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Aging and long term behaviour of composite tubes

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Abstract :

This paper will discuss results from studies undertaken by IFREMER and EDF over the last ten years. The aim of these studies has been to examine the aging and long term behaviour of glass fibre reinforced epoxy composite tubes for cooling water system applications. First, aging of resins and composites in water is discussed. Results from tests to establish the kinetics of resin hydrolysis are used in a simple model to predict composite degradation with time, and correlated with results from panels immersed for 8 years at 20, 40 and 60°C. Then results from creep tests on tubes under internal pressure with closed ends, lasting up to 18 months are given. Creep strains are shown to be lower than those measured in similar tubes with free ends reported previously. Damaged and assembled tubes have been tested. Finally current research activities are discussed.

1 INTRODUCTION

Thin wall filament wound glass fibre reinforced composite tubes are being used extensively today, but these structures have been available for over 40 years. Early applications were mostly military, such as missiles and rocket casings (e.g. Kies 1962), but they can now be found in chemical engineering plants (Mallinson 1988), fishing boats (Croquette 1992), offshore platforms (Gibson 1993), and many other industrial cooling systems. In oil and gas production the main use is small diameter low pressure pipe for water flood systems. Williams (1999) reports that Shell now has over 2250 kilometres of FRP (fibre reinforced plastic) piping materials in service round the world. Much of the development work for these applications was performed in the 1960's and 1970's (e.g. Bax 1970, Spencer 1978).

The main incentive for using FRP pipe systems to replace steel is their good resistance to corrosion, and failure rates in sea water in service have been shown to be significantly lower for FRP (de Bruijn 1996). It was mainly for this reason that in 1991 EDF (Electricité de France) decided to introduce composite circuits in their new nuclear power station at Civaux near Poitiers. The circuits involved bring river water to cooling and fire systems and the stringent safety requirements for such applications required extensive full scale testing at EDF and the CEA (French Atomic Energy Authority). Several collaborative research projects were also run. The present paper presents an overview of results from one such project, with IFREMER, but results from other studies on glass/epoxy tubes with the Applied Mechanics Laboratory, (LMARC) in Besançon (Maire 1992, LeMoal 1993, Thiebaud 1994, Perreux 1995, Suri 1995), Ecole Centrale in Paris (Bai 1996), and on glass/polyester tubes at ENS Cachan (Ghorbel 1996) are also available.

The collaboration between IFREMER and EDF focused on long term behaviour and aging. At the IFREMER Brest Centre glass/epoxy pipework has been used successfully for nearly 30 years in a sea water distribution system, but for the power station application the safety authorities required guarantees concerning the long term behaviour. A programme of aging and creep tests was therefore initiated and results from the first phase were presented at DURACOSYS in 1995 (Baizeau 1995).

In the first part of the present paper the aging of resin and composite samples will be discussed. In 1995 results from 3 year immersion aging of composites were described. Results after 8 years will now be presented, and the basis for a simple lifetime prediction method based on resin behaviour will be shown.

The second part of the paper concentrates on the behaviour of tubes under internal pressure, including creep behaviour of undamaged and damaged tubes. Tubes assembled by mechanical and adhesive sys-

tems have also been tested. Finally current research areas and future requirements are discussed

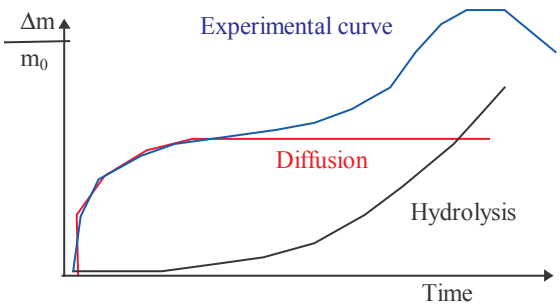
2 AGING OF EPOXY RESIN AND GLASS/EPOXY COMPOSITES IN WATER.

The degradation of composites in water may result from many different mechanisms, involving the fibre, fibre-matrix interface and matrix resin. In order to treat aging practically simplifying assumptions are therefore necessary. One approach is to determine, for each mechanism, a characteristic time before which the mechanism can be ignored but beyond which it plays a significant role in the durability of the material. This approach will be illustrated below for the case of wet aging of glass reinforced anhydride cured epoxy, by considering the hydrolysis of the matrix.

2.1 Resin properties

Anhydride cured epoxies contain esters which are susceptible to hydrolysis. The chemical reaction is: RCOOR' + H_2O → RCOOH +R'OH. The hydrolysis of the polymer leads to molecular chain breakage and water molecules can fix to the material. This leads to an increase in sample weight of 18 g/mole of broken chains. The resin weight change will therefore be a monotone function of the number of breakages. A simple weight measurement should therefore enable quantitative information on the kinetics of hydrolysis to be obtained. This assumes that weight gain due to water diffusion into the polymer can be separated from the overall weight change, (and that other damage does not occur simultaneously) which can be ensured by using very thin specimens. Figure 1 shows this schematically.

