Adhesives in Extreme Environments

SAA Seminar held on 7 April 2011 at the Society of Chemical Industry [SCI] 15, Belgrave Square, London

This meeting was only the second time this subject has been covered before by the Society for Adhesion and Adhesives – the first was in December 1991: 'Adhesion in Hostile Environments. It is a difficult area because suitable surface preparation and long term durability are also essential and for long periods of time; a very challenging day for all concerned.

The first paper of the day was *Bone adhesives: challenges and developments* by David Farrar from the Smith and Nephew Research Centre at York. This paper and some others presented “wish lists” for the properties needed. He said that there was not only a need for a “bone glue” that could hold badly broken bones together during the healing process but it also needed to be biodegradable. Some target to start with!

David said that there was no such adhesive at present. He mentioned bone cements and bone void fillers such as PMMA. These are useful but cannot be described as bone adhesives. He then presented a “wish list” of the properties desired.

David then mentioned glass-ionomer cements, or GIC’s, and discussed the problems with the present versions of these. He also mentioned the need for surgeons to be able to mix these properly, but also quickly, and the need for an adequate work life. Work is continuing on these as progress is being made and he hopes that a suitable adhesive will be developed in the foreseeable future.

The second paper, by Dr W. Palin from the Biomaterials Department at the University of Birmingham was entitled, *Surface interactions of dental biomaterials*. Dr Palin mentioned that dental amalgams (‘silver’ fillings) have been the most successful for the last 150 years. Most of us have some! They have good fatigue resistance and toughness and are easy to use but have the disadvantage that they use mercury and so their usage is declining rapidly. The most viable alternative are the resin-based composites, the so-called ‘white fillings’, but these can fracture due to interfacial degradation within the material. Silane coupling agents are commonly used in these materials. He said that reliable adhesion between the variable-nature of different surfaces in dentistry relies on either chemical or physical alteration of one or both surfaces or by using an entirely different composition to the bulk material as an intermediary layer. A suitable bonding adhesive is needed as the bulk material has no affinity for tooth structure. The treatment process to ensure a good bond sounds complicated and this paper needs to be read in detail. The process also seems time – consuming while patients are in the dentist’s chair!

The third paper, entitled *Overview of the challenges for bonding in the oil and gas industry* was given by Dr. John Harris from MERL Ltd.

Following on the oil spill problems of last year this was a very relevant paper to all the oil companies. John said that the applications related mainly to bonded and

unbonded flexible pipes and pipe joints. The pipes consist of layers of elastomer and reinforcements that are bonded together, the reinforcements being either fabrics or steel cables depending on the pressure requirements.

Bonding is also used to attach the end connectors to the body of the hose. There are Specifications and recommended practices established for this work.

Pipe joints can be a problem as increasing use is being made of composite pipe for fluid transportation; lines that can be hundreds of miles in length. Many pipe connections are required, which must be made in the field, during installation.

Flexible joints consist of spherical shaped layers of metal and rubber bonded together. These joints are used at the top of risers and carry high axial loads and are able to resist the internal pressure of the system.

Bonded seals are used in down-hole applications, such as packers where bonding is required between an elastomeric component and rigid [metallic or thermoplastic] substrates. Temperature requirements may be extreme and the chemical environment aggressive requiring special enhancements to achieve the required bond strengths.

Insulation layers are bonded to pipe and equipment used in subsea processing and fluid transport. Bond integrity must be maintained for the life of the operations and must withstand the elevated temperature conditions of the fluids involved.

Composite Repair systems have been developed for pressurised pipe systems that rely on adequate bonding being achieved and maintained.

John then described durability testing and test methods and said that adhesives are being increasingly used in a diverse range of applications. See the full paper.

The fourth paper was give by Ewen Kellar from The Welding Institute, Cambridge. This paper had the title, *Thermal extremes-a review of adhesives tolerant in thermal survival*. Ewen covered a wide range of available adhesives in his talk.

He began by describing the 'High Achievers'. Ewen showed a thermal stability diagram indicating the limited range of temperature over which RT epoxies, cyanoacrylates, acrylics and pressure sensitive adhesives (PSA) were useful. This range was only from about -40^{o}C to +100^{o}C; some types could cope with -160^{o}C. Polyurethanes were better at the cold end and some can be used from -200^{o}C to about +140^{o}C. Heat–cured epoxies and anaerobics showed a range of -50^{o}C to +250^{o}C with some able to go down to approximately -160^{o}C. The most expensive range i.e. hybrid epoxies, polyimides (PI), bismaleimides (PBI), cyanate esters and silicones could cover the range from -200^{o}C to about +325^{o}C and in a few cases up to +400^{o}C. The low temperature materials often showed poor toughness. The high temperature materials showed greater stability. Fortunately there is a wide range of choice but the best material for each job must be chosen carefully.

