INFLUENCE OF THE FIBRE/MATRIX INTERFACE ON THE LONG TERM DYNAMIC AND ENVIRONMENTAL STRESS CRACKING BEHAVIOUR OF GLASS/EPOXY COMPOSITES

Virginie LIETARD, Patricia KRAWCZAK and José PABIOT

ECOLE des MINES de DOUAI, Department of Polymers & Composites Technology,
941 rue Charles Bourseul, BP 838, F-59508 DOUAI, FRANCE
http://www.ensm-douai.fr e-mail: plastics@ensm-douai.fr Fax:+33 3 27 71 25 25

SUMMARY: The mechanical behaviour of unidirectional glass/epoxy composite materials has been investigated in air & water, at ambient & higher temperatures under bending loading (static & dynamic) as a function of the interface quality. The results highlight the combined effects of the environment (air/water), the temperature (from 40°C to 90°C), the sustained load and the interface quality on the durability of the composite materials studied. It appears also that using the time-temperature equivalence principle in order to predict lifetimes at very long term is not so easy, because of the changes in damage mechanisms which occur within the temperature and stress ranges investigated here for the loading mode chosen.

KEYWORDS: interface, glass fibres, polymer matrices, environmental stress cracking (ESC), creep, dynamic fatigue, durability, water

BACKGROUND

Experience shows that the quality of the fibre/matrix interface is likely to very strongly influence the durability of glass/resin industrial composite parts: Previous studies, carried out on glass/epoxy industrial piping in dynamic fatigue under internal hydraulic pressure, have shown that the choice of the reinforcement sizing could multiply or divide by 30 the lifetime of the part [1]. Extensive efforts have been made up to now in order to analyse, understand and explain the damage mechanisms involved at the interface, on the basis of different approaches: Fracture mechanics and macromechanics [2], micromechanics [3] or physical chemistry [4], taking into account in the last case some hydrolytic ageing effects.

Nevertheless, when industrial parts such as pipes or tanks are used under internal pressure in nuclear power plants or offshore platforms, the main problem is that the degradation of the composites is the result, at the same time, of their mechanical fatigue, of their contact with the medium contained inside the pipe and of the synergy of these two external aggression types, that is to say, of environmental stress-cracking effects. These phenomena are thus likely to

induce catastrophic unpredictable failures, even under very low stresses and in neutral media (i.e. non aggressive fluids). Such environmental stress-cracking effects are not limited to composite materials, they exist also for metals and plastics, but are amplified and more complicated in the case of reinforced plastics [5-9], because of the heterogeneity of these materials and the necessity to take into account fibre-matrix bonding effects (interface).

In that context, this paper aims to investigate the influence of the fibre/matrix interface on the long term behaviour of unidirectional glass/resin composite materials submitted to environmental stress-cracking conditions under imposed mechanical loading in water and at higher temperatures. The effect of the loading mode (static or dynamic fatigue) is also considered. The present work is a part of a wider research program on environmental stress-cracking, where, among others, cracks initiation and propagation phenomena are investigated thanks to fracture mechanics [10].

EXPERIMENTAL MEANS

The basic study is carried out on two unidirectional E-glass/DGEBA epoxy (DETDA curing agent) composite materials made by filament winding in the same thermomechanical conditions (same curing cycle), but with a unique difference of constitution: the nature of the fibre reinforcement sizing. Two formulas, likely a priori to produce extreme variations of mechanical behaviour, have been chosen because of their incidence on fibre-matrix bonding: an optimum commercial reference, called «epoxy specific», and no sizing. The materials have similar fibre contents of 76,5 (±0,5) % by weight, but a void content and a glass transition temperature slightly different, respectively 3,5% and 130°C for the epoxy specific sized material and 1,6% and 111°C for the unsized material, the short term mechanical properties being the same (bending strength of 1050 MPa and bending modulus of 39 200 MPa). A third formula is used for dynamic fatigue with a «polyvalent» sizing. Mode I cracks initiation and propagation energies of the materials are measured as described in [2].

