Hygrothermal effects on interlaminar strength and cracking of thick Graphite-Phenolic Laminates

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Fluctuations in hygrothermal ambient conditions, which comprise an intensive drying cycle, were found to affect the interlaminar residual strength of thick woven Graphite Phenolic laminates and induce surfacial interlaminar cracking in some cases. Specimens, which were cut from thick (~45mm) Fabric Graphite–Phenolic panels, perpendicular to the laminate plane, were exposed to drying conditions (40°C, 23%RH). Results showed high moisture loss associated with free shrinkage. After returning to room conditions (RC), significant free residual shrinkage strains were measured. Flexural three point bend specimens (3PB), in which the fabric layers are normal to the beam length were tested to failure. A reduction in residual interlaminar strength was found and attributed to the "restrained shrinkage mechanism", which induces tensile stresses near edge surfaces. Such mechanism which may cause interlaminar cracking in panels, are driven by the following processes: 1.) Water as a by product of the curing process which reduces the fiber matrix interfacial bonding strength. 2.) Interlaminar free shrinkage during drying. 3.) Near edge diffusion-drying process, causing interlaminar tensile stresses due to the restraining effect of the thick panel interior core. 4.) Low interlaminar tensile strength of the Graphite-Phenolic composite.

Taking into account the above interactive processes, 3PB specimens of two Graphite Phenolic composite systems were tested to failure at three stages in the above HT histories. A comparison between the two materials as obtained from the bending specimens proved to be a good indicator for the relative endurance of thick panels to interlaminar edge cracking. SEM micrographs of the fracture surfaces showed two microstructure differences which may control the macro interlaminar strength-cracking behavior: a.) The weaving pattern (plain vs. satin) and b.) The fiber surface morphology, which controls the fiber-matrix interfacial bond. The 3PB testing procedure serves as a simple straight forward methodology for selecting the optimal material for composite panels which undergo hygrothermal exposure. Current efforts are focused on modeling the HT behavior for quantitative predictions of interlaminar cracking process in composite panels.

Keywords: Phenolic - woven Graphite composites, Hygrothermal effects, Interlaminar cracking, Restrained shrinkage

1. Introduction

The complexity of hygrothermal effects on the mechanical properties of composite materials [1-6] is mainly due to the multiple scales and the large number of material parameters involved. Consider for example the basic problem of a uniform temperature change of a single unidirectional fiber composite, caused by natural cooling after matrix polymerization. The difference between the coefficients of thermal expansion of the fiber and matrix is a source of a residual stress field. This field is spatially non-uniform in the transverse plane near the fibers, uniform in the far field and also uniform *along* the fibers. In addition, local stress concentrations occur near the fiber edges (edge effects). The residual uniform field depends mainly on material properties only (moduli and thermal expansion coefficients) but the local fields depend on the *fiber size* (scale).

When a thick laminate (panel) made of multiple plies are manufactured, each with its own effective properties (different fiber orientations), the cooling stage in the manufacturing process yields two new sources of residual stresses in each ply: a uniform field due to their different thermal expansion and a "local" one near the edges of the *layers*. Again, the uniform field depends mainly on material (layer) properties but the latter is a function of the *layer thickness*.

Cooling rate and spatial temperature uniformity is also important. It is evident that material near the composite plate edges is cooled faster than its inner part, leading to thermal edge

stresses. This locality involves a scale related to the *plate thickness*. However, these stresses are transient, and if the cooling process is slow enough, their permanent effect may be reduced significantly.

Humidity and temperature fluctuations (HT loading history) during service add additional scales and complexity to the above problems, especially for Phenolic matrices, since water is a generic part of the polymerization process. Humidity transient changes may permanently affect the fiber-matrix bond strength, which is localized at a very small scale related to the adhesion interphase. In addition, new residual stresses are formed by restrained expansion (or shrinkage) of the plate thickness near its edges. As a result, interlaminar cracks may be formed, coalesce and cause an unacceptable damage to the structure.

Different time scales are also involved in the HT loading, since thermal changes have one typical scale (in our case, of the order of minutes to few hours), while humidity changes may cause transient stress fields with a time scale of days, weeks or even years. Thus, the design for durability of Graphite-Phenolic thick plates (panels) involves many time and spatial scales, as outlined briefly in table 1. As will be shown, nanosclae processes are also important but are excluded from this study.

Fiber-matrix interphase	$\sim 10^{-7}$- 10^{-6}
Fiber diameter	$\sim 10^{-5}$
Fiber bundles	$\sim 10^{-4}$
Layer	$\sim 10^{-3}$
Panel Thickness	$\sim 10^{-2}$
Panel planar dimensions	$\sim 10^{-1}$-1m

Table 1: Scales of various morphological characteristics in fiber composites (in meters)

Interactions of the above with strong non-isotropic behavior complicate the analysis and design even further. Moreover, developing testing methodologies from which the proper characteristics can be drawn is not straight forward. For example, how to plan a testing procedure which will establish the "interlaminar strength property" is one of the open problems, since direct mechanical testing of full scale thick panels is not practical. In fact, the notion of strength and failure in this case can be defined by more than one criterion: is it one crack of specific macro size or a group of crack (damage) of a certain extent. More than one criterion can be defined here, even if only the inerlaminar property is considered.