Critical factors to consider are: thermal degradation, expansion coefficient difference between adhesive and substrate, the required glass transition temperature, modulus

increases as temperature falls and strength decreases as temperature increases. As temperature decreases adhesion strength usually decreases.

Ewen then described the 'Low Achievers'.

He described some epoxies often used for PCB's that are stable at low temperatures but brittle and some similar epoxy/phenolics. He mentioned some polyimides that were stable over a wide temperature range and silicones that show good flexibility down to -60°C and lower. It all comes down to "horses for courses" and the lowest cost for the required performance.

Ewen went on to describe a number of severe in-service applications at both high and low temperatures. An excellent paper that needs to be read to cover the large number of specialises uses mentioned. Ewen can supply a copy if you contact him: e-mail: ewen.kellar@twi.co.uk

The fifth paper was given by Bernard Sikkel of 3M UK PLC and had the title: *Safety in the skies. Innovation in adhesives and sealants qualified to aerospace FST requirements*.

Bernard said that the adhesives and sealants discussed might not seem to qualify for consideration under extreme environments, except that fire was one of them.

He proceeded to mention several materials that have been qualified to Aerospace FST requirements to meet this situation. Fire, smoke and toxic fumes can all kill passengers and crew so cabins have special requirements for materials used. These are laid down by the Regulatory Bodies such as the Federal Aviation Administration (FAA) and the European Aviation Safety Agency (EASA).

He went on to discuss some new materials developed by 3M. These were 3M Scotch Weld® 3460 low density void filler, used at the edges of honeycomb panels and within the panels at bolt positions in some cases. He said all non-metallic materials need to be tested and he described some methods. Bernard also discussed other new materials, 3M AF-3070, 3M-9300 B/A FST, a new adhesive for interior cabin applications, and 3M Scotch Weld 3550: a 2-component bulk or cartridge dispensed low density void filler.

Paper 6 entitled, *Adhesive performance in hostile chemical environments* by Phil Duke from DSTL, Porton Down was given by Steve Shaw from the same establishment.

Steve said that a potentially damaging environment, not always considered in as much detail as some others, is the effect of chemicals that come into contact with a bonded joint during its service life. These can include fuels, icing inhibitor compounds, and hydraulic fluids in aircraft applications through to chemical warfare agents. These can damage polymers and adhesives of many types and need to be tested against the materials proposed for a given design.

Steve went on to say that he would discuss the effect of compounds such as solvents, acids and alkalis i.e. what could be called 'ordinary' chemicals together with more toxic and potentially damaging systems such as Toxic Industrial Chemicals (TIC's) and chemical warfare agents. He highlighted the manner in which such

chemicals could impact polymer/adhesive behaviour. He also discussed the effect of such chemicals on the bulk adhesive characteristics. Steve finally discussed procedures and guidelines for enhancing chemical resistance in structures subjected to various chemicals together with some decontamination compounds that can be helpful to mitigate their effects.

Paper 7, the final paper, was given by Dr Bill Broughton from NPL, Teddington. His title was *Adhesive qualification for extreme environments: standards and test methods*. Bill's paper covered virtually all the topics in the previous papers and a full copy would be needed to select the topic of concern in each case. Bill can be contacted at the National Physical Laboratory, Teddington, TW11 0LW.

He mentioned humidity, temperature, [hygrothermal ageing], pressure, seawater, and salt spray, weathering, photo oxidation, high–energy radiation, environmental stress cracking and synergistic effects of mechanical stress in combination with chemical agents. Chemicals covered were solvents, including paint strippers and cleaning agents, acids and alkalis, and aircraft products [gasoline, jet fuel, grease and de-icing fluids]. He also discussed accelerated ageing procedures and the use of design of experiments for analysing durability data. Bill also covered adhesion testing for dental and prosthetics [including bone implants and tissue grafts]. He concluded with an examination of new technologies such as the use of optical fibres for chemical sensing and atomic force microscopy and nano-indentation for interfacial characterisation. His presentation was primarily concerned with test methods and standards associated with the use of adhesives in chemical [including water] environments.

Altogether a challenging and useful day