The mechanical behaviour is investigated under constant loading in 3-point bending at 60°C and 90°C in air and in water. The equipment used is a creep testing stand, making it possible to apply through a beam a constant load at the midspan of a test coupon of 70x15x3 mm mean dimensions, simply placed on two supporting points 52 mm apart and with fibres oriented in the sample long axis direction. A heat-regulated chamber or bath allows the exposure of the test coupon to a certain environment (ambient air or demineralized water) and at a given temperature. Before loading of the test specimen, it is kept during one hour in the environment chosen (air or water) in order to achieve a full thermal stabilisation. Loading is achieved quickly (< 5 s), smoothly and with a good reproducibility with an electric jack. The maximum deflection is recorded continuously as a function of time until final failure by means of a displacement sensor attached to the load pad.

On similar samples, 3-point bending dynamic fatigue tests are carried out at constant amplitude of deflection, at a frequency of 1,5 to 2 Hz and room temperature. The maximum induced stress is recorded continuously as a function of time by means of a load sensor attached to the load pad.

RESULTS

Effect of environment and temperature

First the effect of the liquid environment (water) on the creep behaviour until failure has been investigated on the basis of a comparison with the behaviour in air in the same conditions. Tests have been carried out at the same loading level corresponding to 50% of the short term bending strength, at both temperatures of 60°C and 90°C.

The creep curves (**fig.1**) obtained for both sized and unsized materials show some particular features:

- in air, the strain does not vary a lot, neither at 60°C nor at 90°C, and a saturation appears at long term which augurs no damage initiation, as was predictable under such a relatively low loading level of 50% of the short term strength;
- in water, the strain increases very rapidly after a period of slow variation similar to the behaviour noticed in air; it leads to failure after very short times (for example about 2 min and 40 h, respectively for unsized and sized materials at 90°C, while no damage appears in air after two months;
- the effect of temperature is very pronounced in water, as failure times are reduced by 1,5 to 2 decades (depending on the material) at 90°C compared to 60°C, while no significant effect occurs in air except the stiffness modification.

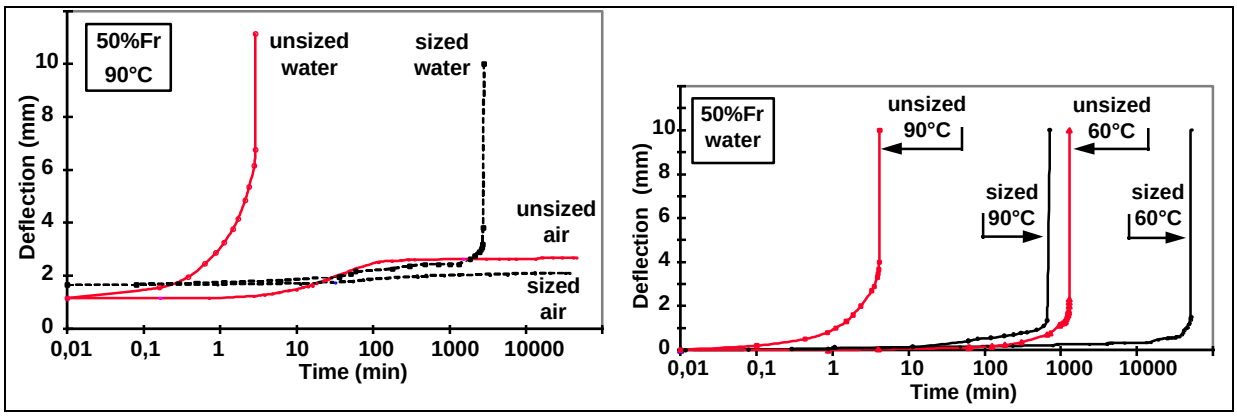

Fig.1: Bending creep curves of unsized and sized materials: Effect of (left) environment at 90°C and (right) temperature in water

It is thus confirmed that the nature of the environment has a great influence on the long term behaviour of composites submitted to a permanent mechanical stress; water in particular can induce catastrophic hardly predictable failures, as it has been already shown [11].

Effect of the interfacial quality

Furthermore, the effect of the interfacial quality on the mechanical behaviour under permanent loading in hydrothermal conditions has also been highlighted: the creep curves (**fig.1**) show that, for a same hydrothermal environment and a same loading level, the ability of the composite to deform increases and that lifetimes are reduced by 1.5 (at 60°C) to 3 decades (at 90°C) when reinforcement fibres are unsized.

