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EFFECT OF INTERNAL MOISTURE CONTENT ON THE T_G VALUES OF CFRP RODS

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ABSTRACT

DMA tests are used for the material charaterisation of CFRP tendons for civil engineering applications and to assess the high temperature behavior of CFRP prestressed structures by measuring the glass transition temperature T_g. The glass transition temperature is sensitive to the moisture content of the CFRP tendons and standard test methods (e.g. ASTM D7028 (ASTM 2007)) have not yet qualitatively addressed the effect of small moisture content variations from environmental conditions in the T_g values. The effect of the internal moisture content on the T_g values of two CFRP rods with different diameters and manufacturing process is evaluated. Lab conditioned specimens with varying drying time (9, 15, 36 and 210 days) and thus moisture content are tested to study the effect of small lab conditions variations in the glass transition temperature and the sensitivity of the DMA testing. Exposed specimens at 60°C for roughly 3 years are also investigated to record effect of greater moisture absorption on the T_g values. Two heating runs were conducted for every test to differentiate post-curing effects and mass weight measurements were recorded before and after each heating run. A linear relationship between the mass loss of the specimens due to drying at vacuum and during the heating runs with the glass transition temperature T_g was observed. Post-curing effects could not be clarified even for the dry specimens. The exposed specimens showed a reduction in T_g of 38°C that was reversible after drying. It is recommended that the use of T_g values to infer the degree of curing should be carried out on dry specimens.

KEYWORDS

CFRP, DMA test, Material Characterisation, Environmental Conditions.

INTRODUCTION

Composite materials such as CFRP (Carbon Fibre Reinforced Polymer) rods are increasingly used in structural applications as a proactive measurement against steel corrosion. However, despite being non-corrosive, the structural behavior of CFRPs depends on the performance of the polymer matrix. When exposed to wet environments, the matrix tends to absorb water and consequently swells and plasticizes. The matrix also softens at high temperatures. The softening of the matrix can lead to a degradation of the mechanical properties. Thus the performance of CFRPs is dictated not only by the carbon fibres but also by the chemical stability of the epoxy.

In the civil engineering industry, material characterization methods are being proposed to assess the matrix performance i.e. Interlaminar Shear Test Methods (ILSS), and network structure of composite materials i.e. Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). These test methods are well-known in mechanical engineering applications (naval and aeronautical), where FRP laminates are widely used, but are relatively new in the civil engineering field.

DMA tests measure the temperature at which the epoxy in a CFRP tendon moves from a glassy to a rubbery state. This point is termed the glass transition temperature, T_g, and is used to study the high temperature behaviour of CFRP reinforced and prestressed structures and to infer the degree of cross-linking. In a DMA test, the specimen is subjected to a minor sinusoidal oscillation as a function of time and temperature by applying a small sinusoidal force. This force can be applied longitudinally (uniaxial tension or compression), transversally (bending mode) or in a torsional mode. Dynamic mechanical properties such as the storage modulus, E', loss modulus, E'', and loss factor, $\tan\delta = E''/E'$, are derived from DMA tests and different T_g values are obtained from the relevant plots of E', E'' or $\tan\delta$ vs temperature. The storage modulus E' represents the stiffness of a viscoelastic material and is related to the elastic energy stored during a loading cycle whereas the loss modulus E'' represents the energy lost during a loading cycle. As shown in Figure 1, the $T_{g\text{-}onset}$ value is determined from tangent lines associated with the initial slope of the storage modulus (at the point where there is a drop in modulus (2)) and a slope after softening that is extrapolated from the inflection point (1). $T_{g\text{-}loss}$ and $T_{g\text{-}tan\delta}$ are defined as the temperatures where the peak E'' and $\tan\delta$ values are recorded respectively (see Figure 1). The definition of $T_{g\text{-}onset}$ can be subjective as the tangent lines from the inflection point and the initial slope are open to interpretation and it depends if the values are plotted in a linear or a log axis. Therefore, the $T_{g\text{-}tan\delta}$ and $T_{g\text{-}loss}$ definitions are preferred to deliver a better accuracy and consistency.