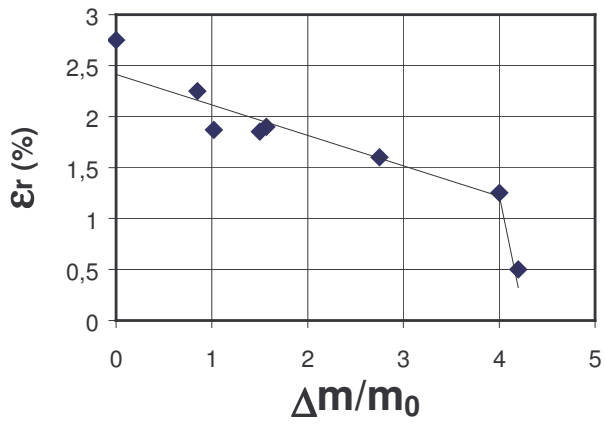
Figure 1 Resin weight change during immersion



Samples of epoxy resin (diglicidyl ether of bisphenol A, DGEBA) with methyl tetra hydrophthalic anhydride (MTHPA) were immersed at three temperatures, 60, 70 and 80°C. A kinetic model was used used based on the following assumptions: the reaction is homogeneous throughout the material, the kinetics are of second order (one with respect to the ester functions concentration, one with respect to water concentration), and solubility of water varies little with temperature. The time to reach a given degree of advancement depends on the water content, which can be calculated for all temperatures using an Arrhenius model and an activation energy calculated from the resin weight gains at different temperatures. The determination of a critical level of hydrolysis leading to mechanical property changes is then required.

By measuring the failure stress and strain as a function of water absorbed on samples of resin aged in water at 60°C, a critical value of percentage weight gain (and hence of hydrolysis) corresponding to a drop in mechanical properties was determined, Figure 2.

Figure 2. Failure strain versus % water absorbed.



For the epoxy/anhydride system studied here that value is around 4%. By introducing this critical value (4% water absorbed in the resin) in the kinetic model a lifetime can be determined for the matrix hydrolysis mechanism. This varies from several centuries at 20°C to less than one year at 80°C. These characteristic times show that matrix hydolysis is not a problem under normal operating conditions but may become critical at elevated temperatures.

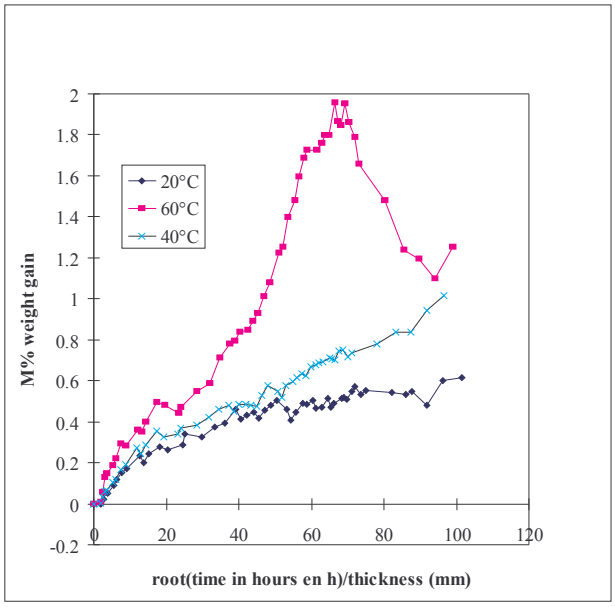
2.2 *Composite panel weight gain*

Figure 3 shows the results from 8 year immersion in distilled water at different temperatures (20, 40 and 60°C) of 3 mm thick composite panels, filament wound at ±55°. The curve for immersion at 60°C shows a similar form to those in Figure 1, with an increase in weight gain after about 3 years. However it should be noted that of the five panels tested at 60°C two showed a more rapid increase in weight gain than the other three. This will be discussed further below. Tg measurements were made periodically by DSC, then after 7 years specimens at each temperature were removed and dynamic mechanical analysis was performed in 3 point flexure (temperature increased at 2°C/minute). Results are shown below, Table 1, indicating that the glass transition temperature of 60°C aged samples (which showed the large increase in weight) has dropped significantly. Similar drops in Tg were measured by DMA on aged resin samples, Figure 4.

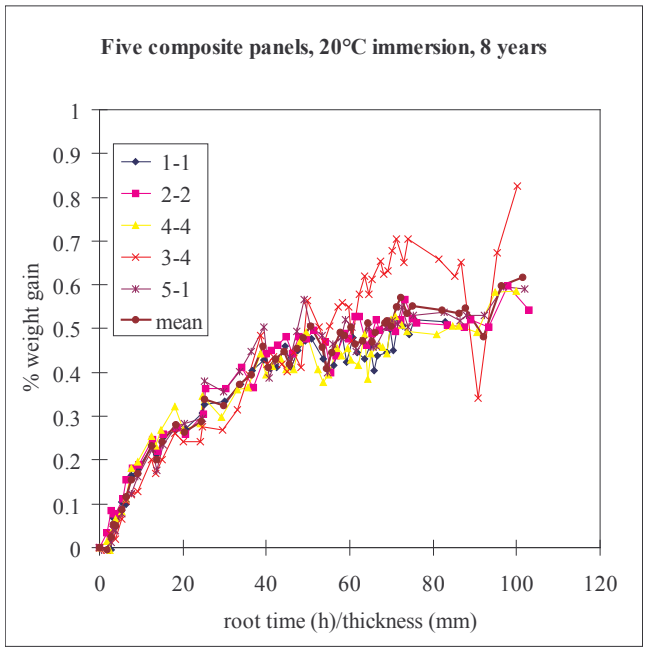
Table 1. Glass transition temperatures, °C (DSC & DMA), aged composite panels

