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Durability Study of Pultruded CFRP Plates under Sustained Bending in Distilled Water and Seawater Immersions: Effects on the Visco-Elastic Properties

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***Abstract*—**This paper presents effects of distilled water, seawater and sustained bending strains of 30% and 50% ultimate strain at room temperature, on the durability of unidirectional pultruded carbon fiber reinforced polymer (CFRP) plates. In this study, dynamic mechanical analyzer (DMA) was used to investigate the synergic effects of the immersions and bending strains on the visco-elastic properties of (CFRP) such as storage modulus, tan delta and glass transition temperature. The study reveals that the storage modulus and glass transition temperature increase while tan delta peak decreases in the initial stage of both immersions due to the progression of curing. The storage modulus and T_g subsequently decrease and tan delta increases due to the matrix plasticization. The blister induced damages in the unstrained seawater samples enhance water uptake and cause more serious degradation of T_g and storage modulus than in water immersion. Increasing sustained bending decreases T_g and storage modulus in a long run for both immersions due to resin matrix cracking and debonding. The combined effects of immersions and strains are not clearly reflected due to the statistical effects of DMA sample sizes and competing processes of molecular reorientation and postcuring.

***Keywords*—**Pultruded CFRP plate, bending strain, glass transition temperature, storage modulus, tan delta.

I. Introduction

THE Fiber Reinforced Polymers (FRPs) that are used in civil engineering rehabilitation works are produced by the continuous fibers that are embedded in the polymer resin matrix. The desirable characteristics of FRP materials are derived from the fibers that possess better mechanical properties than the polymer matrix. Polymers, however, have established themselves as matrix materials for composites in many engineering applications. The merits of polymers for the role as the resin matrix include light weight, low density, high corrosion resistance, low elastic modulus and can be used, either in solution or molten, to impregnate the fibers at pressures and temperatures which are much lower than those which would be required for other materials, such as metals [1]. However, polymers do not provide high performance mechanical properties at right angles to the fiber direction, which make unidirectional composite materials such as CFRP inherently anisotropic. They also absorb water, which can modify the composite properties and compromise the adhesion between the fibers and the matrix, so weakening the composite [1]-[5].

The most used resin matrix for high performance carbon fiber reinforced composites (CFRP) is the thermosetting epoxy based polymer. Epoxy provides a resin with low shrinkage, high adhesive strength, excellent mechanical strength and, chemical resistance[1].Numerous research works have reported that water ingress in the epoxy resin depresses glass transition temperature by plasticizing the polymer network [5]-[7]. It is generally known that water penetrates into the polymer resin by osmosis and occupies the free volume as Type I water molecules. The water molecules are subsequently bound to polymer chains by the formation of hydrogen bonds and exist as Type II water molecules [6].

The formation of hydrogen bonds depends on the polarity of the final chemical structure of the cured epoxy. The literature has shown that amine hardeners give rise to high resin of high polarity than anhydride based hardeners [8], [9]. The interchain hydrogen bonds in the polymer cause chain scission and hydrolysis as reported by [10], [11].The notable effects of bending strain on the polymer matrix include delamination, cracking and change in free volume fraction of the composites [12]-[14].

It has been shown that CFRP moisture uptake in seawater immersion is enhanced by the damages caused by blisters in addition to the process induced defects. The progression of postcuring enhances mechanical properties of CFRP /epoxy composite. The reduction in the free volume causes the decrease in the moisture uptake of the composite in both water and seawater immersions.

This paper focuses on the synergic effects of the moisture uptake and bending strain on the visco-elastic properties of the unidirectional pultruded CFRP composites. The variations of glass transition temperature, storage modulus and tan delta peaks of CFRP with immersion time under sustained bending strain were investigated using Dynamic mechanical analyser (DMA).