In this study, an experimental procedure (methodology), for evaluating the hygrothermal durability of thick Graphite Phenolic Material (GPh), made from woven layers is described. Specifically, the aim is to develop a relatively simple experimental procedure, which will help in choosing the most durable material composition from a given set of combinations. Another, longer range objective is to provide a baseline for an analytical model which will predict the interlaminar macrocracking characteristics (initiation, coalescence, growth rate etc.) as a function of basic mechanical parameters and the hygrothermal process variables.

During its service life, composite Phenolic panels are going over temperature and humidity changes, which may affect their mechanical performance. When put in a dry environment, the region near the edges is dried first due to the hygrothermal diffusion type processes, while the inner part is practically unchanged. Interlaminar tensile stressing and cracking mechanisms are activated under exposure to hygrothermal variations, due to the restrained shrinkage mechanisms [4]. In extreme cases, *microcracking* processes initiate, propagate and coagulate into severe interlaminar *macrocracks* which have a significant adverse effect on the mechanical performance of the laminate. It was found in our preliminary investigations that these mechanisms may prevail in GPh panels with certain lay-up compositions and may be attributed to a.) High anisotropy of the Graphite fibers, b.) Low transverse and interlaminar

strength of the GPh system due to weak fiber-matrix interfaces and c.) Internal high initial moisture content.

2. **Testing methodology**

The raw material is a thick composite plate (panel, 320x220x45mm), composed of 120 layers of woven (±45°) GPh fabric, as shown in figure 1.

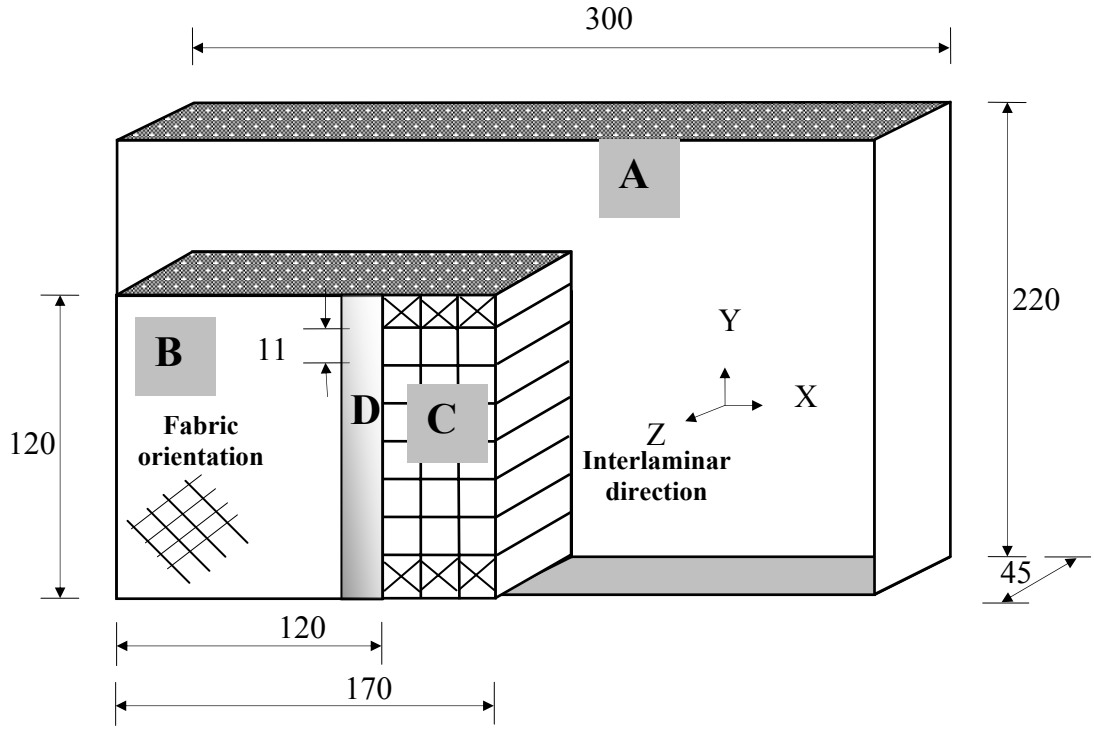


Fig.1. Illustration of specimen cutting procedure. All dimensions in mm. A block B (120x170) was cut first from a thick (45mm) panel A. Three slices (C), for 9 specimens from each, were then cut for three HT loading histories. The block B was dried as a panel. Then, its residual properties were examined by slicing (D) for 6 additional specimens