Aging temperature	Initial state DSC	10 months DSC	22 months DSC	35 months DSC	7 years DMA
20°C	129	130	129	131	116°C
40°C	129	130	129	132	119°C
60°C	124	123	119	115	86°C

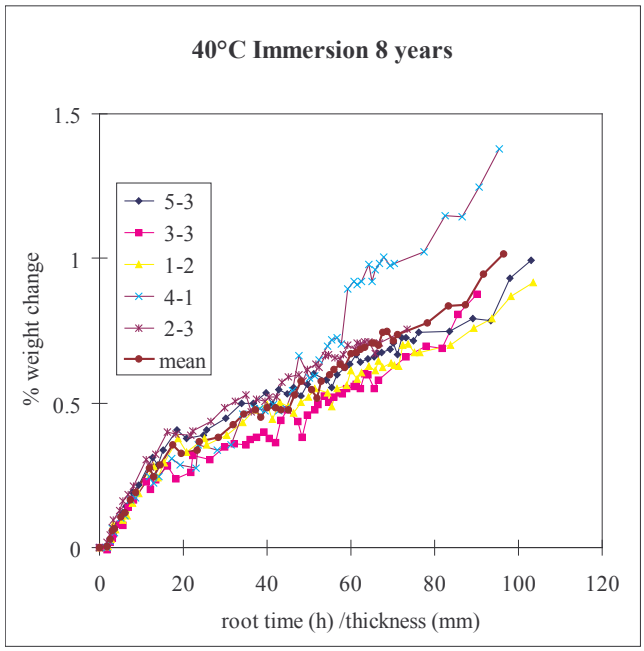
Figure 3. Weight gains, 20, 40 and 60°C, 8 years.



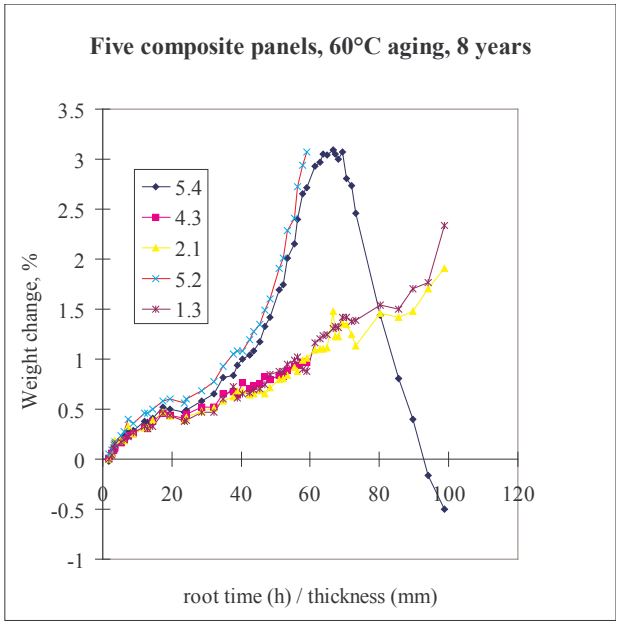
a) All panel means



b) 20°C immersion

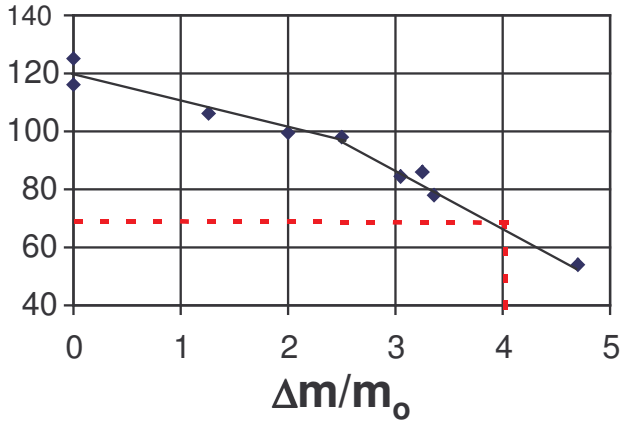


c) 40°C immersion



d) 60°C immersion

Figure 4. Change in resin Tg (°C), 60°C aging.



Scanning electron microscopy was performed on polished sections and fracture surfaces of regions on the exterior and centre of specimens at all three temperatures. Figure 5a shows the specimen thickness and it is apparent that some voids are present. Specimens aged at 20°C showed no evidence of interfacial debonding after 7 years. Those aged at 40°C show some signs of interface debonding on the surface but not in the centre, while those aged at 60°C show very close to the surface (in a 0.2 mm thick skin layer) clear interfacial degradation, Figure 5b, but again in the majority of the thickness of the specimens there is no evidence of debonding, Figure 5c.