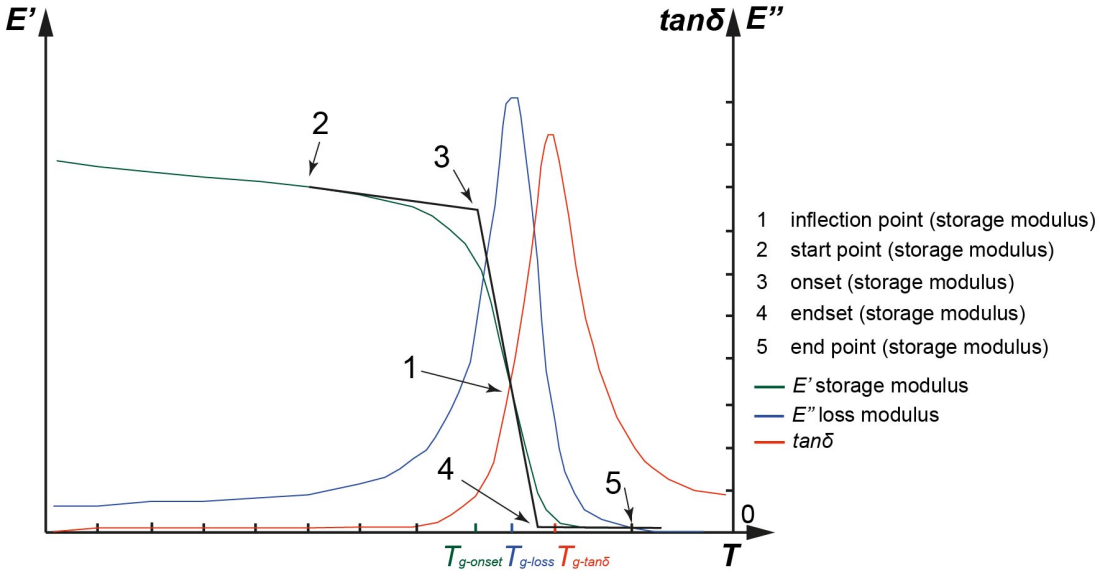

Figure 1: Definitions of glass transition temperature: $T_{g\text{-}onset}$, $T_{g\text{-}loss}$ and $T_{g\text{-}tan\delta}$.

The glass transition temperature is sensitive to the initial moisture content in CFRP tendons. However, standard test methods (e.g. ASTM D7028 (ASTM 2007)) have not yet qualitatively addressed the effect of small moisture content variations due to environmental conditions on measured T_g values. This can lead to variations in the DMA T_g values for the same material when tested in different lab conditions. This is important when DMA tests are being used to infer the level of curing since deviations in the T_g values due to the initial moisture content can lead to erroneous conclusions about the level of crosslinking density in the epoxy of CFRP specimens. A decrease in the T_g value with increasing moisture content has been experimentally recorded (Birger et al. 1989; Nogueira et al. 2000; Chateauminois et al. 1995). It has been suggested that, as a general rule of thumb, a decrease in T_g of around 20°C could be expected for a 1% increase in moisture content (Wright 1981). A drop in T_g values of up to 34°C has been observed for CFRP laminates conditioned in humid air (RH= 95%) at 50°C for 960 hr with a 1.7% moisture uptake and a reference T_g value of 135°C (Birger et al. 1989). Similar findings have been reported for GFRP although proved to be reversible after drying of the exposed specimens (Chateauminois et al. 1995, Robert and Benmokrane 2010). However, the reversibility of the plasticising effect is dependent on the epoxy system and irreversible decreases of up to 15°C have been reported elsewhere (Chateauminois et al. 1990). Chateauminois et al. (1995) showed that the width of the $\tan\delta$ plot increases and the $\tan\delta$ value decreases with increasing moisture content. A linearly decreasing relationship between the T_g and mass uptake of GFRP specimens was reported irrespective of the exposure temperature

(range 70-90°C). A weight loss of up to 60% of the initial water content for the exposed specimens was recorded when the transition to the rubbery state was acheived and a change in the desorption rate was found analytically. This change in the desorption curve was not clear under high DMA heating rates due to the shorter drying time. Plasticising effects will not be reversible if the CFRP specimens are exposed to high temperatures close to the wet T_g values where additional degradation mechanisms can take place.

The influence of different internal moisture contents on the glass transition temperature of CFRP samples is assessed in this paper by undertaking DMA tests on specimens that have been subjected to different drying regimes. The post-curing effect during a heating run is evaluated. The reversibility of plasticisation effects and irreversible degradation mechanisms are also studied by testing CFRP specimens that have been exposed in water at 60°C for nearly 3 years.