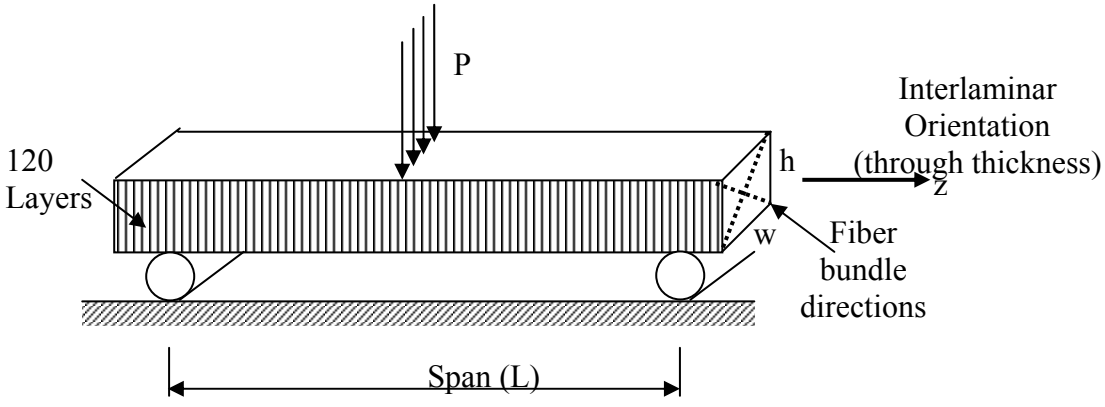


Fig.2: 3PB specimen: loading, geometry and layup configuration (schematic). L=32mm

Two types of materials (denoted as A4 and A5) were tested, having identical Phenolic matrix. The Graphite fabrics were different in two ways: first, weaving of A4 was a "1x1 plain weave" and A5 was a "8 Harness satin weave" and second, the Graphite fabrics were produced by two different fabrication processes. The effect of these differences will be

discussed in more details later. Autoclave curing process was also identical, namely, at 160°C and 14 atm.

To examine the HT effects, the following preparation steps were taken:

a. The panel A was kept closed in a plastic bag at room temperature (23°C) at all times.
b. The panel (~45mm thickness) was cut through a cross section far from its edges. Note that the cutting direction is 45° from the fibers directions (fig.1). Preliminary tests were conducted on specimens cut along the x and y directions but no difference in testing results were obtained. However, for tracking purposes, the "x" notation has been kept in the following.
c. Inner slices (part C in fig.1, 11mm thick) were taken by a second cut parallel to the first
d. The inner slices were cut into beam specimens of a square cross section (11x11x45mm).
e. Additional specimens (5x11x45) were used for hygrothermal shrinkage and weight loss measurements.
f. Three point bend (3PB) testing for interlaminar (z direction) strength measurements were conducted.
g. The bisected panel (part B in fig.1, 120x120x45mm) was hygrothermally exposed and inspected for near surface microcracks initiations, expansions and coalescence.

The mechanical 3PB (fig.2) and panel tests were conducted at four stages during the hygrothermal history:

a.) 38 days in room conditions sealed in bag at 23°C (RC) - denoted as **orcx**,
b.) 3 days at RC, and 14 days at 40°c and 23% relative humidity (*drying*), denoted by **dcx**
c.) 3 days at RC, 14 days of drying and 21 days of recovery at RC, denoted as (**drcx**).
d.) To find the equivalence between the performance of specimens and panels, the panel was cut *after* a **drcx** history (part D in fig.1) and its "made of" specimens were tested to interlaminar strength – denoted as **drcxp**.

The above timescales were chosen in accordance with the characteristic times for the completion of the diffusive processes inside the specimens, as obtained from the shrinkage and weight loss measurements, as shown in figs.3,4. The specimens with the first three HT histories were taken from the same original set (fig.1), i.e., 18 specimens were cut at the same time and divided into three groups of 6 for each history point (**orcx**, **dcx** and **drcx**).

Since cutting process involved water cooling, all specimens were given a three days period of "adjustment" at RC before HT exposure was started. All recorded time variables above *include* this period.