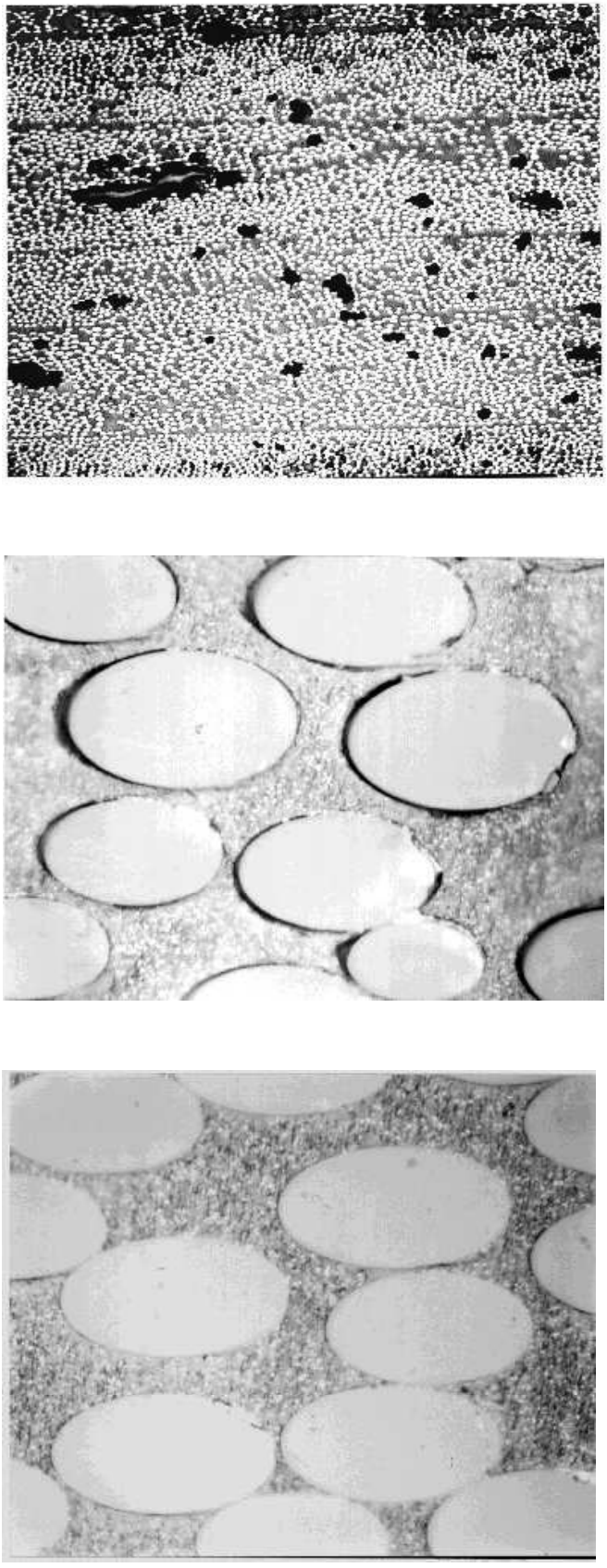


Figure 5. SEM photos 60°C aged panels after 7 years' immersion,
a) all thickness
b) outer surface (0.2mm skin layer)
c) centre

Given these results it may be justified to assume that the bulk of the specimen is degrading in a homogeneous manner and to apply the kinetic model of resin hydrolysis to predict an order of magnitude of the state of hydrolysis in the composite panels. This would suggest that when the composite has reached a weight gain around 1.6 to 2% (when the 40% by mass of resin matrix in the composite is at 4% weight gain plus the uncertain contribution of voids which will fill up with water) then there will be a drop in mechanical properties. This weight gain is achieved after a few years at 60°C but not after 8 years at 40°C (Figure 3). The predicted time for a 4mm thick resin panel to reach 4% water content is 55 years. The influence of this weight gain on composite mechanical properties will be discussed in section 2.4 below.