EXPERIMENTAL PROCEDURE

Materials

To study the effect of the internal moisture content on the measured T_g values, two groups of CFRP tendons, groups C and D, were used. The tendons had the same epoxy and carbon fibres but a different diameter, manufacturing process and preconditioning regime. The material properties and main differences between the two tendon groups are summarized in Table 1. Group C tendons were manufactured uncoated for research purposes. The group D tendons were a commercial product and had an outer sand coating layer to improve the bond between the tendon and the concrete. This means that there was an additional in-line production step during pultrusion, where an extra epoxy layer was applied, sand particles were sprayed and further curing followed. All the tendons were produced by the same manufacturer and the core tendon had the same curing regime. The exact details of the curing process are confidential but during the curing process a maximum temperature of 195°C was reached. For comparison purposes, the outer sand coating layer on the group D tendons was gently removed with a blade to avoid misinterpretation of the DMA results due to the additional external resin layer.

Table 1: Material properties of the group C and D CFRP tendons.

Specimen Type	C	D
Matrix/Epoxy Hardener	EPR 4434/EPH 943	EPR 4434/EPH 943
Fibres	Tenax UTS 5631	Tenax UTS 5631
Voume fraction	0.64	0.64
Diameter (mm)	4.2	5.4
Manufacturing process	Uncoated	Originally sand coated
Pre-conditioning	Dried in the oven at 60°C for 2 years and exposed in water at 60°C for roughly 3 years	Stored in lab conditions
	Previously tested in torsion	Not tested previously

Experimental Programme

The group D samples were tested to study the effect of internal moisture content on the T_g values. Therefore, the CFRP samples were dried in a vacuum oven at 80°C for 9, 15, 36 and 210 days and subsequently tested in a DMA machine. Two samples were tested after each drying time and two samples previously stored in the lab were used as control specimens. Group C samples were used to study the effect of sustained exposure to moisture on the glass transition temperature and thus on the network structure of epoxy. These samples were extracted from a 300 mm long CFRP tendon that was previously tested in torsion within the elastic range (Toumpanaki et al. 2015) after immersion in water at 60°C. The specimen had been stored in an oven at 60°C for roughly 3 years to reach a dry condition before exposure in water. The central 200 mm region of the specimen was fully immersed in

distilled water whereas the ends of the specimen remained unexposed. One 'dry' control specimen for this group was therefore cut from the unexposed ends.

Two heating runs in the DMA machine were carried out for all samples from both groups. A second heating run was adopted to differentiate between the post-curing effect and the drying effect in terms of any increase in the T_g value. All samples were weighed with a digital balance with a 0.0001g accuracy before and after every heating run.

DMA tests

The glass transition temperature T_g was measured using DMA. The DMA tests (Eplexor 500 from Gabo Qualimeter, Germany) were performed under 3 point bending mode at a 10 Hz frequency and ramp rate of 2°C/min from 23–210°C. The maximum load cell capacity in the majority of DMA tests was 150 N. A dynamic amplitude of 0.008% was superposed on a static load of 0.023% flexural strain. All CFRP rod samples from both groups were 50 mm long. For consistency the $T_{g\text{-}tan\delta}$ definition was adopted for comparison purposes.

EXPERIMENTAL RESULTS

The glass transition temperature versus mass loss as recorded before and after each heating run for the group D specimens are depicted in Figure 1. All the $T_{g\text{-}tan\delta}$ and mass loss values are summarized in Table 2. The notation used is A-#-B-# where the first letter denotes the group D CFRP samples, the first number is the storage days at 80°C in a vacuum (i.e. 0 for the control specimens), the second letter is either 'a' or 'b' to identify the specimen tested after the same storage conditions, and the number, 1 or 2, is indicative of the 1st or 2nd heating run respectively.The group D lab-conditioned specimens yield an average $T_{g\text{-}tan\delta}$ = 143.5°C and for the 'dry' specimens $T_{g\text{-}tan\delta}$ = 171.1°C after the 1st heating run. A maximum increase of 29°C is observed between the lab-conditioned and dried specimens after the second heating run. This was attributed to a –0.68% mass loss due to drying in a vacuum and during DMA testing. The $T_{g\text{-}tan\delta}$ values were found to increase linearly with the mass loss according to Eq. 1.

$$T_{g\text{-}tan\delta} = -41.47\,\Delta M + 140.2 \quad (1)$$

In Figure 2 the $T_{g\text{-}tan\delta}$ value is plotted against the mass loss for the group D specimens. A post-curing effect during the 1st and 2nd heating runs cannot be clearly isolated since moisture evaporation is observed during both runs. In the dry specimens dessicated in a vacuum for 210 days, the $T_{g\text{-}tan\delta}$ increases by 1.3°C on average after the 2nd heating run and 0.04% moisture evaporation and this change is also consistent with Eq. 1. This suggests that either the CFRP tendons were fully cured or that any potential post–curing effect takes place gradually during the heating runs and so cannot easily be discerned. From Table 2 it is observed that the control specimens and the specimens tested after 9 days have not yet reached the fully dry conditions even after the second heating run. A third heating run could yield even higher $T_{g\text{-}tan\delta}$ values associated with moisture evaporation up to –0.68%. Hence, the results from a second heating run to assess the degree of curing in CFRPs should be used with caution since the increases in the $T_{g\text{-}tan\delta}$ values can be related to moisture evaporation rather than additional curing effects. It is therefore important to weigh specimens before and after each DMA test to try to differentiate between these two phenomena that influence the glass transition temperature.