Nevertheless, when under monotonic short term loading the fracture mode is of flexural type, due to the normal stresses induced by bending, delayed fractures appear in creep, which are

either of flexural type, or of delamination type, due to the shear stresses induced by transverse forces, or of coupled flexure-delamination type, with or without fibre pull-out. In the case of the sized composite two damage modes can thus be distinguished (**photo**):
- (F) clean flexural fracture without fibre pull-out,
- (FD) clean fracture with a flexure-delamination coupling and ply separation.
In a same manner in the case of the unsized composite, three damage modes are observed:
- (FP) clean flexural fracture with fibre pull-out,
- (D) pure delamination with ply separation,
- (DP) partial fracture in flexure with delamination without ply separation and with fibre pull-out.

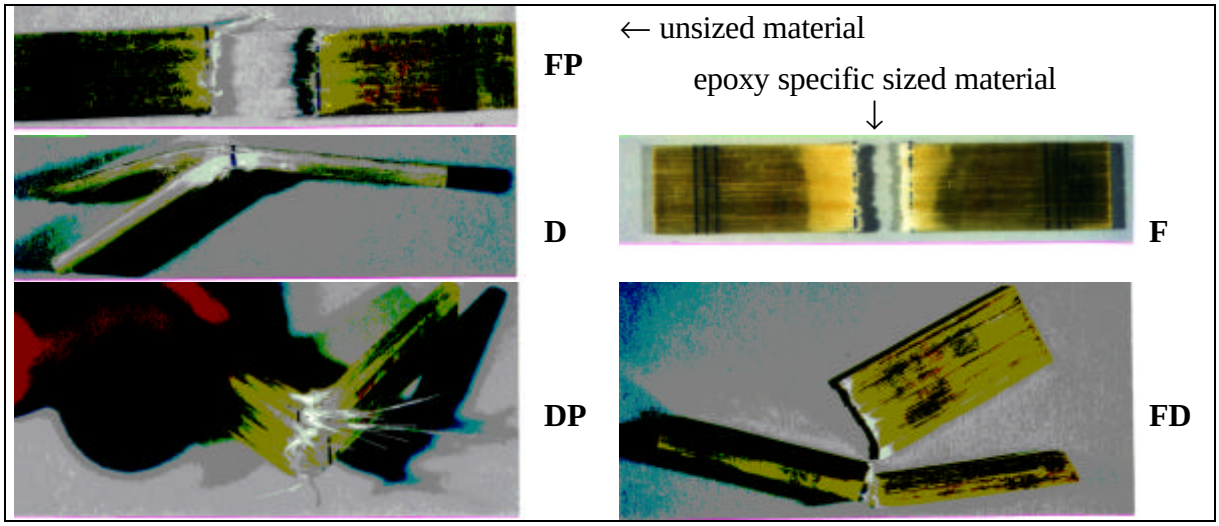

Photo: Fracture modes of the unsized (left) and sized (right) materials

It will be shown hereafter (**fig.2**) that, for a given temperature, delamination appears mainly after long times (low loads) and is more frequent for the unsized material than for the sized one. That means that the decrease of the shear strength at the fibre-matrix interface due to ageing is far quicker for the unsized material.

The SEM analysis of the fracture surfaces confirms also the existence of specific damage modes according to the interfacial quality, whatever the fracture mode may be (flexure or delamination):
• when the fibre reinforcement is sized, the presence of large areas of resin on the fibre surface confirms a damage propagation through the resin, which is the sign of a good interfacial adhesion retention;
• when the fibre reinforcement is unsized, the glass fibres are mainly smooth, the sign of a damage propagation along the fibre-matrix interface and of an interfacial adhesion loss under the combined effects of a mechanical stress and a water environment.

The behaviours observed as a function of fibre sizing are very complicated to explain because:
• of the 3-point bending loading mode imposed, inducing, on the one hand normal stresses in the fibre direction (maximum at the surface which is in direct contact with the fluid), on the other hand shearing stresses (maximum at the mid-plane and high enough to generate damage during ageing, even if low because of the large span length chosen);
• of the lack of knowledge about the chemical nature of the «epoxy specific» sizing and its distribution around and along the fibres;
• of the differences measured between some characteristics of the materials tested, especially void content and glass transition temperature.

The higher void content of the sized composite could thus contribute to the decrease of its interlaminar shear strength. In a same way, the lowest glass transition temperature of the unsized material could be the origin of the highest ability to deform noted at high temperature: Indeed a change in the behaviour of this material has been observed from 90°C, when tested at different temperatures under monotonic 3-point bending. Near the glass transition temperature the easiest chain mobility enables higher and easier deformations, and the mechanical behaviour of the unsized material, which was brittle initially, changes as a consequence into a viscoelastic/plastic behaviour with yield point.