II. Materials and Experimental Procedure

A. Materials

The materials used in this study were unidirectional pultruded carbon fiber reinforced polymer composite (CFRP) plates with the width and thickness of 25mmx1.43mm produced at the Laboratory for FRP Composites and

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Structures (LFCS), Harbin Institute of Technology China. The two primary raw materials for the manufacture of CFRP plates were 7 µm diameter PAN-based carbon fibers (TC-36s, Tairyfil Brand carbon fiber, from the Formosa Plastics Group Production, Taiwan, China),with density, tensile strength and modulus of 1.80 g/cm^3,4.9 GPa,250GPa respectively. The epoxy resin used was the Oligomeric prepolymer diglycidyl ether bisphenol-A (DGEBA) (manufactured by Xing-Chen Chemicals Co., Ltd., Wuxi, China). The resin curing agent (hardener) was methyl hexahydrophthalic anhydride (MeHHPA) manufactured by Jiaxing, China. The curing accelerator was a tertiary amine (tris (dimethylaminomethyl) phenol (DMP-30), (manufactured by Changzhou Shanfeng Chemical Industry Co., Ltd., Changzhou, China).The tensile strength and Poison's ratio of the cured epoxy system were 3.5GPa and 0.35 respectively.

B. Sample Conditioning

The bending fixture (see Fig. 1) for realizing sustained flexural strain of CFRP plate was specifically designed to cause out of plane deformation of the CFRP plate with the maximum strain being at the mid length of the specimen. The CFRP samples of dimensions 250mmx25mmx1.43mm were inserted onto the bending fixture and immersed in water and seawater at room temperature (25°C) using enclosed plastic conditioning chambers. The water was distilled, while artificial seawater was prepared in accordance with ASTM D1141.

Fig. 1 Bending fixture for CFRP plates

C. Dynamic Mechanical Analysis (DMA) Tests

After 2,4,12 and 20 weeks of immersion, the visco-elastic properties of the conditioned and control CFRP samples were tested using Dynamic mechanical analyzer (DMA) instrument (Q800 DMA 2980) manufactured by TA instruments Inc USA. The DMA tests were carried out using the single cantilever clamp at a constant load frequency of 1Hz, and a heating rate of 5°C/min from 23°C to the maximum temperature of 200°C. The test samples were cut from the mid-point of the strained and unstrained immersed samples. The average sample dimensions were 35mm x8mm x1.43mm and three samples were tested for each data point.

III. Results and Discussions

A. Glass Transition Temperature

The effect of moisture ingress is clearly shown in Figs. 2 and 3 to cause increase in glass transition temperature within the first 2 weeks of immersion in both water and seawater. The glass transition temperature indicates an increase of about 6% after 2 weeks followed by the dramatic decrease of about 8% after 20 weeks for the strained samples in seawater and water immersions. The anomalous trend is shown for (50% strain samples) in seawater. The T_g of these samples slightly increases for the last data point at time (t=20weeks) while the water immersed samples under the same strain level show significant decrease. Increasing level of strain causes further decrease in glass transition temperature for water immersion while seawater immersed samples under the same strain level show anomalous trend. However, no significant difference in the rate of T_g depression is indicated for both immersions. The unstrained samples in seawater immersion show a higher rate of degradation of T_g than the water immersed samples. The percentage difference of about 7% between the water and seawater unstrained samples is indicated after 20 weeks of immersion.