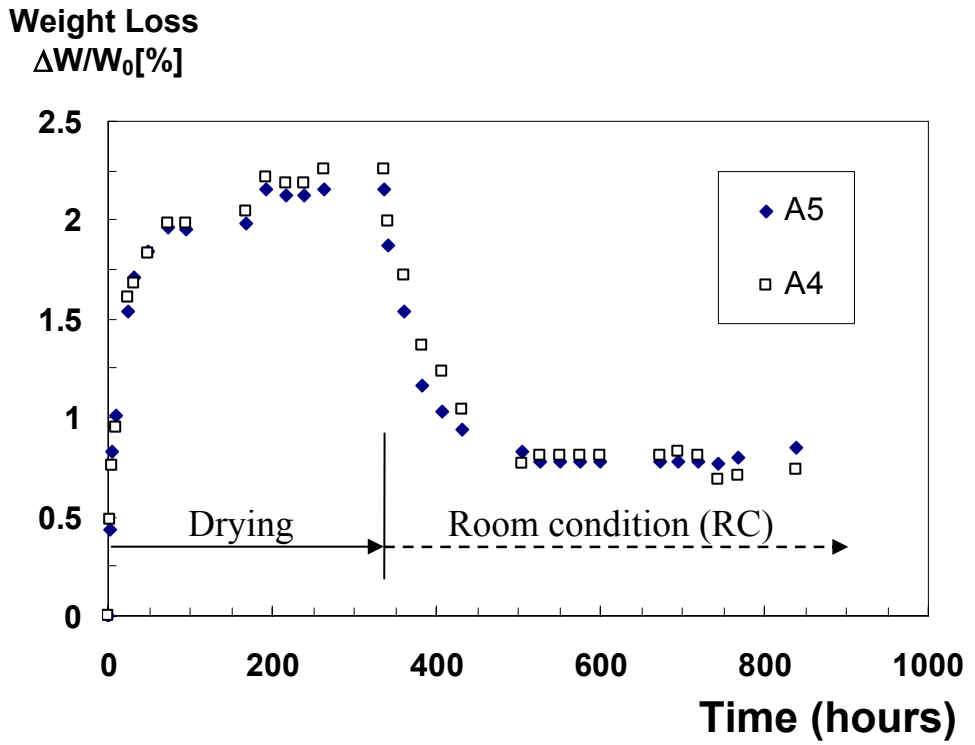
3. Test results

3.1 HT weight and dimensional changes

The weight loss (or gain) vs. time of a 5x11x45mm specimens under pure hygrothermal loads is shown in fig. 3 for the composite systems. Common exponential curves are observed, with a characteristic time of about two to three weeks, which justifies the choice of the specific timescales t(**dcx**) and t(**drcx**). Only partial weight recovery is observed at t(**drcx**). This may be due to the fact that heating (cooling) time scale is much smaller than the one for humidity, so that the recovery time interval between (**dcx**) and (**drcx**) was done essentially at 23°C while drying period (**dcx**) was at 40°C. Another possibility is that part of the water diffusion is irreversible, such as from locations where the water is trapped and is in micro-local compression. No significant difference between the two materials (A4 and A5) is observed.

The hygrothermal interlaminar (z direction) free shrinkage strain is shown in fig.4. A distinct difference between the two materials is seen, mostly during the initial drying stage.

Since the matrix of the two systems is identical, the above difference may be due to different fiber-matrix interfacial shrinkage and will be discussed later. Note also that the HT shrinkage is in the order of interlaminar failure strain of these materials, and cannot be ignored.



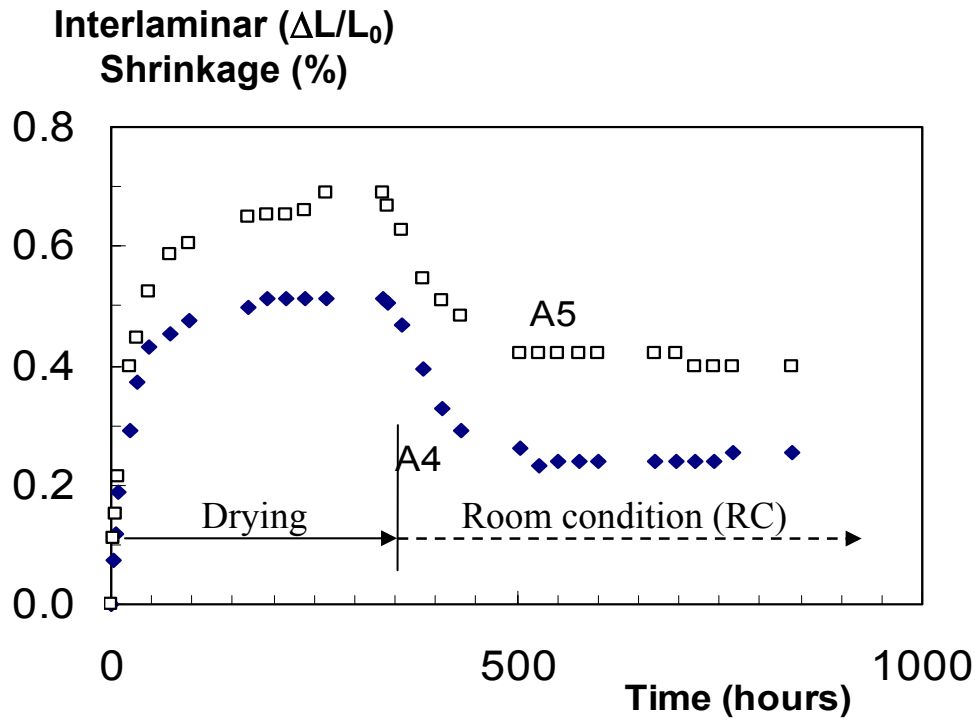


Fig. 4: Shrinkage through the thickness direction during the hygrothermal history

3.2 Three point beam tests

The 11x11x45 specimens were used as beams for the flexure tests. Results for A4 and A5 are shown in figs 5 and 6, respectively. It shows the stress-deflection relations of three stages in the HT history (**orcx**, **dcx**, **drcx**) for the beam specimens, which were cut at "zero time" (part C in fig.1). Test results of specimens which were cut from the panel at the **drcx** stage (denoted as **drcxp**) were also tested for comparison, which reflects the net restraining effect. From fig. 5 it is seen that for A4, the interlaminar flexure stiffness is changing dramatically by the drying exposure (three fold increase from the original to the driest state). On the other hand, the ultimate flexure strength is almost invariant, while the ultimate strain is affected accordingly. The behavior of A5 is significantly different. There are considerable differences in strength too, showing the highest value at the initial (**drcx**) stage, while the (**drcxp**) specimens show the lowest strength. The strengthening seen in (**drcx**) mechanism in not clear, but the weak case can be explained by interlaminar macrocracks which were observed on the panel z surface due to the restrained shrinkage mechanism. It is seen that A4 exhibits a "ductile" response and sustains higher flexural stresses, as compared to the brittle behavior of A5.