In short, these results show that the fibre-matrix interface quality is both an important and complex factor in the environmental stress-cracking damage phenomena of composite materials: In environmental stress-cracking conditions at constant stress and in water, the epoxy specific sizing ensures a better long term strength, the lifetimes being strongly reduced without sizing; on the contrary, early failures are induced by a significant interfacial damage. Nevertheless the damage induced by the simultaneous actions of mechanical and hydrothermal ageing is also dependent upon parameters, other than the presence and chemical nature of the coupling agents, which are likely to modify the environmental stress-cracking behaviour:

- morphology of the interfacial region, which is closely related to the glass fibre topography, to the sizing composition and its deposition conditions,
- proper control of the manufacturing of the composite (for given thermomechanical and technological conditions).

Structural mechanisms and behaviour prediction

When different loading levels are applied, it is possible, not only to monitor the strain variations as a function of time, but also to plot the lifecurve (stress vs. time-to-failure) of a material submitted to simultaneous actions of a mechanical stress and a liquid environment at a given temperature, providing experiments are carried out until final fracture.

The results obtained at 5 different temperatures between 40 and 90°C are reported on **fig.2**, where the applied loading is given in term of maximum bending stress. Trend lines are drawn for each ageing temperature in order to improve the results presentation. Moreover the corresponding fracture mode (descriptions detailed previously) is indicated for each point.

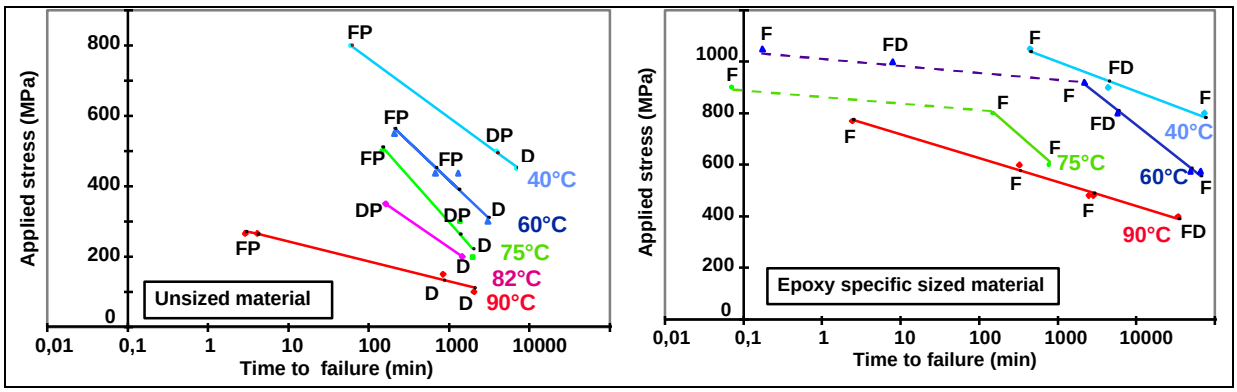

Fig.2: Time to failure as a function of sustained load in environmental stress cracking conditions for (left) unsized and (right) sized materials

Behaviour of the unsized material

Even if the fracture modes of the unsized glass-epoxy composite are different for each temperature according to the stress level applied, three regions can nevertheless be defined, for which a unique fracture mode is associated. A schematic and approximate representation of these three regions is given on **fig.3**:

- the mode of clean flexural fracture with fibre pull-out (FP) and the mode of pure delamination with ply separation (D) appears respectively for higher and lower stress levels, the former reaching the delayed tensile strength of the fibres, the latter reaching the delayed shear strength of the fibre-matrix interface;
- the mixed mode of flexure & delamination without ply separation and with fibre pull-out (DP) is associated to intermediate stress levels and constitutes a transition between the two previous extreme modes.

The notions of higher and lower stress levels are defined for each ageing temperature in relative values with respect to the short term 3-point bending strength at the considered temperature. Considering the approximate limits of the different regions of fracture modes, the high and low levels correspond to bending stresses respectively higher than 50% and lower than 30% of the short term strength of the material.