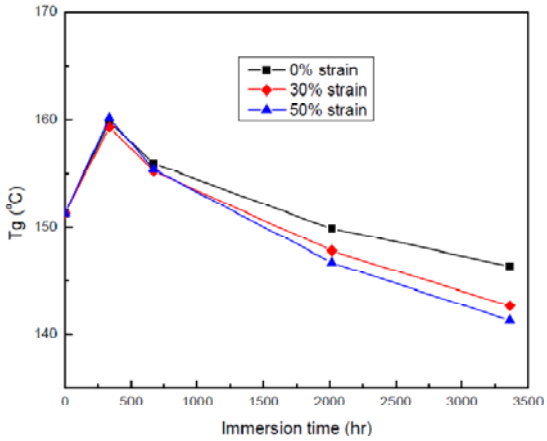


Fig. 2 Variation of glass transition temperature with water immersion time

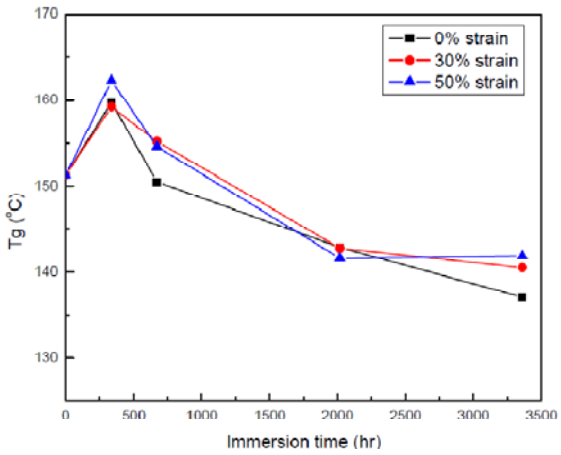


Fig. 3 Variation of glass transition temperature with seawater immersion time

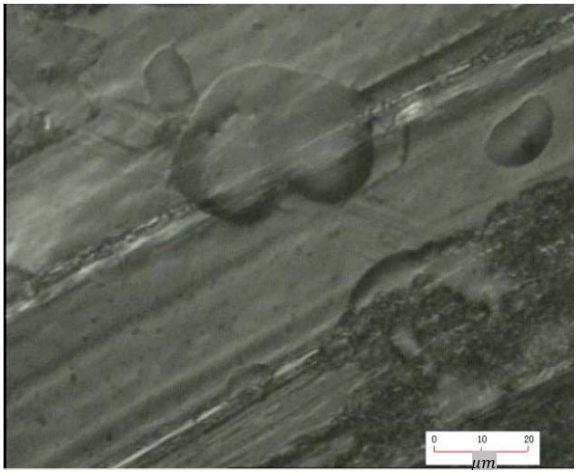


Fig. 4 Blisters on the CFRP surface of unstrained seawater samples

Water absorption by polymers causes plasticization in the short-term and hydrolysis, saponification, and chain scission in the long-term through attack of network linkages [10], [11]. These processes induce higher levels of molecular mobility that lead to the decrease in T_g, although the situation becomes complicated by progression of cure due to immersion in aqueous solutions such as seawater and water [10]. Glass transition temperature depends on a number of factors such as molecular weight and free volume. The variation of T_g with molecular weight can again be related to the free volume. As the molecular weight decreases, the density of chain ends increases. Since each chain end is assumed to contribute a fixed amount of free volume, increasing molecular weight reduces free volume and in turn increases T_g [15]. Increasing length of polymer chain segments enhances chain stiffness and requires large free volume for the molecular mobility hence, any structural change that increases the segmental volume requires a larger free volume per segment and results in a larger T_g [15].

Therefore, the increase in T_g exhibited after 2 weeks of immersion is attributed to the progression of cure (post curing) that may lead to the increase in length of the polymer chain segment, and reduction in the free volume and ultimately provides the stiffer polymer chains. The small free volume and chain stiffness inhibit molecular mobility and increase glass transition temperature of CFRP. The subsequent decrease in T_g is due to the onset of resin plasticization process as water content increases. The progression of plasticization results in the increased free volume of the matrix that facilitates the polymer chain mobility hence lower glass transition temperature.

The sustained bending causes reorientation of polymer chains also reported by [13], [14], [16] that hinder polymer chain mobility and raise T_g of the composite. Therefore the increase in T_g in the first 2weeks of immersion in the strained samples may be due to the coupled effects of molecular reorientation and postcuring. Nevertheless, it is evident that the effects of postcuring are dominant since unstrained samples also exhibit increase in T_g after 2weeks of immersions. In addition, damages associated with sustained bending strain such as micro cracks and debonding enhance moisture diffusion by wicking. Therefore depression of T_g in a long run may also be due to resin plasticization as a result of wicking. The significant reduction in T_g for the unstrained seawater samples is attributed to the damages caused by the rupture of blisters on the CFRP plate surfaces shown in Fig. 4, as a result of high osmotic pressure.