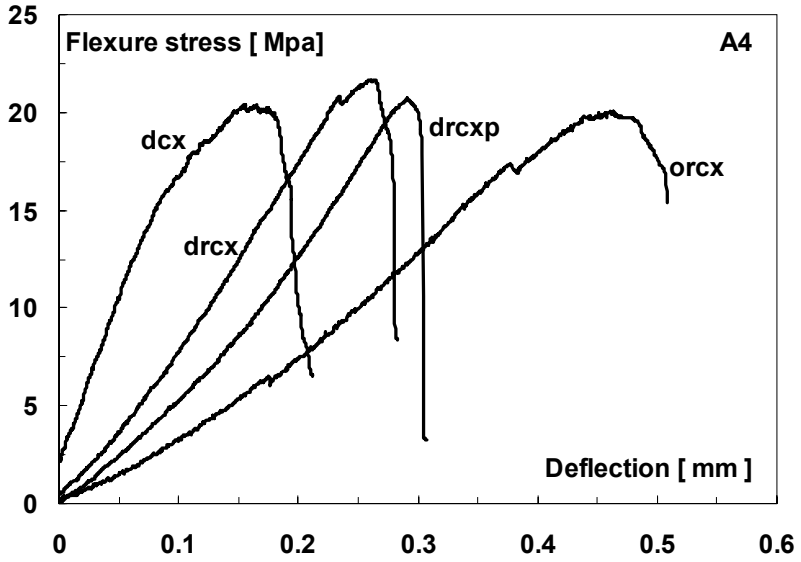


Fig. 5: Typical stress-deflection curves for material type A4.

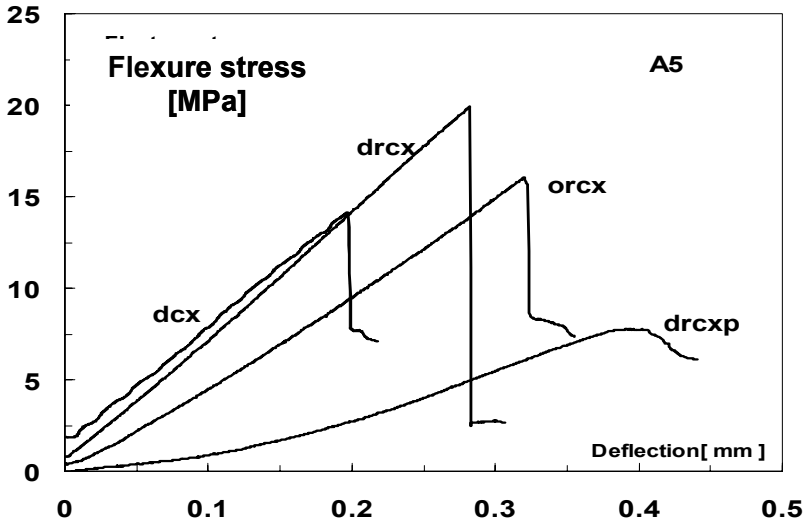


Fig. 6: Typical stress-deflection curves for material type A5

A diagrammatic comparison for the strength is shown in figure 7 and table 2 for all cases, where each value is the average of 6 specimens. The "over recovery" of A5, as seen in **drcx** vs. **dcx**, where the strength is comparable to A4 (~20MPa) is especially remarkable. Another significant result is the panel behavior of A5, which is the lowest of the four cases, both in stiffness and strength. This is due to the appearance of both micro and macro cracks. These cracks may be the reason for the high statistical strength dispersion of A5, when compared to A4, as shown in table 2. The panel macrocracks effect can be clearly seen in the **drcxp** results of fig.7.

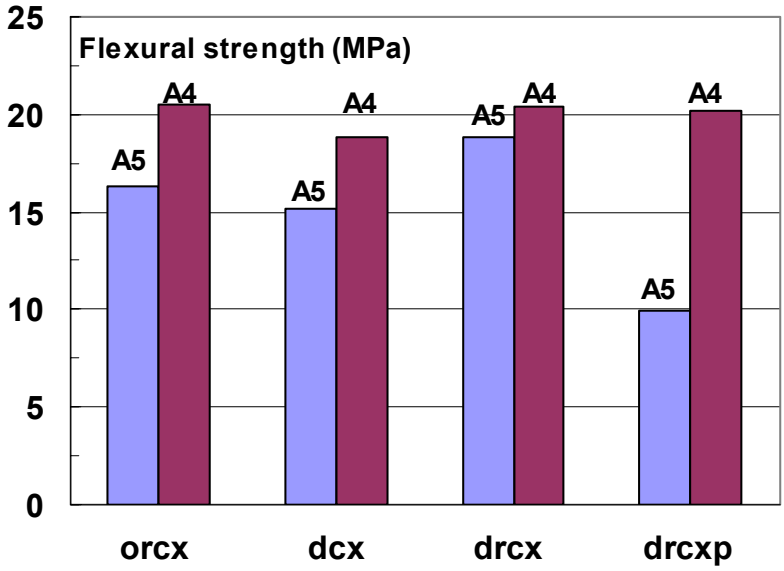


Fig. 7: Flexure interlaminar strength of A4 and A5 for 4 hygrothermal histories.

