

First Workshop on Corrosion of Polymer Materials

September 2004

The first activity organised by WP19, a Workshop on Corrosion of Polymer Materials, was incorporated into its inaugural meeting. This included seven most interesting presentations by leading exponents in the field. The first presentation was a short overview of the topic by Rudolf Morach. He began by reiterating the claim often heard from the plastics industry that "plastics do not corrode" but went on to explain that this is not so. Indeed there are analogies with the corrosion of metals, which can occur in many forms including uniform corrosion, localised corrosion, erosion corrosion, radiation induced corrosion, etc., and, in the presence of mechanical loading, stress corrosion cracking and corrosion fatigue. Long chain polymers are also susceptible to various forms of corrosion. These substances have 2-way bonds between the chains. Up to 10 chemical substances are added to polymer melts, including stabilisers, plasticisers and UV absorbers. The additives fit between the long chains from which locations they can be leached out, leading to the embrittlement and premature aging of the material. In the case of food containers, such processes can adversely affect the contents. Polyethylene is susceptible to uniform corrosion while Amorphous Acrylonitrile Butadiene Styrene Terpolymer (ABS) and composites can be prone to selective corrosion and pitting. As with metals, the occurrence of stress corrosion cracking in polymers requires a susceptible material, a crack-promoting environment and critical stresses. Polyethylene can crack in the presence of wetting agents and tensides (surface active substances); polystyrene can crack in heptane and acetone vapours; while copolymers can crack in olive oil. Some interesting statistics were presented from the analysis of 5000 failures of plastics components, some of which were due to faulty processing or poor design, as follows:

Stress corrosion cracking	25 %
Fatigue	15 %
Poor design	14 %
Creep relaxation	8 %
Chemical attack	7 %
UV attack	6 %
Thermal degradation	4 %
Others	21 %

The most commonly used test of susceptibility to stress corrosion cracking of polymers involves the exposure of stressed specimens under constant load to the environment of interest. Curves are plotted of time to failure versus applied stress at each of several different temperatures (e.g. 40 °C, 60 °C and 80 °C). A number of important questions must be addressed by the new working party. For example: what are the mechanisms of polymer corrosion; what is the influence of additives and processing; and how can long-term behaviour be predicted from short term testing? This latter point is of particular interest for water piping in houses, where unexpected failures sometimes occur after 10-20 years, depending on the characteristics of the water being carried. Dr Morach suggested that polyethylene should be studied to begin with, but if that doesn't work out attention should be turned to polypropylene and, if necessary, the application of protective coatings to plastics.

The next speaker was Dr Bernhard Blümich of Aachen Technical University, Germany. His presentation concerned new tools for investigation and testing of polymer performance. In particular, he described the NMR-Mouse, a portable nuclear magnetic resonance-based device. Nuclear magnetic resonance is most often used in medical applications because it is safe and, unlike X-rays, provides information about soft tissue. However, applications of NMR in polymer science have been in progress for 20 years, culminating with the development of the NMR-Mouse. This is a portable instrument, which measures the resonance decay function, T_2 . It can be used, for example, to monitor the degradation of plastics insulation on wires. Features, such as oil penetration, can be revealed by the colour contrast of the output. A resolution of about 0.1 mm is available at present, but this is expected to improve in future. The NMR parameters are different for under-cured and over-cured polymers and the technique can be used to monitor aging and water take-up of polymers. The NMR signals can also be analysed to provide information about crystalline and amorphous regions in polymers, and on changes that occur due to deformation or on annealing at 80 °C (i.e. 40 °C below the melting temperature). NMR can be used to detect defects in glass fibre reinforced composites. In fact, anything that modifies the plastics matrix through the ingress of chemicals can be detected by NMR monitoring. The equipment is commercially available and can even be used to make measurements in the proximity of metal components such as steel wires in car tyres or for coatings on steel.