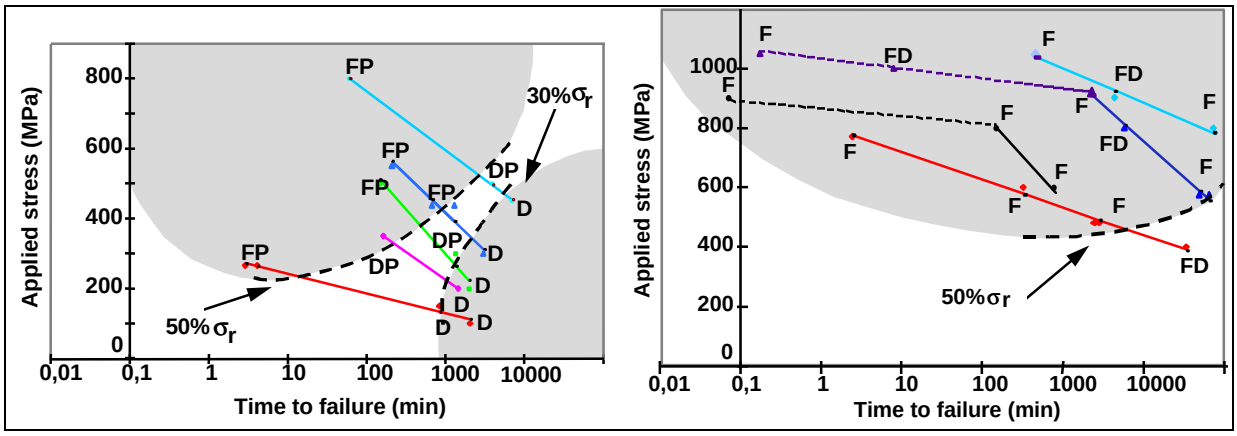

Fig.3: Regions of major damage mode for (left) unsized and (right) sized materials

A multiplication of the number of tests, especially at lower stresses to obtain longer times-to-failure, could make it possible to define more accurately the position of the above mentioned zones and the lifecurves associated to each fracture type. Nevertheless it seems possible at first to bring together the present observation and the hypothesis made by PHILLIPS [8], according to which it is necessary to distinguish three different stress/environment/lifetime ranges: a first one independent of the environment, a second dependent on both the stress and the environment, and a last one independent of the stress.

These three ranges appear here clearly for the unsized composite for which:

- at shorter lifetimes (less than about 1000 min), the clean flexural fracture (FP), similar to that observed for a dry material under short term monotonic bending loading, is associated to a domination of mechanical damage processes on water absorption related processes;
- at longer lifetimes (higher than about 1000 min), the delamination fracture (D), revealing a significant interfacial damage, reflects a major contribution of damage processes related to hydrothermal ageing;
- at intermediate lifetimes, the mixed fracture mode in flexure and delamination without ply separation and fibre pull-out (DP) constitutes the transition between highly mechanical and highly hydrothermal damage processes.

However one should keep in mind that environmental stress-cracking involves a coupling of mechanical and hydrothermal ageing, without which no fracture could occur so rapidly. As previously described, for the same stress levels leading to a rapid and clean flexural failure under the combined actions of mechanical and hydrothermal ageing, the only thermomechanical ageing in air generates neither rupture nor significant mechanical damage for short times (**fig.1**).

Similarly, on the basis of an analysis of the water absorption curves of the unsized material, which shows no saturation due to complex absorption mechanisms, the approximate determination of the times τ_D characteristic of water diffusion processes at 60 and 90°C ($960<\tau_{D(90°C)}<1080$ min and $15360<\tau_{D(60°C)}<17340$ min) clearly shows that, at longer times, the only knowledge of the diffusion processes related to hydrothermal ageing is not sufficient to predict the damage mechanisms linked to the combined actions of a water immersion and a constant mechanical loading.

As a consequence, if diffusion phenomena at shorter times are obviously not sufficient to induce in the unsized composite a genuine hydrothermal damage of the fibre-matrix interface, especially in the sample heart where the shear stresses are maximum, they can nevertheless be sufficient to accelerate damage processes, inducing, locally at the surface where normal stresses are maximum, plasticisation and differential swelling phenomena which are respectively accompanied by an increase of molecular mobility and a decrease of mechanical cohesion on one hand, and by the creation of internal mechanical stresses on the other hand. Similarly at longer times, the only effect of an hydrothermal ageing would not be enough to produce such a catastrophic delamination failure. The existence of a mechanical damage, even if slight, created at the very beginning of the material loading, can ease indeed the hydrothermal damage processes through an acceleration of the diffusion processes along the microcracks induced mechanically.