	orcx	**dcx**	**drcx**	**drcxp**
A4 (aver)	20.45	18.86	20.36	20.22
A4 (C.V.)	2.5%	5.0%	2.7%	2.7%
A5 (aver)	16.35	15.20	18.81	9.95
A5 (C.V.)	4.0%	7.5%	5.0%	24.1%

Table 2: Average (MPa) and dispersion of flexure strength

3.3 Micrograph study

To find the mechanisms which cause the above differences between the two materials, fractographs of the specimens were taken at each hygrothermal state. SEM micrographs of A4 and A5 surfaces after drying is shown in fig.8, which reveals a good adhesion between the Phenolic matrix and the fibers for A4 and almost no matrix around the fibers for A5. The fracture pattern is seen in figure 9, which shows the wavy bundle arrangement of A4 (plain weave), where macrocracking was not detected, as compared to the flat layer structure of A5 (satin weave), which allows for a macro cracks to develop.

Further details of the macrocrack morphology of panel A5 at the **drcxp** state can be seen in fig 10. This interlaminar failure is a consequence of the combined thermal+drying exposure and the edge restraining effects. Fibers are seen without any matrix attached to them, which is a sign of poor fiber-matrix adhesion, leading to interfacial microcracking in the A5 and is also compatible with fig.8 above. Further insight can be can be gained by higher magnifications as in figs.11-13 where fiber surfaces of A4 and A5 are compared. Fig.11 shows that the A5

fibers are smooth while A4 is relatively "warty", which improves interfacial bonding. A higher resolution micrograph is seen in fig.12, showing that the "warts" are not just matrix particles but an inherent part of the graphite fiber. An even more convincing picture is seen in fig.13, which is focused at the fiber-matrix interface for the two materials. The "warty" fiber surface has "blueprints" which are clearly seen on the matrix surfaces for A4.

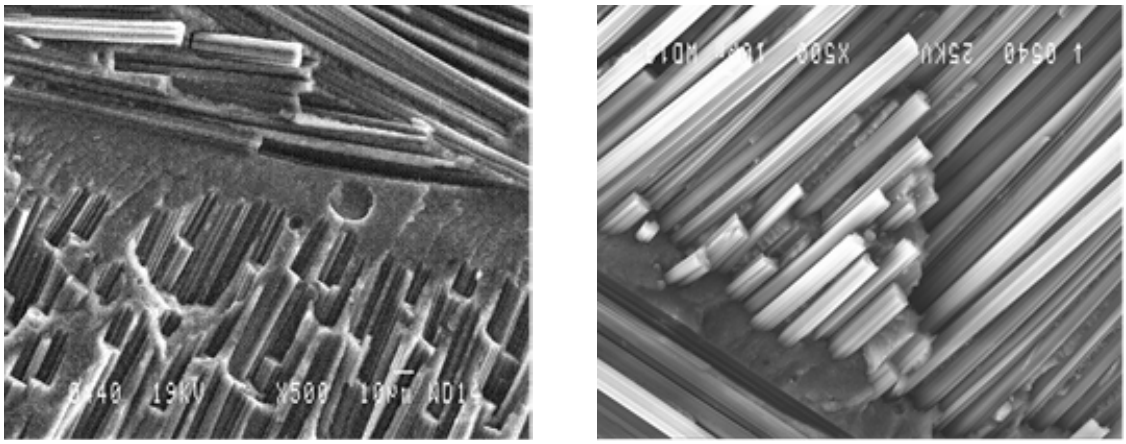


Fig.8: A4 (left) vs A5 (right) SEM micrographs of the fracture surface of beam specimens at the dried stage. Notice the adhesive (matrix) phase in A4 (x500).