The model proposed by [17] was used to predict the variation of T_g with diluents media diffusion. The glass transition temperature of the moisture saturated polymer according to the media diluents model is given by;

$$T_{gwet} = \frac{a_e V_e T_{ge} + a_w (1-V_e) T_{gw}}{a_e V_e + a_e (1-V_e)} \quad (1)$$

$$V_e = \frac{1}{1+0.01M\left(\frac{\rho_e}{\rho_w}\right)} \quad (2)$$

where T_{ge} and T_{gw} are the glass transition temperature of epoxy and water respectively, volumetric expansion coefficient $a_e = 3(a_{re} - a_{ge})$where a_{ge} and a_{re} are the thermal coefficients of expansion of epoxy in glassy and rubbery states respectively, ρ_e and ρ_w is the density of epoxy and water respectively, a_w is the thermal coefficient of expansion of water and M is the moisture content of the epoxy. Assuming the negligible effects of postcuring of the epoxy for $a_w = 4x10^{-3}/^{o}\text{C}, T_{gw} = 4^{o}\text{C}, \rho_e = 1.2g/cm^3, \rho_w = 1g/cm^3$ and $a_e = \sim 6x10^{-4} cm^3/cm^{3\,o}\text{C}$ [18]. According to the model and the experimental data, the calculated (T_g)s are shown in Table I for water and seawater. It is indicated that calculated values are higher than experimental values. This is because the model does not include factors to cater for the reduction in water uptake due to the decrease in free volume of the resin matrix when subjected to bending strain.

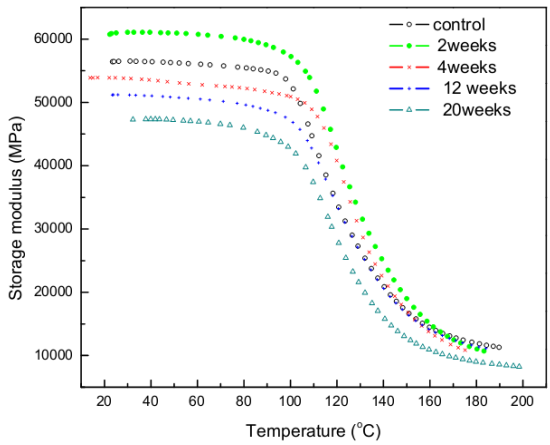
TABLE I
PREDICTED AND TESTED GLASS TRANSITION TEMPERATURE OF THE SATURATED CFRP COMPOSITES UNDER VARIOUS BENDING STRAINS

Strain level	Water		Seawater	
%	T_{gEXP} (°C)	T_{gCAL} (°C)	T_{gEXP} (°C)	T_{gCAL} (°C)
0	146.36	147.78	137.06	146.61
30	142.60	148.28	140.50	147.94
50	141.25	149.11	141.88	149.26