Dr Michael Rudschuck, Head of the Wear Group at the German Institute for Polymers (DKI) in Darmstadt, Germany, spoke about research requirements in connection with the stress cracking of polymers. He said that damage to plastics items can be predictable (due to poor design, etc.) or unpredictable (due to aging, corrosion or solvent-induced crazing). Stress induced crazing is a phenomenon that only affects polymers. Other factors that affect polymers include light and radiation, micro-organisms, mechanical loads and chemical influences. On their own, mechanical loads and chemical influences are relatively easy to control but both together can lead to unexpected behaviour. Stress cracking occurs due to the conjoint action of internal stress and a crack releasing medium and nothing quite the same exists for metals. It is a purely physical process, with no chemical action, which results from swelling, the development of crazing, and cracking of the component. The dissolution of polymers in solvents involves no chemical reaction, simply dissolution. All injection-moulded plastics items have high internal stresses, which can be released by the occurrence of stress cracking. To minimise the risk of such damage, notches and other stress concentrating features must be avoided. Edges should be rounded to avoid high stresses and production methods must be optimised, e.g. by slow injection. All sorts of substances can promote the cracking, including cleaning agents, disinfectants, and plasticisers from other components. To make matters worse, the manufacturer never knows to what kinds of media the component will be exposed in service and failures can occur after years, or on first use of plastics. For example, oil can cause crazing of polycarbonate filter cartridges (although polyamide 11 is more resistant to oil). Soap can be enough to cause craze cracking in polymethyl methacrylate (PMMA), which means that any threads must have a well-rounded profile, and superglue causes crazing of ABS polymers. The use of lubricants can cause crazing during the forming of polymers, so must be avoided at all cost during injection moulding. Tables are available that give the susceptibility of polymers to crazing in a wide range of different media. However, skin lotions can include mixtures of different components that can wreak havoc with plastics, but their effects are difficult to predict from the tables. In all cases, the external medium interacts with stresses (either internal or external) to increase the rate of growth of crazes as a function of the local stress intensity. This means that the most commonly used test methods, bent strip tests and tensile tests, are irrelevant. The literature on craze cracking dates from the 1970s and, in Dr Rudschuck's opinion, it is high time that it was revisited. A great deal of catching up needs to be done by the Polymer Corrosion Working Party.

The Swedish Corrosion Institute in Stockholm has had a group on corrosion of polymers for many years, and Karin Jacobson from that establishment gave a talk that had been co-authored by her colleagues Stefanie Römhild and Gunnar Bergman. This concerned the corrosion of glass-fibre reinforced polymers (GRP), which are widely used in the chemical industry when titanium won't do, e.g. for 35% HCl. Unfortunately, even polypropylene degrades under sufficiently aggressive conditions (such as 99% chlorine), but if the corrosion rate is known, it should be possible to include a corrosion allowance at the design stage. The important thing is to keep the HCl away from the load-bearing glass fibres. The diffusion front of HCl through the polymer can be established by the microscopic examination of polished sections. Nevertheless, GRP demisters in a flue gas scrubber have collapsed because of corrosion and there is a clear need for systematic studies. Some work has been done, and this has revealed that the depth of attack of GRP in ClO₂ depends on the exposure time, ClO₂ concentration, and temperature. Twice as much damage occurs at 35 °C as at 15 °C. The type of resin used is also important because different vinyl esters perform differently. In areas where there is a substantial amount of glass compared to resin, cracks can form more readily and can penetrate more deeply. Stress corrosion cracking is an important consideration for glass reinforced polymers and can occur where acid has access to the fibres in the matrix. The tensile stress must be less than the 0.2 % proof stress. In one case, at a pulp mill, stress corrosion cracking due to ClO₂ resulted in the failure of a GRP pipe lined with 3 mm thick polyvinylidene fluoride (PVDF). This thickness was less than the 4 mm that had been specified. However, there are few data on diffusion through fluoropolymers so it is always difficult to estimate the correct thickness for protection. What is more, the failure occurred at a joint where the stress corresponded to the 0.6 % proof stress, sufficient to initiate stress corrosion cracking by ClO₂. A very costly failure affected a GRP line 8 km long that was used to carry HCl. This occurred after only 2 years in service due to through wall stress corrosion cracking. The crack is believed to have initiated either due to impact during installation or as a result of excessive clamping forces. The resin was too brittle for the application and diffusion along the fibres is more rapid than through the polymer. Dr Jacobson ended her talk by reporting a few more serious problems with GRP. Delamination was one of these. This shows as a colour change due either to curing defects (as a consequence of the incorrect curing temperature) or attack of the glass fibres by water or acid. Micro-delaminations can very easily grow into macro-delaminations in poorly cured regions. Osmotic blisters (boat pox) occurs due to the penetration of salt water into the GRP, assisted by osmotic pressure originating from the lower salt content in the GRP than in the external environment. Regrettably, plastics are not impermeable and are by no means standardised. Polypropylene can contain literally anything and may suffer swelling or shrinkage depending on the environment. In one case, a 12-year old petrol storage tank failed when the composition of the fuel was changed by the addition of 3 % methanol. Lastly, one must not forget the risk of galvanic blistering of plastics reinforced with carbon fibres. In this case the fibres can conduct a current and, if in contact with another metal, can create galvanic cells resulting in reactions that cause blisters to form.