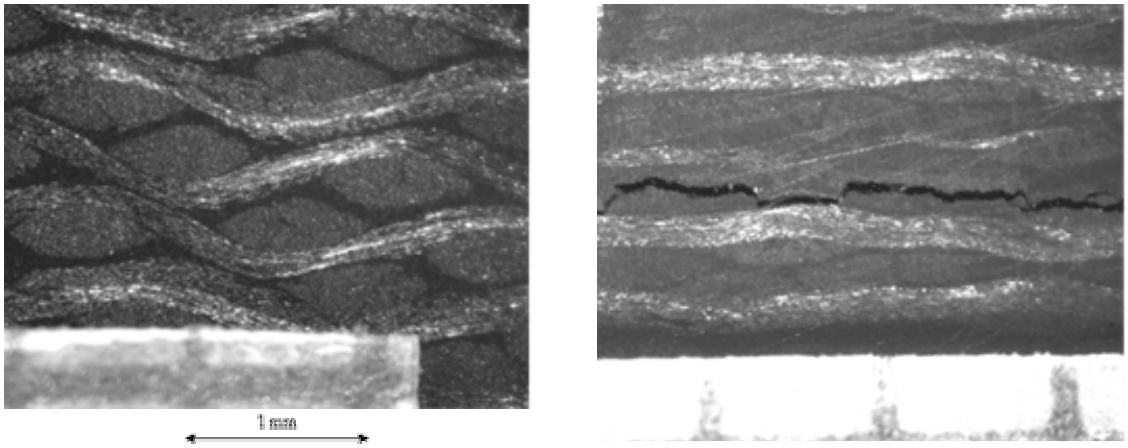


Fig. 9: Micrographs observed at 45° surface of panels after exposure to drying.. Left: Panel A4, no visible cracks after 14 days of drying. Right: Panel A5 – initial cracking detected after less than 24 hours (x40).

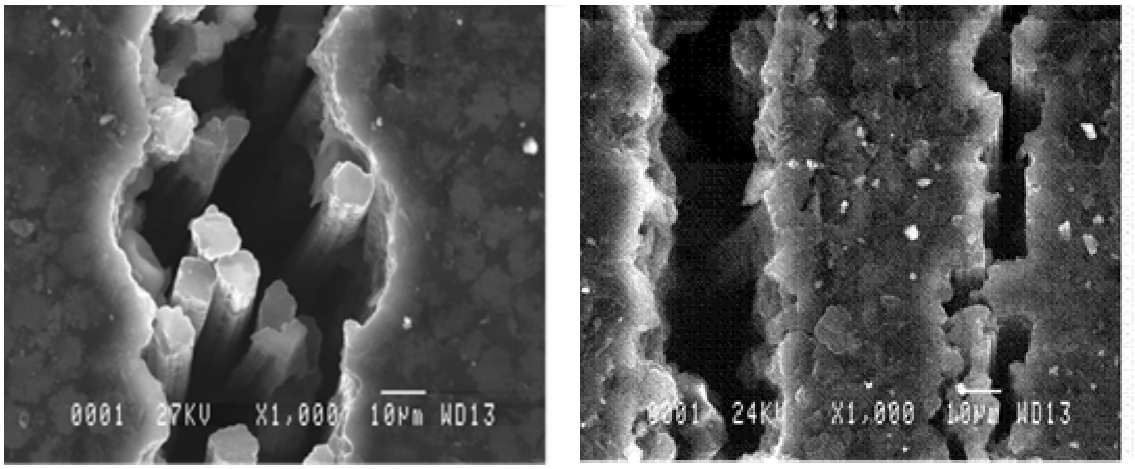


Fig.10: Panel hygrothermal (interlaminar) failure (micrographs observed at 45° surface after exposure to drying). A macrocrack (left) as a coalescence of small interfacial microcracks (right). (X1000)

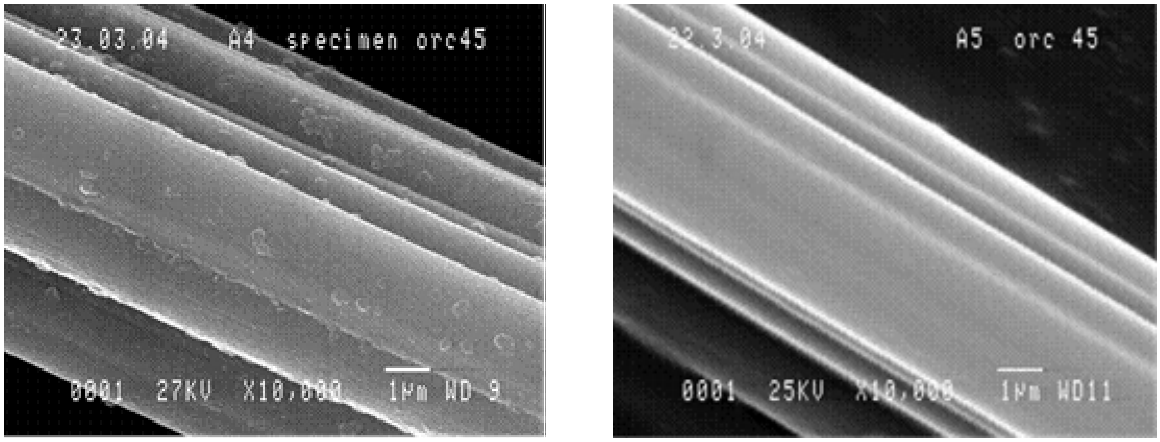


Fig. 11, SEM micrographs of typical fiber textures taken from fracture beam surfaces. Left: for A4 material, right: for A5 material (x10000).

