EUROPEAN MECHANICS SOCIETY

Colloquium Final Report

N. 607 – Marine Aging of Polymers

Dates and location: **28/08/2019 - 29/08/2019, Brest, France**

Chairperson **Peter Davies**

Co-Chairperson **John Summerscales**

Conference fees

- Regular registration fee (early bird) **250.0 €**
- Regular registration fee **300.0 €**

What other funding was obtained? **None**

What were the participants offered? **The registration fees included:**
- The book of abstracts.
- Backpack containing tourist information and maps
- Lunches and Coffees on both days
- Welcome meal at Brest Marina 28th August
- Gala dinner at Oceanopolis aquarium (in association with CFM) 29th August.

Number of members of Euromech (reduced registration fee) **4**

Number of non-members of Euromech (full registration fee) **46**

Applicants (members)

- Peter Davies
- Quentin DEZULIER
- Romain Léger
- Yann MARCO

Applicants (non members)

- Alina Adams
- Michael Adams
- Mael Arhant
- Antoine Bardin
- Haithem Bel Haj Frej
- Herve BINDI
- Guilhem BLES
- Morgane Broudin
- Kipp Carlisle
- Yoan Chevillotte
- Alexandre CLEMENT
- Corentin Coguenanff

- Anthony Comer
- Guillaume Damblans
- Yves DENOS
- Quentin Deshoulles
- Andreas Echtermeyer
- Paul Eisentraut
- Bruno Fayolle
- Christophe Floreani
- Romain Grangeat
- Mikael Hedenqvist
- Corentin HUMEAU
- Frédéric Jacquemin
- Etienne LAIR
- PIERRE YVES LE GAC
- Maelenn LE GALL
- Antoine Le Guen Geffroy
- Gauthier Loubrieu
- Mouton Luc
- Denis MELOT
- Ben O'Sullivan
- Yves PERROT
- Alexandre Portela
- Emmanuel RICHAUD
- Nadeem Riyazuddin
- Colin Robert
- Alban ROBIN
- Marie Schmidt
- Gregg Stewart
- John Summerscales
- Jiri TOCHACEK
- Alexandre Uguen
- Gertjan Vancoillie
- Sam Weller
- Helmut Zanzinger

Scientific Report

Polymer based materials are extensively used in marine applications, from pleasure boat hulls to deep sea thermal insulation of offshore risers. As a result they are subjected to a very wide range of mechanical loading conditions, but the essential feature of all these applications is the permanent presence of water. The first step in developing safe, reliable marine structures is therefore the integration of water diffusion effects into their design. This is usually based on results from accelerated test methods, whose validity may be questioned. Even if this step is valid, recent work has clearly shown that this is not sufficient. Water interacts with applied stress so coupling must also be considered. These two aspects, test acceleration and water/stress coupling, must be fully understood if they are to be used to predict service lifetimes.

The goal of the EUROMECH Colloquium 607 was to bring together actors from different marine application areas who are confronted by these problems, in order to exchange on qualification methodologies, with a particular emphasis on laboratory characterization methods and lifetime prediction.

This is an area which has been studied for over 50 years, with the most widespread approach being immersion of samples in water at elevated temperatures and periodic mechanical testing. The limitations of this approach have been highlighted in recent years, and as polymer applications become more

critical, so the need for more accurate predictions of mechanical behavior becomes more pressing. There is a particular requirement for validated models which are able to include coupling between water diffusion and mechanical stress.
Four key material areas were identified: Unreinforced Polymers, Polymer foams, Polymer fibres and Fibre reinforced polymers. One half-day session was devoted to each, with a keynote from a recognized expert introducing each session.
The Polymer session was introduced by Professor Richaud of ENSAM Paris, who described recent work to integrate wet aging and oxidation in a modelling framework. This underlined the multi-disciplinary nature of research on ageing, it is essential to include polymer chemistry in any simulation but this is not intuitive for mechanical engineers and researchers. Further examples were given in two subsequent presentations in which low temperature ageing and microplastic formation were discussed. The traditional accelerated ageing approach cannot account for environments in which UV exposure, seawater exposure and variable mechanical loads (due to wind, waves and currents) occur simultaneously. One avenue to explore is the development of new instrumentation which allows the actual loading conditions to be measured in service. The application of new portable NMR techniques and the integration of fibre optic sensors could both provide information on the chemical and physical state of the polymer, so that models can focus on the dominant mechanisms. The presentation of these two techniques with examples of their application stimulated considerable discussion.
The session concluded with a study including a chemistry based model linked to mechanical properties, which allows lifetime predictions to be made for thermoplastic elastomers. This showed what is possible when the dominant mechanisms can be isolated, chain scissions in the case presented, and its kinetics can be linked to environmental conditions even when an Arrhenius expression is not valid.