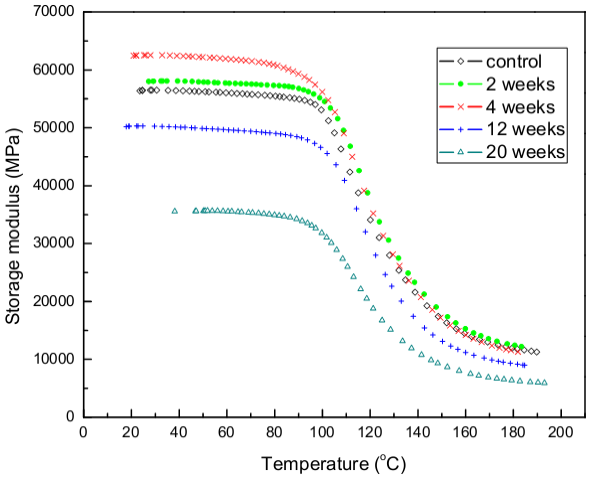
B. Storage Modulus

Figs. 5 (a) and (b) show the storage modulus as a function of temperature at various immersion times with a given strain level. It is shown that the storage modulus increases during the initial stage of immersion followed by the decrease in the long run. The storage moduli for both water and seawater immersions increase to about 8% and 3% of the control value after 2 weeks respectively. After 20 weeks, the unstrained water immersed samples register a decrease of about 8% of the initial value while the unstrained seawater immersed samples show considerable decrease of about 37% of the control value. The increase in the storage modulus in the initial stage of immersion is due to the progression of the postcuring as explained in the previous section. The higher rate of degradation in the unstrained seawater samples is attributed to the high moisture absorption as a result of the

blister induced damages and the fiber-matrix debonding. The degradation of the storage modulus is due to the plasticization and on set of matrix hydrolysis which is expected to accelerate after complete cure of the resin matrix [10].



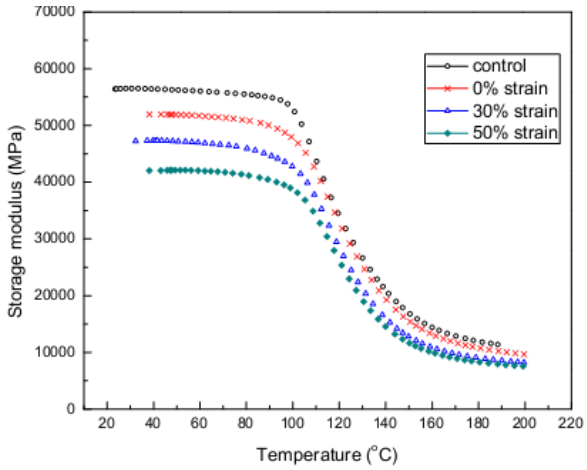
(a)



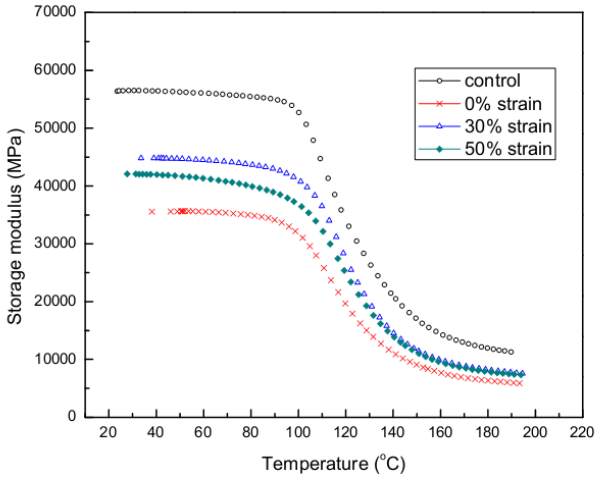
(b)

Fig. 5 Variation of the storage modulus with immersion time (a) unstrained water immersed samples (b) unstrained seawater immersed samples

The effects of sustained bending on the storage modulus is presented by the plots of the storage modulus as a function the temperature with various bending strains at a given immersion time. The synergic effects of the sustained bending strain with immersion time is not clearly reflected in the initial stage of immersion however the effects are pronounced after 20 weeks of immersion in Figs. 6 (a), (b). It is indicated that increasing sustained bending strain causes significant decrease in the storage modulus after 20 weeks in both water and seawater immersions. The low storage modulus of about 25% of the control value is indicated in the highly strained samples (50% strain level) in both immersions. It is worth noting that the unstrained seawater immersed samples indicate the lowest value of the storage modulus of about 37% of the control value after 20 weeks of immersion.