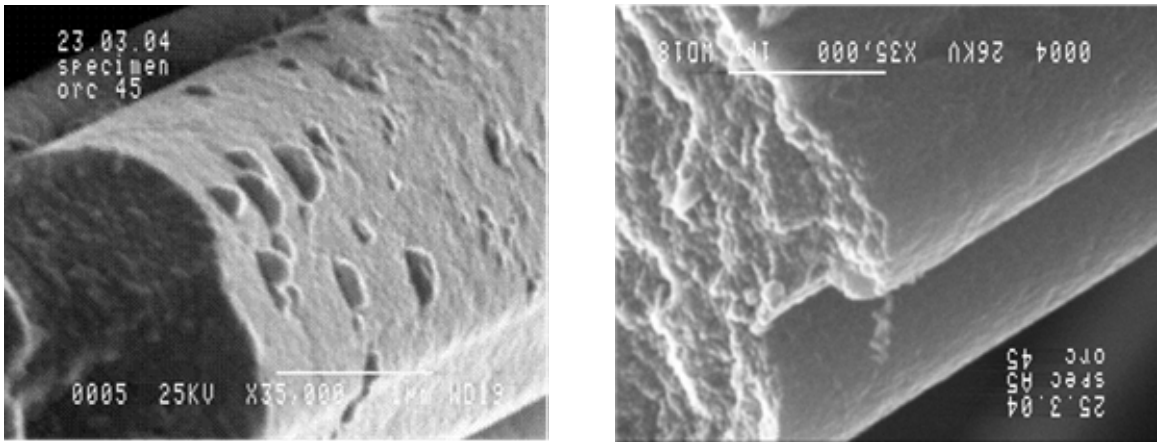


Fig.12., Fiber surfaces of A4 (left) and A5 (right) materials taken from fractured beam surface. Notice the relative "warty" surface of A4. (x35000)

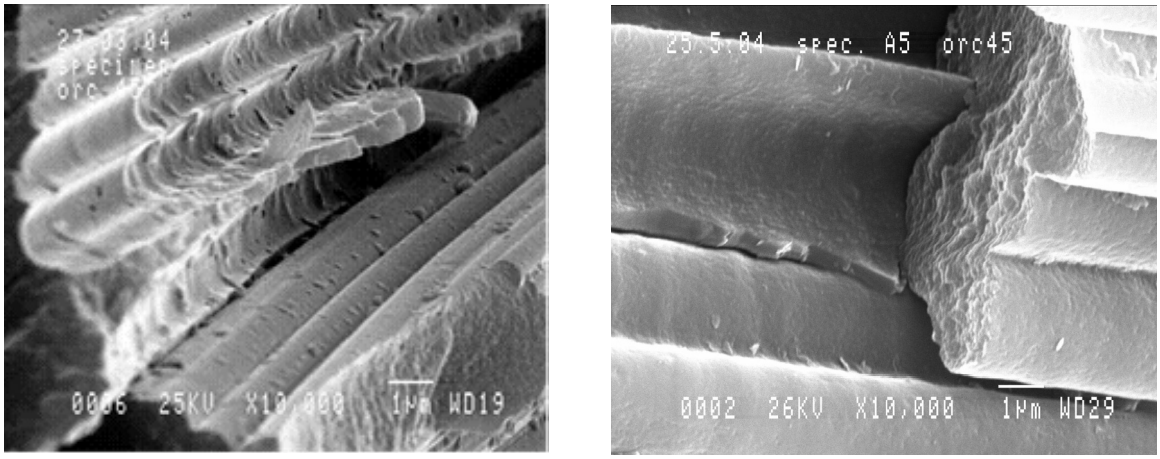


Fig.13: Fiber surface replicas on the matrix of A4 (left) and A5 (right). Notice the relatively smooth interfacial surfaces of A5. (x10000)

4. Summary and Conclusions

A systematic testing methodology for comparative evaluation and assessment of hygrothermal effects on residual strength and cracking characteristics for different Graphite Phenolic (GPh) systems was established. Two materials (denoted by A4 and A5), representing two types of compositions were investigated. More specific conclusions are as follows:

1. Intense drying exposure was found to change significantly the interlaminar mechanical characteristics and cracking sensitivity of thick GPh panels. The cracking process is attributable mainly to interlaminar tensile stresses induced by restrained shrinkage mechanism

2. All GPh specimens suffer from high water loss during drying, causing a free interlaminar shrinkage in a scale which is comparable to the failure strain.

3. The response to a pure hygrothermal cycle (no mechanical loading) is not fully recoverable, at least in the first hygrothermal cycle. The residual free shrinkage is smaller in material A4 than in A5.

4. A significant difference in mechanical performance between the two groups of GPh panels were found, which may be defined as Drying Sensitive Material (DSM) – (A5), as compared to Drying Insensitive Material (DIM) – (A4).

5. The DSM panels were characterized by interlaminar macrocracking detected during drying and reduced residual strength after drying. The DIM panels exhibit no cracks and invariable strength. The DSM material exhibit brittle force-deflection curves, while DIM showed a "ductile" force-deflection behavior.

6. The difference between the DSM and DIM may be attributed to two morphological factors: a.) fiber surface texture - in case of interfacial microcracking, and b.) weaving pattern - in case of macrocracking process.

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