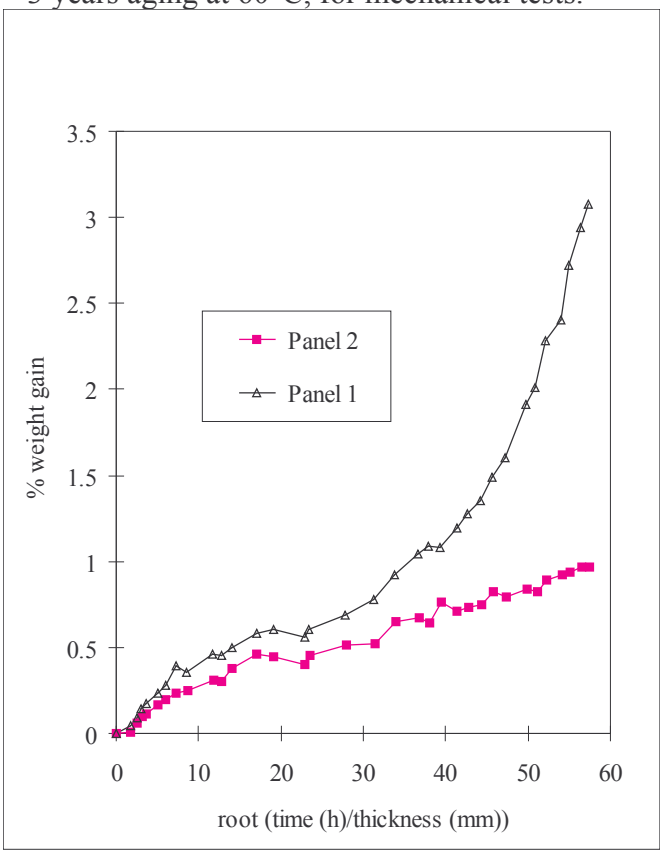
2.3 Correlation with behaviour of tubes

Samples taken from tubes fully immersed for 5.8 years at 60°C were also examined and the same degradation mechanism was observed, a little interfacial debonding near the surface but none in the centre of the tube wall. This suggests that the simplified approach based on resin hydrolysis kinetics, combined with regular checks on glass transition temperature, may provide a useful tool in determination of the service life of these tubes. As tubes in service are only exposed to water on the inside wall there may need to be an adjustment to the weight gain kinetics however, as previous results (Baizeau 1995) indicated that weight increases in this case were much lower than expected based on plate or fully immersed tube results. Some additional tests involving machining of inner and outer layers were performed (Suri 1995) to try to explain this phenomenon but did not clarify the reasons. As far as the degradation mechanisms are concerned this effect should be positive in reducing the degradation rate. Another aspect which can affect the correlation is the presence of voids, high levels of which (>5%) can be introduced during filament winding. Chiou (1996) has also reported anomalies in long term behaviour of tubes, which were attributed to the presence of voids.

2.4 Mechanical property changes after aging

A small number of flexure and short beam shear tests were performed on samples taken from the panels aged at 60°C after 3 years. Two panels were tested, one which had shown a rapid increase in weight gain (to 3%), while the other had only gained 1% weight, Figure 6. These should therefore be above and below the critical weight gain corresponding to loss in resin properties (Figure 2).

Figure 6. Weight gains of two panels removed after 3 years aging at 60°C, for mechanical tests.



The reasons for the difference are not yet clear and are being studied, but may be caused by formulation or curing differences (the two panels which gained weight the fastest come from the same panel). It should be noted however that after 8 years the remaining panels at 60°C had also gained 2% weight or more (Figure 3). In flexure there is a clear drop in strength for both, Table 2, but this property is governed by the surface degradation (interface debonds). In interlaminar shear however, governed by shear of the resin in the centre of the sample, the loss in strength is only significant for the sample with high weight gain.

Panel	Flex strength, MPa		ILSS, MPa	
	35°	55°	35°	55°
Reference (unaged)	410	127	44	19.5
Panel 1 (3%)	231	87	30	13
Panel 2 (1%)	302	120	43	18.5

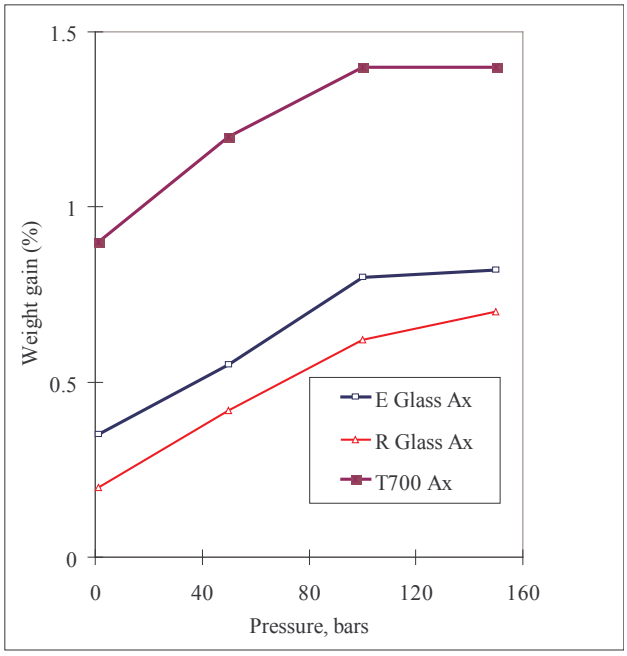
Table 2. Results from tests on composite panels after 3 years at 60°C

Further projects are now underway to develop this model further, including tests in which tube and resin samples of the same epoxy with three hardeners, (anhydride, aliphatic diamine and aromatic cycloamines) are being aged at different temperatures. Studies of the degradation of fibre-resin interfaces are also being performed. This may have a short characteristic time and be the critical degradation mechanism in some cases.

