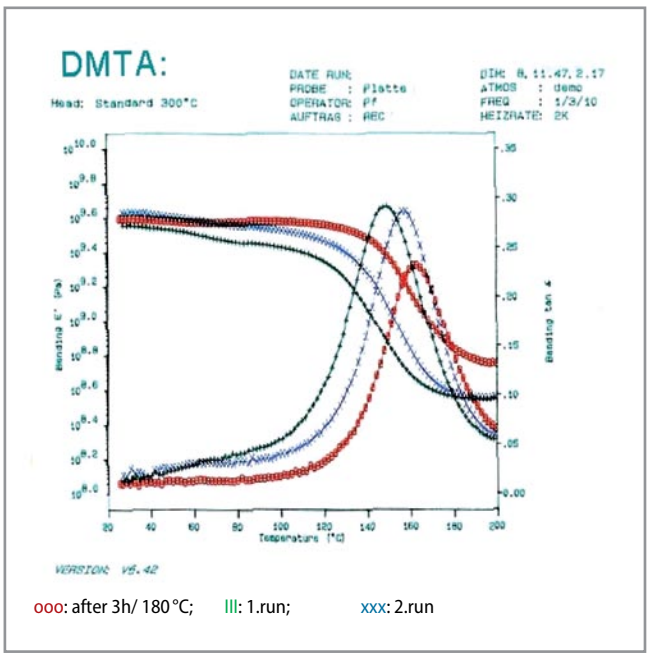


FIGURE 6 MDSC spectra of a typical epoxy matrix



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

FIGURE 7 DMA curves at various crosslinking densities of an epoxy system

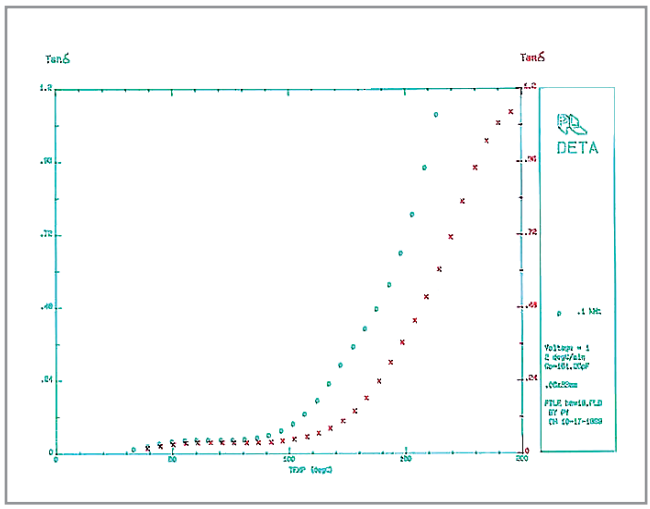


FIGURE 8 DETA of a composite cured at different temperatures

is a very useful parameter. The peak maximum of tan δ is defined as tg of the cured resin (Figure 7). DMA is an extremely sensitive and useful technique but has the obvious disadvantage of sample geometry and preparation.

In the presence of polar groups in the polymeric materials (e. g. epoxy and PU), this DEA 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 $\delta = \varepsilon''/\varepsilon'$ 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 (Figure 8).

DETA (Dielectric Thermal Analysis) 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 a composite 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 as well as 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 composite material. MDSC, DMA and DETA /3/ have proved as powerful techniques for quality assurance of polymeric matrix.

ACKNOWLEDGEMENT

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