(a)



(b)

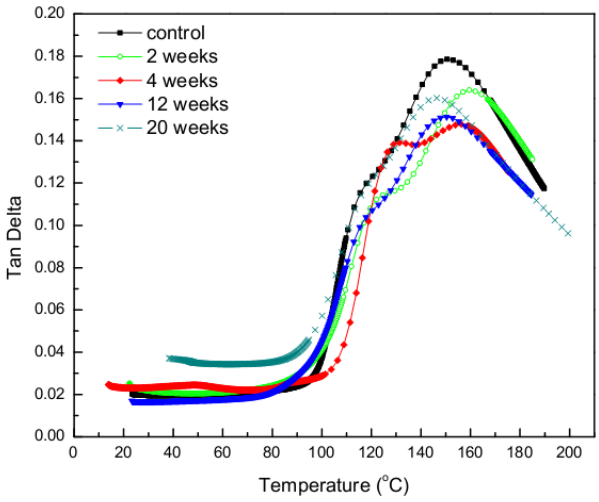
Fig. 6 Variation of the storage modulus after 20 weeks of immersion (a) distilled water immersion (b) seawater immersion

The decrease in the storage modulus with high sustained bending strain is due to the enhanced moisture absorption as a result of damages induced by high sustained strain. High strain may cause the formation of microcracks in the resin and delamination of the composite. These enhance moisture absorption by wicking and consequently a high rate of matrix degradation due to hydrolysis is experienced. The dramatic reduction in the storage modulus in the unstrained seawater samples is related to the high water uptake of the composite as a result of the damages by the blisters [19]. High moisture diffusion enhances matrix hydrolysis and account for the significant degradation of the storage modulus.

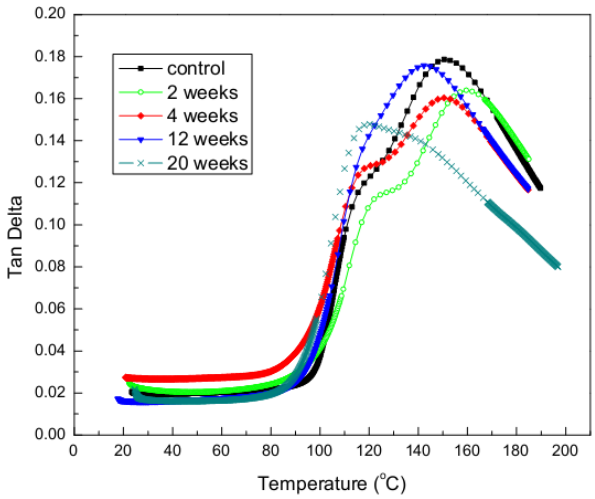
C. Tan Delta

The variation of tan delta peak with immersion time is presented in Figs. 7 (a) and (b). As shown, the peak values of loss tangent curve initially decrease followed by the increase. The decrease is shown to occur within 2 weeks of immersion and further immersion leads to the increase in the peak value. In the initial stage of immersion, two peaks are seen to appear

in the loss tangent curve. However, for the unstrained seawater immersed samples, the peak of loss tangent curve is lower than the preceding peak at time t=20weeks.



(a)

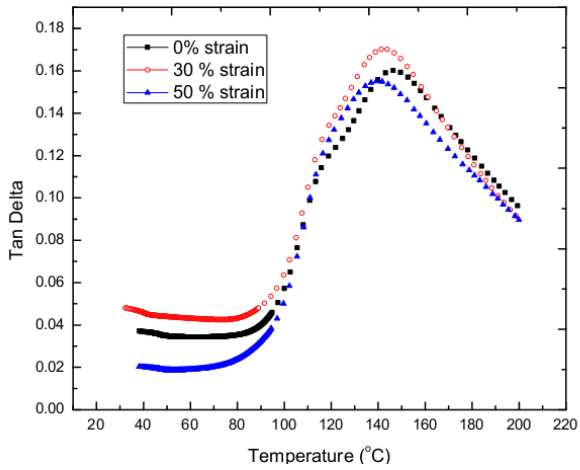


(b)