The storage modulus E' and tanδ values versus temperature curves for one unexposed and two exposed group C specimens are shown in Figure 3. The notation used is A-B-# where the first letter denotes the group C CFRP samples, the second letter is either 'a' or 'b' for the exposed samples and 'c' for the unexposed sample, and the number, 1 or 2, is indicative of the 1st or 2nd heating run respectively. The $T_{g\text{-}tan\delta}$ values and mass losses recorded after each heating run are summarised in Table 3. The $T_{g\text{-}tan\delta}$ values of the exposed samples in the first run are roughly 38°C lower than the $T_{g\text{-}tan\delta}$ of the unexposed sample. The 2nd runs of the exposed samples yield $T_{g\text{-}tan\delta}$ values in the same range as the $T_{g\text{-}tan\delta}$ value from the 1st run of the unexposed sample. The moisture induced decrease in $T_{g\text{-}tan\delta}$ could be attributed to reversible plasticising moisture effects. Additional degradation mechanisms are not observed and the T_g values of the wet specimens are well above the exposure temperature of 60°C. This is also indicated by the decrease in the width of the tanδ plots between the 1st and 2nd runs for the exposed samples. The mass loss recorded after the 1st run is representative of the mass at saturation for the group C CFRP specimens exposed at 60°C (Toumpanaki et al. 2015). The $T_{g\text{-}tan\delta}$ value in the second run for the unexposed specimen is 8.6°C higher than the first run and associated with a loss of 0.10% of moisture. This is a

twice the theoretical glass transition temperature change of 4.15°C that would be predicted based on Eq.1 and might indicate that the group C was not fully cured during the manufacturing process.

Table 2: $T_{g\text{-}tan\delta}$ and mass loss during the DMA heating runs- Group D experimental series.

	$T_{g\text{-}tan\delta}$	ΔM (%) before DMA test	ΔM (%) after 1st run	ΔM (%) after 2nd run
D-0-a-1	143.6	N/A	-0.333	
D-0-a-2	159.8			-0.388
D-0-b-1	143.3	N/A	-0.225	
D-0-b-2	155.9			-0.282
D-9-a-1	157.0	-0.397	-0.397	
D-9-a-2	161.3			-0.452
D-9-b-1	157.9	-0.363	-0.419	
D-9-b-2	160.2			-0.476
D-15-a-1	158.3	-0.385	-0.440	
D-15-a-2	163.0			-0.495
D-15-b-1	159.2	-0.406	-0.746	
D-15-b-2	169.0			-0.848
D-36-a-1	163.2	-0.522	-0.578	
D-36-a-2	167.8			-0.578
D-36-b-1	164.7	-0.512	-0.568	
D-36-b-2	167.8			-0.624
D-210-a-1	171.0	-0.608	-0.631	
D-210-a-2	172.5			-0.675
D-210-b-1	171.2	-0.618	-0.643	
D-210-b-2	172.3			-0.684