2.5 Accelerating tests with pressure

While raising temperature is often a convenient way to accelerate aging tests, increasing hydrostatic pressure may also be used. This may be more appropriate for applications such as underwater pipelines, and some tests have been run to look at how pressure affects diffusion kinetics in these materials. Examples of results for the same epoxy resin with three different fibre types, for specimens cut from filament wound tubes wound at ±55°, aged at 60°C are shown below, Figure 7.

Figure 7. Weight gain after 150 days at 60°C as a function of pressure.



This figure shows that there is a significant effect of pressure for all three materials, with an increase in weight gain as pressure is increased up to 100 bars. Further increase to 150 bars does not appear to have a significant effect. This effect of pressure is related to the porosity common to filament wound materials.

3 CREEP OF TUBES AND TUBE ASSEMBLIES UNDER INTERNAL PRESSURE LOADING

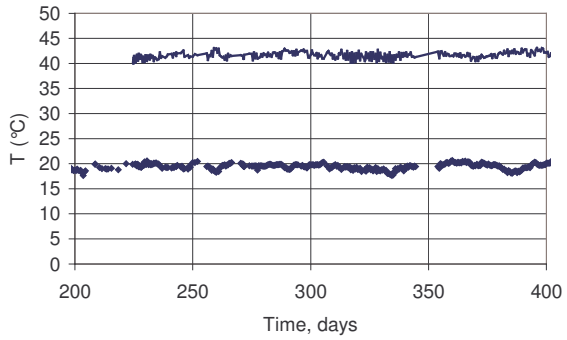
Two series of tests have been performed to investigate the long term behaviour under internal pressure. A total of 24 tubes, each 1 to 1.5 metres long, has been tested, Table 3. The internal diameter is 150 mm, wall thickness is nominally 5 mm. The first phase of the project, a series of 12 creep tests on tubes without internal liner and loaded with free ends ($\sigma_z = 0$) at different temperatures and pressures, was described by Baizeau et al. at DURACOSYS 95 (1995). A description of the second phase, which involved tests on tubes with internal liners, will now be presented. The aims of these tests were to establish the influence of creep on residual stiffness, to compare the free end and fixed end loading conditions, to examine how damage affects subsequent creep behaviour and to see how bonded and mechanical joints behaved.

Series	Pressure MPa (σ_q)	Temperature, °C (Number)	Duration Creep/ Recovery	Details
1.	2.7 (38)	25, 40, 55	12m/1m	All type
No liner	4.0 (56)	25, 40, 55	9m/1m	A
Free ends	2.7 (38)	25, 40 (2), 55	6m/2.5m	
σ_z=0	5.4 (76)	55 (2)	6m/2.5m	
2.	0.8 (11)	20 (3)	17m/1m	A,B,C
With liner	1.7 (24)	40 (5)	17m/1m	A, B, D1-3
Fixed ends,	3.8 (53)	40	10m/1m	B
$\sigma_z=\sigma_q/2$	3.8 (53)	60 (3)	10m/1m	A (2), C

Table 3. Summary of creep tests performed
A: Straight tube, B: Mechanical joint at centre, C: Tulip adhesive joint at centre, D: Damaged
Hoop stresses applied to damage:
D1 35 MPa, D2: 67 MPa, D3: 130 MPa

Long term testing of tubes requires a number of precautions to be taken. First, the temperature and pressure must be continuously monitored. An extract from the temperature log is shown in Figure 8.

Figure 8. Extract from temperature log.



The 20°C chamber was installed in an existing test laboratory with temperature and humidity regulation and posed no particular problems. The 40°C and 60°C chambers used heated air blowers with three thermocouples per chamber to regulate temperature and maximum (exceptional) variations of 8°C were recorded at 60°C. The pressure was also recorded throughout the tests, and could be regulated to within ±2 bars at the highest pressure. In addition to following the pressures and temperatures it is also necessary to record the strain response by strain gauges throughout the creep and recovery cycle. This requires a reliable data logger which can handle over 100 strain, temperature and pressure channels. A *Scorpio* logger was used here, which allows low current impulsion strain gauge excitation, minimising local heating problems. In addition a dummy gauge was bonded on an identical tube section in each temperature chamber to allow strain gauge drift to be measured. Photo 1 shows one of the creep chambers.

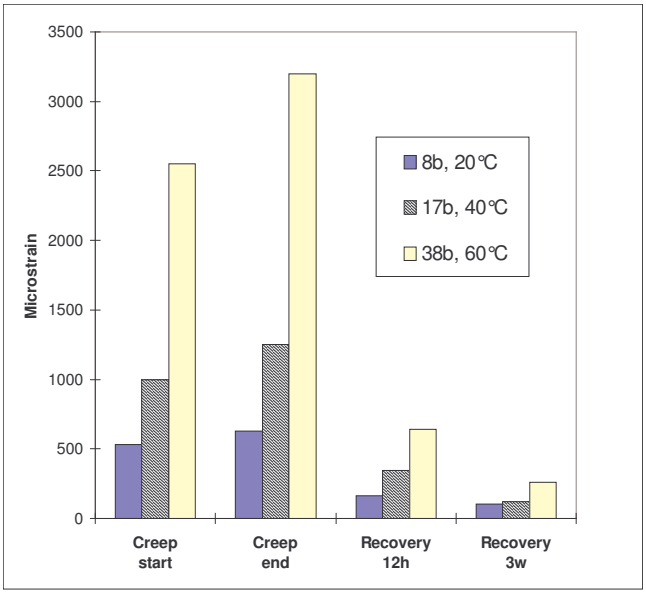
Photo 1. 20°C creep chamber with tubes of type A, B and C.