Like metals, plastics can be prone to microbially influenced corrosion (MIC) and a presentation by Professor Paul Linhardt of the University of Technology in Vienna discussed strategies for its prevention. Professor Linhardt went to great pains to stress that he is not really a specialist in polymers, having come from the corrosion of metals side of things. He held that the ISO definition of corrosion (see ISO 8044:1999) relates only to metals and recommended that for a broader definition one must look to that of Mr Spähn in the 1980's. He defined corrosion as "all processes involving the components of the material and medium which cause mass transport across the phase boundary and which may cause deterioration of the material (or failure of the system)". Microbes can survive over the temperature range -12 °C to +110 °C and can lead to the development of potentially corrosive environments.

To make matters worse, they can tolerate a wide range of pH values, salinity and pressure provided that nutrients are available to an extent $> 10 \text{ mg L}^{-1}$ (C_{org}). They can also survive in environments containing more than 2 mg L^{-1} of free chlorine. Several basic modes of MIC were outlined, as follows:

1. Modification of the complete medium to give H_2S or NH_3 ;
2. Modification of the phase boundary by biofilms (the most important one);
3. Deterioration of protective coatings due to MIC as a precursor to corrosion of the underlying metal;
4. Indirect MIC as a consequence of using too high a temperature or biocide concentration in an attempt to eliminate microbe for hygienic reasons.

Biofilms can vary in thickness over the micron to centimetre range. They often accommodate synergistic mixed populations. They contain between 50 % and 95 % water, together with an extra-cellular polymeric substance (EPS) that glues the microbes to the surface. Biofouling is impossible to avoid in open systems, attachment to the surface being controlled by signalling molecules that are "quorum sensing". However, the speed of fouling depends on the surface roughness and type of material. Biofilms can clog pipes, and can cause microbial influenced corrosion due to the chemical modification of the phase boundary, together with stagnant flow conditions within the biofilm layer. The MIC of polymers can occur due to:

1. Direct attack of the polymer chain;
2. Leaching of small molecules;
3. The ingress of small molecules from the biofilm into the polymer chain.

The attack is usually by stereo selective enzymes and crystallinity plays a role (the more crystallinity, the less easily attachment occurs). The propensity to attack depends on the polymer:

- Polyethylene is relatively resistant (but additives may adversely affect this);
- Polypropylene is rumoured to be susceptible to stress corrosion cracking due to copper ions, which may accumulate in the biofilm from the environment to a sufficiently high level to cause cracking;
- Polystyrene is very stable;
- Polyvinyl chloride loses mass due to the loss of plasticisers, resulting in poor properties;
- Polyesters have stability which depends on their acid components;
- Polyimides (PI) can be degraded under chemical conditions by both bacteria and fungi
- Synthetic polymers with molecular weights in excess of 1,000 are generally considered to be stable, although degradation has been reported with molecular weights of up to 20,000

Microbially influenced corrosion can affect the appearance and the protection provided by organic coatings since biodegradation can give rise to diffusion pathways, allowing the flow of electrolyte to the underlying metal. Alternating current electrochemical impedance spectroscopy may be used to check the barrier properties of such coatings. There exists a standard (EN ISO 846: Plastics I Evaluation of microorganisms) which is suitable for fungi, but not for microbes. Curiously, there are relatively few published case histories of microbially influence corrosion of polymers. This seems very different compared with the situation for MIC of metals, where published case histories are common, and Professor Linhardt regards this as an area in which WP19 might make an important contribution in coming years.

