

DIELECTRIC MONITORING OF DEGRADATION IN E-GLASS REINFORCED EPOXY COMPOSITE

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ABSTRACT

In the investigation of the hygrothermal degradation mechanisms, a torsional-DMA technique and dielectric spectroscopy are used to analyse the changes in E-glass reinforced epoxy composite properties taking into account the used conditioning. The conditioning medium is distilled water at 70°C. The degradation of the matrix can be characterized by the glass transition and characteristic frequency shifts while the fibre/matrix bonding degradation is attributed to the elastic modulus changes at low temperature and the interfacial dielectric behaviour at low frequency.

1. INTRODUCTION

In sub sea oil industry and related applications, Glass Fibre Reinforced Plastic (GFRP) is considered a suitable material system offering good chemical resistance and good mechanical properties. In addition, the non conductive and non magnetic properties (through thickness) of the material enable monitoring of water content in crude oil by means of Nuclear Magnetic Resonance NMR. Durability is required to make this application successful.

However, the sub sea environment is humid and corrosive, leading to degradation of polymeric composite material. Therefore, an understanding of the degradation mechanisms is crucial to predict the life time of the composite material in this application.

It is necessary, in this application, to quantify and qualify the dielectric properties during the functional life time of the pipe material.

Generally, the dielectric loss factor is used to characterise the quality of dielectric material and the dissipation of electric energy inside the material. In composite materials, almost all physical properties are strongly depending on the quality of the interfacial bond where composite constituents interact chemically and mechanically [1].

This paper focuses on dielectric dissipation as a performance criterion, introducing some fundamentals of dielectric properties, mechanical properties, characteristic (relaxation) frequency and polymer glass transition.

Further, this paper attempts to bridge the mechanical, chemical and electrical disciplines. A unified model merging electrical and mechanical domains is proposed.

In the current work, dielectric and mechanical properties of E-glass fibre reinforced epoxy material are measured in the presence of water uptake at 70°C using, respectively, dielectric spectroscopy and torsional dynamic mechanical analysis (DMA). The tested composite is laminate built of six layers of glass woven (0/90) fabric reinforced epoxy. In addition, unreinforced epoxy specimens are used to distinguish the effect of water

diffusion and temperature on the matrix and on the fibre/matrix interface. The glass fibre is assumed to be unaffected by the degrading medium.

2. MODELLING

This section focuses on the analogy between the dielectric and mechanical properties of the given material, in the out-of-plane direction of the composite laminate. The reliability of this analogy when those properties undergo a change or degradation is investigated as well.

The combination of temperature and water diffusion has generally a large effect on the polymer properties [1]. In fibre reinforced polymeric material, the hygrothermal effects are generally dependent on fibre direction. Moisture concentration has a negligible effect on tensile strength and modulus values in the fibre direction [2]. Both the tensile strength and the modulus in the transverse direction however decrease by a significant amount due to moisture uptake. The transverse lamina properties are matrix dominated [2]. Therefore, it is obvious that the hygrothermal effects on the composite material should be evaluated through the thickness of the test material.

2.1 Dielectric and mechanical models

The through-thickness dielectric and mechanical properties of the laminate are assumed to be equal to the properties transverse to the fibre in a unidirectional lamina. From the assumption that the glass fibres are isotropic and have a negligible dielectric loss compared to the epoxy resin, the complex permittivity, e^* , at a constant temperature, of one unidirectional lamina is modelled according to Debye relaxation circuit [3].

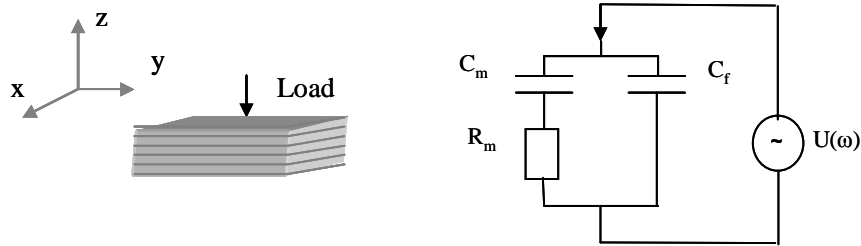


Figure 1: The through-thickness equivalent circuit of the composite laminate in harmonic electric field $U(\omega)$.

In figure 1, C_m and R_m are, respectively, the capacitance and resistance of the matrix. The capacitance of the fibres is denoted by C_f .

According to the above circuit,

$$e^*(\omega) = V_f e_f^* + (1 - V_f) e_m^* \quad (1)$$

where the complex permittivity of fibre is denoted as e_f^* , and e_m^* is the complex permittivity of the matrix.