Pressure tests were also performed on the tubes before and after this cycle. These involved subjecting tubes to low pressure cycles with two loading conditions, fixed and free ends (i.e. with and without axial stress), and allowed the influence of the creep cycle on residual stiffness to be assessed.

3.1 Creep results

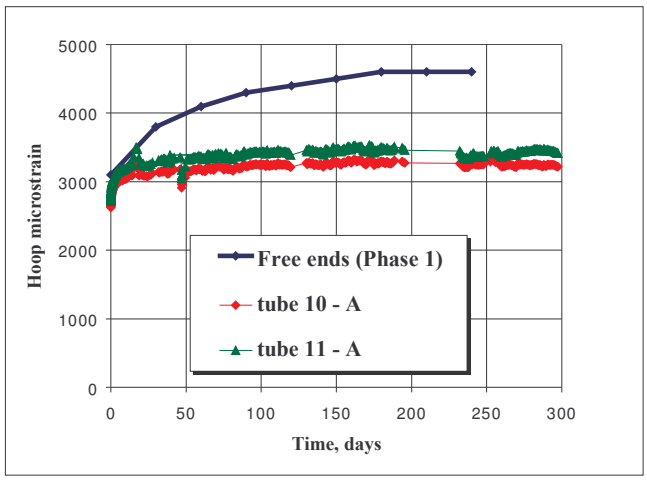
Given the large amount of data collected, there is only space here to show some examples of the creep behaviour. Figure 9 shows strains measured at the start and end of creep and recovery.

Figure 9. Creep hoop strains (10 months 38 bars, 17 months 8 & 17 bars) and recovery (1 month)



At first sight these creep strains appear low, lower than creep under free end loading conditions reported for Phase 1 of the project, Figure 10. The biaxial stress state apparently reduces the hoop deformation, and a ply stress analysis suggests shear stresses are higher in the ply for free end conditions (LeBras 1995), which may explain the difference. From a practical viewpoint free end loading conditions are subject to friction due to the need for a joint between the sleeve and the tube so fixed end load conditions are easier to control experimentally.

Figure 10. Creep of two fixed end tubes and one with free ends, 60°C 38-40 bar.



3.2 *Influence of damage*

Different levels of damage were introduced into three tubes by loading under internal pressure. The procedure for these tests was the following:

First, the tubes were pressurised at EDF. The pressures (hoop stresses) chosen were:

D1 19 bars (35 MPa), just above the first acoustic emission recording, at the elastic limit.

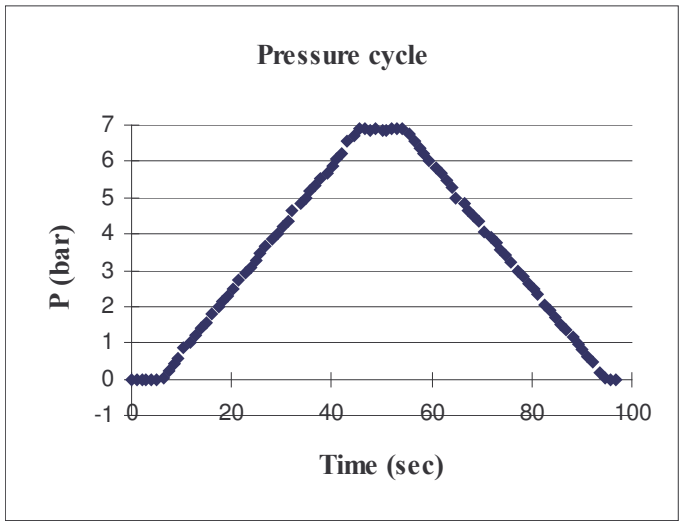
D2: 38 bars (76 MPa), an intermediate damage state

D3: 76 bars (130 MPa), corresponding to extensive damage.

These values should be considered in relation to the pressure at failure by leakage (weeping) of these cylinders at 197 MPa (LeBras 1995).