The next presentation was again by Michael Rudschuck of the German Institute for Polymers in Darmstadt, this time speaking on behalf of his colleague Robert Brüll who was unable to attend the meeting. The topic was the failure analysis of corroded polymer components and it began with some statistics: of the 65,000 tonnes per year of polymer pipes, 40 % are made from polyolefins. The corrosion mechanism of these pipes involves free radical oxidation to give organic acids, esters, etc., all of which are characterised by specific infra red absorption characteristics. Long term exposure tests would be too time consuming to be used for quality control processes so precise analytical methods have been developed instead to establish which reactions lead to degradation of the pipes. The work started 6 months previously on the red pipes used for domestic hot water installations in which large cracks up to 1.5 cm deep had formed in a 2 cm thick pipe wall. Fourier Transform Infra Red (FTIR) spectroscopy revealed a gradient of hydroxyl-containing degradation products through the pipe wall. A variation of molecular mass from 544,000 at the unaffected outer wall to 200,000 - 280,000 within 0.01 - 0.1 mm of the inner wall was also detected, showing that the degradation products are relatively small molecules. Spectra were recorded from thin slices taken through the pipe wall. These showed that the degradation products are located very close to the inner surface. Effort will be directed towards the identification of the additives responsible for specific absorption troughs and to determine the activity of the radical scavengers. Black spots have been found to coincide with increased carbonyl concentration. Mid-infrared (MIR) imaging using a 64x64 diode array to map across the image seen in the light microscope has confirmed that the degradation started at the inner surface, as expected, leading to visible morphological changes. It was stated that the presence of copper ions can accelerate the degradation and because of this the use of copper pipework in installations that include polypropylene is forbidden. Other ions such as lead are also bad for plastics pipes and there appears to be a direct link between metal corrosion and the degradation of polymers. Copper ions act as catalysts for the degradation, so only very small amounts are needed. In mixed polymer/metal heat exchanger systems, oxygen can diffuse through the polymer, allowing corrosion of the metal parts and releasing metal ions that promote knock-on corrosion of the polymer parts.

The final presentation of the workshop, on weathering and fatigue of thermoplastic polymers, was given by Philippe Castaing from the CETIM Technical Centre for the Mechanical Engineering Industries in Nantes, France. This focused on the effects of water on fatigue, which, it was claimed, is responsible for one-third of all failures of thermoplastic polymers. A study had been conducted of the effects of cyclic frequency and humidity on the fatigue behaviour of glass fibre reinforced polymers. In the presence of very high stresses, polypropylene melts locally at 165 °C, giving rise to holes, which coalesce leading to failure. At lower stresses, cracks can form with accompanying striations in the polymer that differ from those produced during mechanical or thermal fracture in fatigue. Fatigue and weathering tests have been conducted on dog-bone specimens of glass-fibre reinforced polyamide 66 with a density of 1.34, fibre ratio of about 30% and crystallinity ratio of about 30. All of the fibres were oriented along the injection direction to give an anisotropic morphology. The tests were conducted using alternating bending and fully reversed loading. The results for absorbed water contents from 2% to 8% showed that the fatigue behaviour of polyamides is sensitive to moisture. The fatigue limit at 10^6 cycles fell from 42 MPa under dry conditions to 35 MPa under humid conditions (3.5% water). The attack occurred on the interfaces, leading to plasticisation of the matrix without any noticeable effect on the fracture mode. However, after 10^7 cycles, the effect of water on the fatigue strength was less significant.