The session on polymer foams focused on polymers filled with hollow glass spheres. These are widely used both for buoyancy and thermal insulation, so the main loading case is hydrostatic pressure directly linked to the water depth. A keynote from G. Stewart, the technical director of a Scottish industrial company producing these foams provided information on current qualification procedures and their limitations. The common polymer test methods are not suitable to characterize these materials, which require highly specific equipment, notably large pressure vessels. The large dimensions of samples result in long aging times, while deeper water applications (>4000m) and longer durability requirements (>30 years) are adding to the cost of qualification. The following talks in the session addressed some of these issues. Acceleration of tests by increasing temperature is valid over a limited range, then hydrolysis can occur. Increasing pressure can also accelerate water ingress but again there is a limit beyond which diffusion mechanisms change. Finally, the most practical approach is to reduce the sample dimensions, which is very effective for pure syntactic foams (micro-spheres). For foams with mini- and macro-spheres the difficulties remain, as specimens must be large enough to constitute a representative volume.
An additional keynote was added at the end of this session as the programme committee considered that the extensive experience of aging for a very wide range of applications at the KTH Polymer group would provide a focus for discussion on transverse application of test techniques. This was indeed the case, with examples shown from the nuclear industry through to packaging. The difficulty in accelerating radiochemical ageing effects was highlighted by profiling techniques, which revealed very different effects when accelerated test results were compared with results for samples aged in service for 21 years. Automotive fuel line qualification tests were also critically analyzed, and the role of different degradation mechanisms (plasticizer loss, internal cavitation, swelling), for different polymer formulations was clearly shown.

The session on polymer fibres started with a keynote from M. Vlasblom of DSM Dyneema. He focused on creep behavior of HMPE fibres, but developed a methodology to apply creep modelling to predict fatigue behavior of fibre yarns, and then to include temperature effects in predicting rope fatigue behavior. Water and UV exposure are not of primary importance for HMPE but may be critical for other fibres and the papers that followed focused on accelerated tests. Autoclave test procedures were described in studies to obtain data to predict oxidation of PP fibres. Then the effect of water was shown for polyamide fibres, followed by a description of long term creep and fatigue tests performed in water on ropes. The session ended with a detailed case study of the qualification of such materials for floating wind turbine mooring lines.
The session on fibre reinforced polymer composites started with a keynote by Professor Echtermeyer of the Norwegian Technical University. He presented a state of the art on the determination of long term properties for marine and offshore applications. Their approach is to examine the sensitivity of the constituents to the environment individually, both chemically and mechanically, then to develop specific tests to study interfaces within the resulting composite. He concluded that substantial savings in testing costs are possible.
The papers which followed in this session mostly described a more traditional approach (influence of immersion alone), but a range of tests was examined, in particular those focusing on specific failure mechanisms. One example is the study of the influence of seawater aging on interlaminar crack propagation under different loading modes, the aim being to introduce appropriate strain energy release rate values (and their aging sensitivity) into structural calculations of complex composite parts. Results from a European project underway to develop more environmentally friendly bio-composites were also presented. Finally, a paper from the University of Nantes described very recent modelling work, which outlined a methodology to integrate the various composite aging mechanisms into a coupled water/stress environment simulation. This is the Grail for many researchers, and is attracting considerable current interest. Several elements are now available. Modelling of water ingress is now common, many authors rely on Fick but more complex models can be implemented. The effect of water on swelling and local stresses has also been developed and an example was shown here. A considerably more difficult next step is to include damage, and here the introduction of a crack and its influence on water ingress was discussed for both homogeneous and heterogeneous (composite) materials. Deterministic and stochastic approaches were shown. The results are very promising and may enable damage/water/stress interactions to be simulated.

In my opinion the main benefit of this colloquium was to make researchers working on particular materials and applications, aware that many researchers in parallel communities are confronted by very similar problems. Paradoxically, accelerated testing is a central part of research both to develop new high technology marine applications and to understand plastic pollution. These methods are included in qualification procedures across industry but the fundamental understanding of the influence of accelerating parameters on degradation effects remains insufficient. This is even more relevant for applications where strong coupling (water plus pressure, water plus temperature…) induces its own accelerating effects. Several of the papers presented at the colloquium showed original results in this area.

Number of participants from each country

Country	Participants
Sweden	1
United Kingdom	8
France	31
Germany	5
Ireland	2
Norway	1
Czech Republic	1
Belgium	1
Total	**50**

Please send this report in electronic form to the Secretary General of EUROMECH, within one month after your Colloquium.