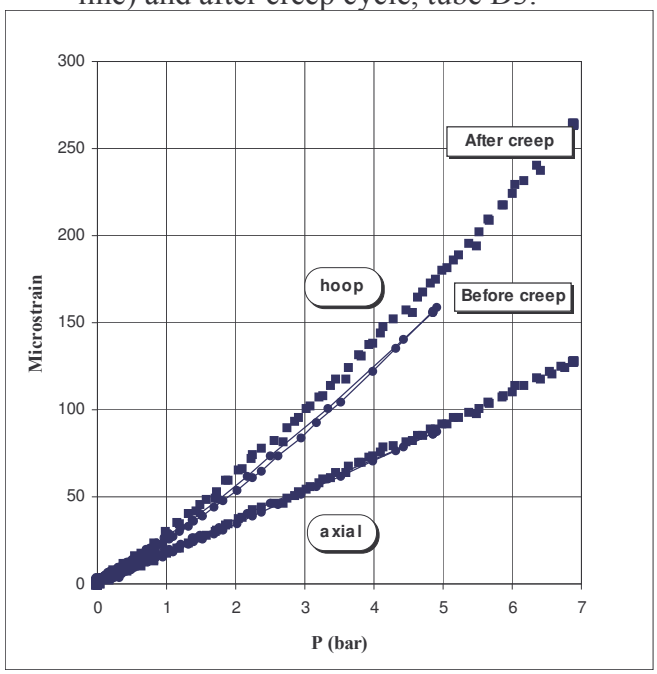
They were then shipped to IFREMER and low pressure cycles (up to 7 bars) were performed to establish their apparent initial stiffness in the damaged state, Figure 11. (Note that the initial 'damaging' pressure cycle resulted in some small permanent hoop strains, which are not taken into account in the subsequent stiffness determination as new strain gauges were bonded at IFREMER, so it appeared that the D2 and D3 damaged tubes were stiffer than the undamaged tubes). The three tubes were then loaded in creep at 40°C and 17 bars for an 18 month cycle, including 17 months of creep and 1 month's recovery. The presence of the damage affected the creep behaviour, increasing the creep strains slightly and causing more scatter in strain readings. At the end of this period a second low pressure cycle was applied to determine apparent residual stiffness.

Figure 11. Low pressure cycle before and after creep.



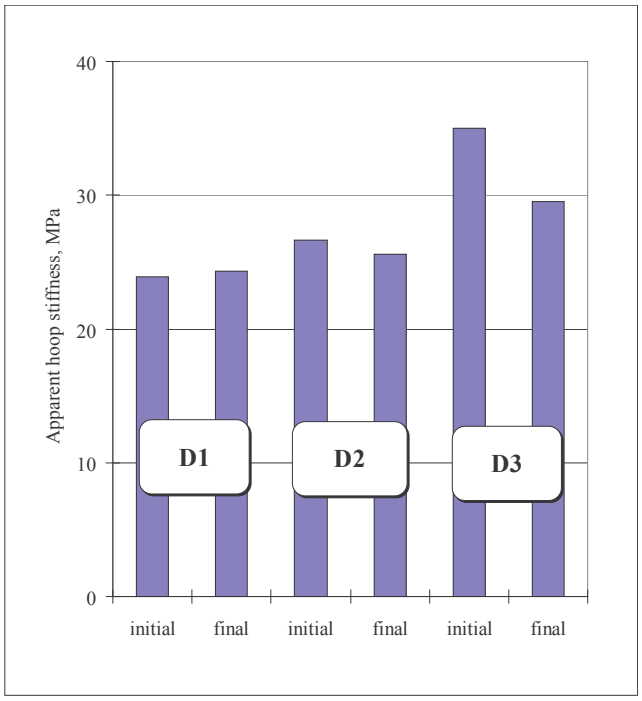
The comparison of the strain gauge response at low pressure before and after creep showed a loss in apparent stiffness for the D2 and D3 tubes, Figures 12 and 13.

Figure 12. Strain versus pressure before (solid line) and after creep cycle, tube D3.



The tube is less stiff in the hoop direction after creep, while the axial response is unchanged (curves superposed).

Figure 13. Apparent hoop rigidities (hoop stress/hoop strain), damaged tubes, before and after creep & recovery cycle.



3.3 Tube assemblies

The bonded and mechanically-joined assemblies behaved in a satisfactory way throughout the tests, and no leaks were noted. The presence of the mid-section joints did not affect the strain gauge recordings. Displacement transducers measuring relative axial displacements of the two half tubes showed no movement.

4 CURRENT AND FUTURE RESEARCH

Research work at IFREMER and EDF is continuing in this area. Current projects are concentrated in three areas.

First, more work is being carried out on the resin behaviour in order to quantify resin degradation kinetics and the influence of hardeners on long term behaviour. Interface studies are also underway.

Second, studies of tolerance of tubes and bonded joints to defects, delaminations and impact damage are being performed. An example is the application of fracture mechanics tests to curved, multi-layer specimens (Ozdil 1999).

The third area is NDT, particularly applied to bonded joints. The use of acoustic emission in-situ is being studied.

Finally, the long term behaviour of composite cylinders under external pressure is also being examined with laboratory tests and deep sea measurements.

5 CONCLUSIONS

This paper gives a brief overview of some of the results available from aging and creep tests performed within a collaborative project between IFREMER and EDF over the last 10 years. The development of a resin degradation model has enabled predictions to be made of the useful lifetime of composite panels and then applied to tubes. Creep tests have shown that creep strains in the hoop direction are lower when fixed end conditions (biaxial stress) are applied than for the free end conditions used in previous studies. Damage introduced by a pressure overload is shown to increase creep strains slightly and apparent stiffness measured before and after tests is shown to decrease. The two assembly systems studied behaved satisfactorily.

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