Because of these various fracture modes obtained under such a 3-point bending loading for the unsized composite at each ageing temperature, it is consequently impossible to warrant the existence of a single damage mechanism throughout the whole lifetime range considered. That means that the behaviours can not be represented only by the trend lines previously drawn to improve data presentation. Unfortunately in the present state of experimentation, there is not enough available data to determine the lifecurves associated to each of the three fields.

Behaviour of the epoxy specific sized material

When the fibres are epoxy specific sized, the resistance of the composite material to hydrothermal ageing under mechanical stress is better: For this reason longer testing times have been required. For lifetimes going up to 7 weeks, two fracture modes appear but no trend could be defined. The clean flexural fracture mode (F) prevails the most often but nevertheless from time to time a mixed mode clean fracture in flexure-delamination with ply separation (FD) occurs. This lack of clear trend, at short as well as at long lifetimes, can be justified by the existence of a random parameter in the material, such as voids and/or non homogeneity of the sizing distribution on the fibre surface, both being difficult to control but generating a decrease of the shear strength of the composite independently of any kind of ageing.

As a result, up to 7 weeks of hydrothermomechanical ageing (from 40 to 90°C), a single damage mechanism seems to mainly dominate the behaviour of the sized composite and to induce a clean flexural fracture. This fracture mode is comparable to that observed for the unsized material at mechanical stresses higher than 50% of the ultimate stress (**fig.3**), even if SEM analysis shows a better fibre-matrix adhesion in case of fibre sizing.

Thus it appears that, for the sized material also, it is possible to find the environmental stress-cracking behaviour range associated to mechanical loads higher than 50% of the short term strength, and for which the prevalence of mechanical damage processes has been isolated for the unsized composite. However as the epoxy specific sizing warrants a higher shear strength, the location of this clean flexural fracture range is extended to longer lifetimes: The lifetimes associated to a clean flexural failure of the unsized composite do not exceed 1000 min while they are approaching 7 weeks for the sized composite. Consequently, due to the extension of the clean flexural fracture mode of the sized material towards higher lifetimes, it is not possible to investigate the damage range governed by hydrothermal mechanisms within a time period initially limited to 10 weeks.

Moreover it must be noted that the point 90°C / 400 MPa (**fig.3**), for which a clean mixed mode fracture in flexure and delamination (FD) has been found, does not seem to be associated to the prevailing mechanical damage mode. The SEM analysis of the fracture surfaces shows indeed some first interfacial debonding and thus confirms the existence of a transition range similar to that of the unsized material, for which the mechanical (related to a clean flexural failure) and hydrothermal (related to a delamination phenomenon) damage processes coexist. One could object that such a fracture mode (FD) within the prevailing purely mechanical damage range has been previously related to the presence of voids: in that previous case however the SEM analysis of the delaminated surfaces had shown a good fibre-matrix adhesion.

Finally, if the determination of the regression lines associated to the single behaviour range observed highlights a similar linear trend for each ageing temperature, some deviations (indicated on **fig.3** by doted lines) appear however at very short times: They can be explained by a limited sensitivity of the experimental method at times lower than one minute. At last, as the mixed mode clean flexure-delamination fractures (FD) follow the same trends as the clean flexural fractures (F) in term of lifetimes, it seems that the delamination phenomena induced by the existence of voids does not modify significantly the clean flexural fracture processes.

Effect of a dynamic loading

The effect of the fibre-matrix interface on the dynamic fatigue behaviour is investigated at first in the less hard conditions, that is to say at room temperature, in air and under imposed strain, while other on-going experiments are reproducing testing conditions similar to those previously chosen for static fatigue.

Tests have been carried out for the three different materials at ambient temperature under the same imposed strain corresponding to 70% of the short term ultimate deflection in 3-point bending. The results obtained (**fig.4**) confirm the effect of the interface on the durability: variations reaching 230% on the number of cycles at damage initiation N_{init} and more than two decades on the final failure N_{fail} are observed, with a good reproducibility (about 10% on the cycle number). Moreover an interesting relationship appears between the mode I crack initiation energy and the cycle number at first damage in dynamic fatigue; such a relationship

has already been noticed for industrial parts (composite pipes under repeated pressure) [1,2,12].