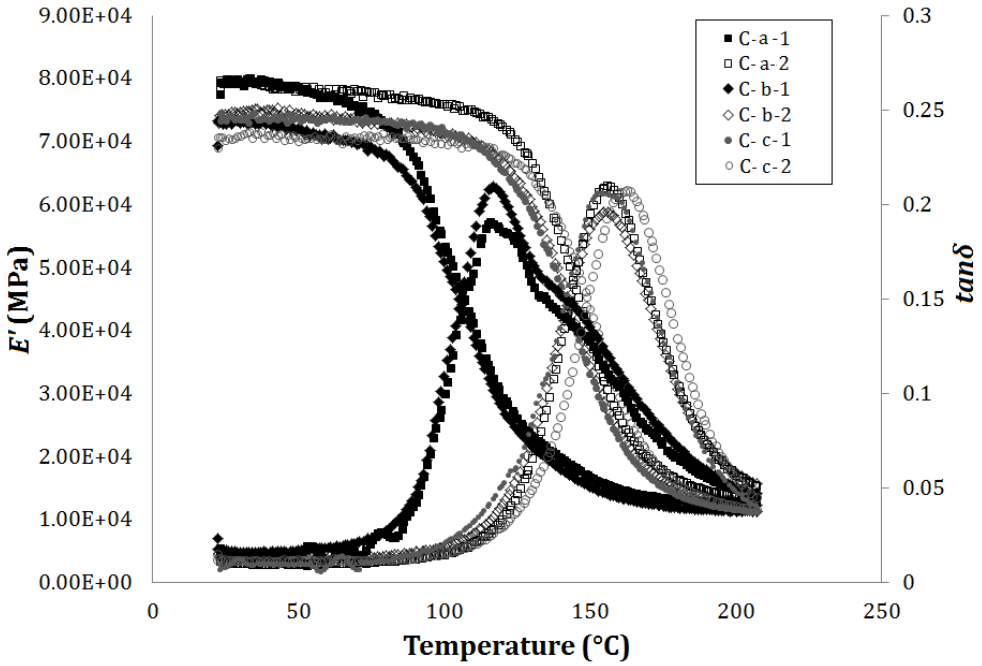

Figure 2: $T_{g\text{-}tan\delta}$ versus mass loss ΔM-Group D experimental series.

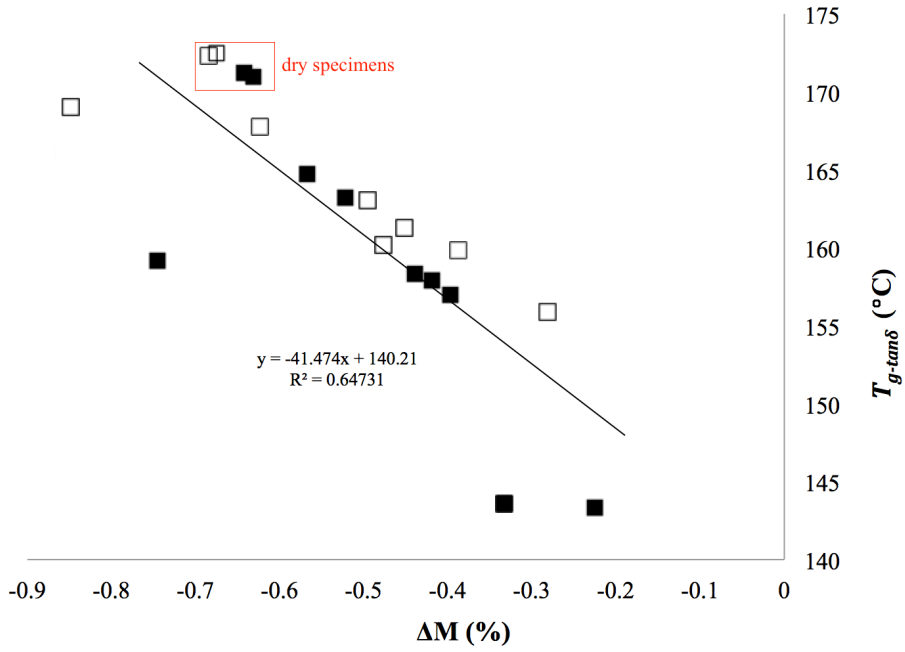

Figure 3: $T_{g\text{-}tan\delta}$ versus mass loss ΔM-Group C experimental series.

Table 3: $T_{g\text{-}tan\delta}$ and mass loss during the DMA heating runs-Group C experimental series.

		$T_{g\text{-}tan\delta}$	ΔM (%)
Exposed in water at 60°C	**C-a-1**	115.8	-2.41
	C-a-2	155.9	-0.04
	C-b-1	117	-2.19
	C-b-2	156.2	-0.10
Unexposed at 60°C	**C-c-1**	154.3	-0.10
	C-c-2	162.9	0.00

CONCLUSIONS

1. CFRP samples with an initial moisture content yield lower T_g values.
2. Due to the high temperature applied (up to 210°C), the use of a second heating run to assess the level of crosslinking density in the epoxy of a CFRP specimen should be conducted on dry specimens.
3. Measured T_g values which are up to 38°C lower than that of a dried reference sample are observed for saturated specimens. This could be important for the fire performance of CFRP structures when the CFRP is exposed directly to humid environments e.g. in retrofitting materials, or when encased in a concrete environment with high humidity.
4. For the CFRP samples tested here, the plasticization effects due to exposure to water are reversible upon drying when the highest exposure temperature is well below the wet T_g value of the CFRP material.

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