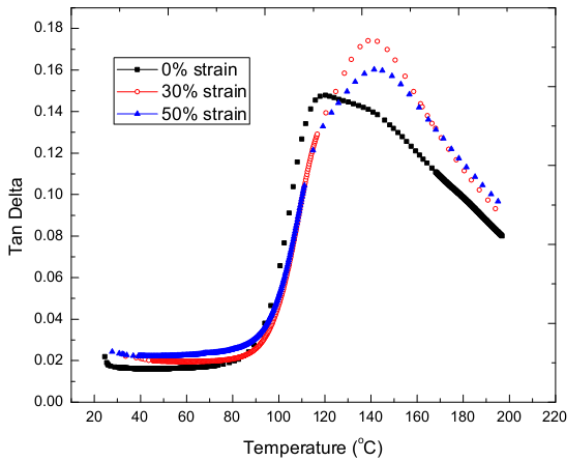
Fig. 7 Effect of immersion on loss tangent curve for the unstrained samples (a) water immersion (b) seawater immersion

The height of the loss tangent peak is related to the degree of mobility of polymer chains at the glass transition temperature, and is used as a measure of energy dissipation. The decrease in the height of the loss tangent peak exhibited by the immersed CFRP samples cannot be well explained with respect to the matrix plasticization [11] rather can be associated with the progression of polymerization (postcure) in the presence of the water molecules. It can be noted that the height of the tan delta peak gradually decreases in the first 4 weeks of immersion, reflecting the effects of progression of cure under ambient conditions. Postcuring increases the crosslinking density of polymer chain segments and reduces the mobility of the molecular chains. The reduced mobility of polymer chains is indicated by less energy loss in the transition region [10]. The moisture present between molecular segments can also reduce segmental interaction and contribute to the decrease in the tan delta peak.

The subsequent increase in the loss tangent peak is an indicative of high degree of chain mobility and high energy dissipation. This can be explained in two perspectives namely the moisture induced plasticization and the interruption of interchain hydrogen bonds. Interruption of interchain segments leads to an increase in the number of mobile chain segments around the T_g, especially in regions of highly packed structure [10], and the consequence is an increase in the height of the loss tangent peak. The two peaks appearing in the initial stage of exposure are attributed to the drying effect of the DMA and non uniform moisture concentration of the samples.



(a)



(b)

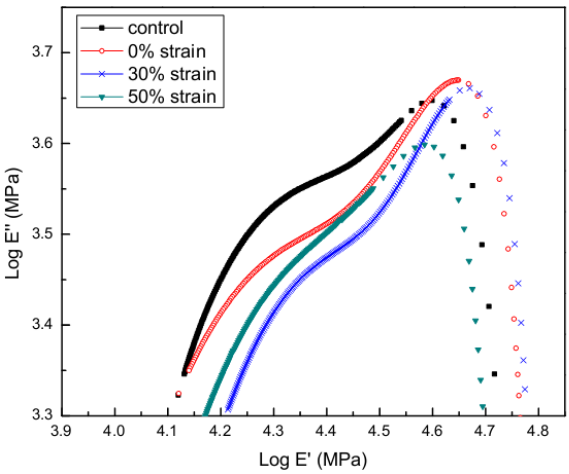
Fig. 8 Effect of strain on loss tangent curve after 20 weeks of immersion (a) water immersion (b) seawater immersion

It is difficult to generalize the effect of sustained bending strain on the peak of tan delta curve for a given immersion because of the scatter of the data. The scatter may be due to the competing processes of postcuring and moisture diffusion. Furthermore, non uniform strain distribution might result in the moisture gradients that affect plasticization and hydrolysis