Material sizing	G_{Ic} (J/m^2)	N_{init}	$N_{20\%}$	N_{fail}
poly-valent	120	700	$4{,}9.10^4$	$6{,}8.10^4$
epoxy specific	204	1300	$2{,}3.10^5$	$>1{,}5.10^6$
unsized	224	2300	$1{,}4.10^4$	$1{,}8.10^4$

N_{init} : cycle number at damage initiation
$N_{20\%}$: cycle number at 20% stiffness loss
N_{fail} : cycle number at failure

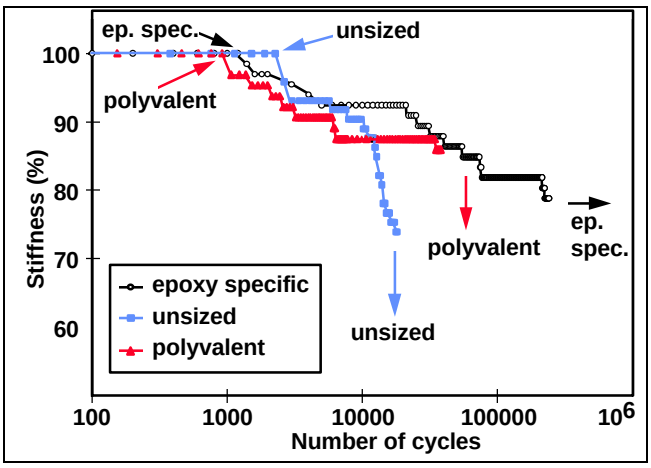

Fig.4 : Dynamic fatigue durability of unsized and sized glass epoxy materials at 23°C

CONCLUSION

It has been shown here for an unsized glass-epoxy composite material subjected to the combined effect of an hydrothermal ageing and a bending mechanical loading with transverse forces, that two extreme behaviour ranges can be defined, for which it is possible to isolate a prevailing damage mechanism among both the mechanical damage and hydrothermal damage, as well as a third intermediate range of transition between the two former ranges. For each ageing temperature in environmental stress-cracking conditions, the application of a mechanical stress approximately:

- higher than 50% of the short term strength leads to a rapid failure with a clean flexural fracture, significant of the prevalence of mechanical damage processes;
- lower than 30% of the short term strength induces damage mechanisms of slower kinetic, closely related to hydrothermal ageing, to which a delamination fracture is associated.

However some slight differences should be introduced in this ranking of the environmental stress-cracking behaviours: When a prevailing damage mechanism, either of mechanical or of hydrothermal nature, governs the final failure mode of a structure (respectively of clean flexural or delamination type), its behaviour is nevertheless not fully independent of the liquid environment or of the applied mechanical stress. The environmental stress-cracking phenomenon really involves an interaction between mechanical ageing and hydrothermal ageing, without which such a catastrophic and rapid failure of the composite could not occur.

The results confirm also that the presence of an epoxy specific sizing improves the environmental stress-cracking resistance of the glass-epoxy composite. The good retention of the interfacial properties allows thus up to 7 weeks ageing under a 3-point bending mechanical stress higher than 50% of the short term ultimate stress and at a temperature going from 40 to 90°C. Within this operating range, mechanical damage processes prevail, which induce a clean flexural fracture of the composite structure. However the presence, very difficult to control, of voids or of heterogeneities of sizing distribution in the material is likely to modify such a behaviour and to induce an additional delamination phenomenon. Furthermore it has been shown also that the full characterisation of the environmental stress-cracking behaviour of the sized glass/epoxy material in a reasonable time period was questionable because of the slowness of damage processes: The prediction of the durability of such composite structures is then all the more difficult.

Finally, regarding the development of a possible prediction model of the environmental stress-cracking behaviour of composites, it has appeared that using the time-temperature equivalence principle and other Zurkhov type laws in order to predict lifetimes at very long times is not so easy, because of the changes in damage mechanisms which occur in the temperature and stress ranges investigated: failure by delamination (D), tensile failure in flexion (F), with or without fibre pull-out (P). In the present work the existence of the different fracture modes is explained by the type of loading (3-point bending) which induces normal stresses and shear stresses. An analysis of the environmental stress-cracking behaviour is in progress under constant tensile loading on the one hand, under constant interlaminar shear loading on the other hand, in order to separate the failure modes. In a same way some dynamic fatigue tests performed in a controlled hydrothermal environment will be completed in the near future.

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