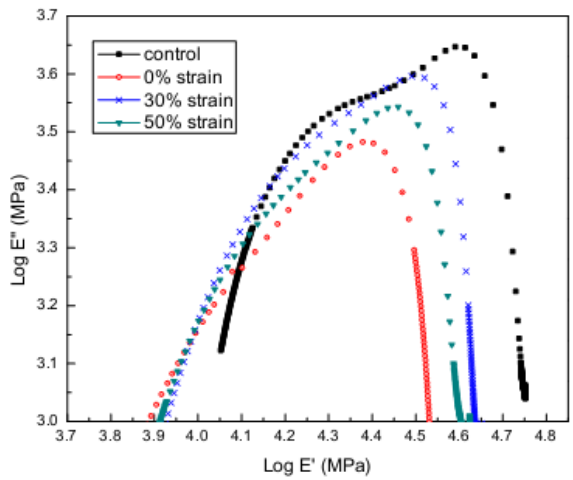
processes. However, comparison of two immersions in Table II shows relatively higher peaks in seawater immersion than water immersion which is an indicative of higher level of degradation and chain mobility in seawater immersion. The unstrained seawater immersed samples in Fig. 8 (b) indicate the lowest peak of tan delta. This is attributed to the damage assisted moisture diffusion by blisters on the CFRP surfaces that account for high moisture uptake hence high plasticization effects.

TABLE II
TAN DELTA PEAK OF CFRP UNDER VARIOUS FLEXURAL STRAINS IN WATER OR SEAWATER

Immersion time (wks)	Seawater			Water		
	0%	30%	50%	0%	30%	50%
0	0.18	0.18	0.18	0.18	0.18	0.18
2	0.164	0.13	0.164	0.164	0.13	0.145
4	0.16	0.167	0.153	0.148	0.167	0.118
12	0.176	0.159	0.174	0.151	0.159	0.159
20	0.148	0.174	0.16	0.16	0.17	0.155



(a)



(b)

Fig. 9 Cole-cole plots for seawater immersion (a) after 2 weeks of immersion (b) after 20weeks of immersion

The Cole-cole plots are presented in Figs. 9 (a) and (b) to assess the variation of material properties with evolution of moisture content after 2weeks and 20 weeks of immersion in both water and seawater. The perfect semicircular plot of Log(loss modulus) against Log(storage modulus) signifies homogeneous material properties while imperfect semicircle implies non homogeneous material properties [16], [20]. Cole-cole plots in Fig. 9 indicate uneven curves in the early stage of immersion. On the contrary, smooth curves are exhibited after 20weeks of immersion. The uneven curves in the initial stage reflect non uniform material properties that may be attributed to the non-uniform moisture distribution and presence of unreacted molecules in the material. The subsequent smoothing of the curves after 20weeks can be explained based on the postcuring process. The progression of postcuring leads to the reduction in the amount of unreacted soluble molecules of the hardener and consequently endows CFRP material with more uniform properties.

IV. CONCLUSIONS

This study presents the durability of pultruded CFRP plates under sustained bending strain immersed in seawater and water at room temperature. The study focuses on the synergic effects of immersion and sustained bending strain on glass transition temperature, storage modulus and tan delta peaks of CFRP composite. The following conclusions are drawn from the study;

1. The progression of the postcuring process due to moisture ingress in both immersions increases glass transition temperature and the storage modulus and reduces tan delta peak of CFRP by increasing the cross linking density of polymer chain segments that limits the mobility of molecules.
2. Water diffusion into CFRP composite in both immersions depresses T_g, and degrades storage modulus and increases tan delta peak by causing matrix plasticization and hydrolysis.
3. The effect of sustained bending strain is overshadowed by the dominance of postcuring but is shown to cause decrease in T_g and storage modulus in a long run due to resin matrix cracking and debonding.
4. The blister induced damages in the unstrained seawater samples facilitate degradation of the T_g and the storage modulus by promoting water diffusion by wicking.

ACKNOWLEDGMENT

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