The matrix volume fraction is simply found as $V_m = 1 - V_f$ for void-free composites. The real part of e^* , denoted by the storage permittivity ϵ' , describes the capacitive behaviour of the material and the imaginary part, the loss permittivity ϵ'' , describes the resistive behaviour. The dielectric loss factor $\tan d_D$ is defined by

$$\tan d_D = \frac{e''}{e'} \quad (2)$$

The characteristic frequency, f_c , is defined as the frequency at which the maximal values of the loss factor occurs.

By analogy to dielectric relaxation behaviour [4], the unidirectional layer is supposed to be loaded by a dynamic mechanical load applied perpendicular to the fibre direction. The complex mechanical modulus, M^* , transverse and in-plane shear directions, can be presented by equation 3 and 4. Those two equations are based on the Christensen model [3].

$$M^* = M_m^* \frac{(1-V_f) + I^*(1+V_f)}{(1+V_f) + I^*(1-V_f)} \quad (3)$$

with

$$I^* = \frac{M_f^*}{M_m^*} \quad (4)$$

where M_f^* presents the complex modulus of the fibre, which is assumed to be purely elastic, and M_m^* denotes the complex modulus of the matrix. The real part of the complex modulus, denoted by the storage modulus M' , describes the elastic behaviour of the material and the imaginary part, the loss modulus M'' , describes the viscous behaviour. The mechanical loss factor, $\tan d_M$, is defined by

$$\tan d_M = \frac{M''}{M'} \quad (5)$$

The glass transition temperature T_g and the dielectric characteristic frequency, f_c , of the materials are further characteristics of the temperature and frequency dependent material behaviour. The above equations require the dielectric permittivity and the mechanical modulus of the matrix, the glass transition temperature, the relaxation frequency and the fibre volume fraction, e_m^* , M_m^* , T_{g_m} , f_{cm} and V_f . These parameters should be determined from the experiments. Literatures values are used for the dielectric permittivity and mechanical modulus of the E-glass fibre.

In this paper, it is assumed that the complex permittivity, e^* , is analogous to the inverse of the complex modulus, $1/M^*$, and the dielectric loss factor, $\tan d_D$, is analogous to the mechanical loss factor, $\tan d_M$. Consequently, an increase in the dielectric permittivity reflects a decrease in the mechanical modulus and an increase the dielectric loss factor means an increase of the mechanical loss factor.

2.2 Diffusion model

The most common approach used to model the water diffusion in polymers is Fick's law applied to simple free-phase diffusion [5]. Base on the Springer model [6,7], equation (6) is used in this research to describe the diffusion of water in both epoxy and glass reinforced epoxy specimens.

$$\frac{M_{\%}}{M_{\infty}} = 1 - \exp(-7.3(\frac{D_z}{h^2}t)^{0.75}) \quad (6)$$

In this equation, t is the immersion time, M_{∞} is the percent weight uptake “at saturation” also called the equilibrium water concentration, D_z is the diffusion coefficient and h is the thickness of the specimen. $M_{\%}$ is the percent weight uptake at time t and is given by:

$$M_{\%}(t) = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100 \quad (7)$$

M_{wet} is the mass of the material after immersion during time t and M_{dry} the initial mass of the dry material. The coefficient of diffusion is considered to be constant in the direction of diffusion, z , and independent of time and water concentration.

The transition time, at which the water concentration reaches the equilibrium, is defined by t_t

$$t_t = \frac{p}{16} \frac{h^2}{D_z} \quad (8)$$

2.3 Hygrothermal effect models

Under hygrothermal conditioning, polymeric material (without fibre) tends to swell due to water diffusion. The thickness change is assumed to be a linear function of the weight uptake within the interval under investigation. In addition, water diffusion results in a reduction in the mechanical properties such as modulus and strength, increases in the electrical conductivity and dielectric permittivity [8].

Based on the analogy between the dielectric and mechanical properties of section 2.1, a change of the dielectric loss factor is reflecting a change, as well, in the mechanical loss factor mechanical. It is shown in [8] that the absorption of the polar water molecules leads initially to a slow increase in dielectric loss factor in fibre reinforced epoxy as a function of water uptake. However, this can suddenly increase because of the development of microcracks according to Cotinaud et al.1982 [8]. This behaviour suggests that beyond a certain water concentration irreversible damage occurs, leading to microcracking or interfacial damage and the creation of a network of free water molecules [8].

In this research and referring to [8], two degrees of degradation are attributed to the change of the dielectric loss factor in out-of plane degradation, and given by,

$$\tan d_D(t) = \alpha(M_{\%}(t)) \tan d_{D0}, \quad t < t_t \quad (9)$$

$$\tan d_D(t) = \tan d_{D0} \sqrt{\frac{t}{t_t}}, \quad t \geq t_t \quad (10)$$

where $\tan d_{D0}$ is the dielectric loss factor of the dry material and α is defined as a function of water uptakes ($M_{\%}$), which is assumed to be reversible and presents the degree of degradation in the first stage of water absorption. Equation 10 presents the irreversible stage, damage, of the hygrothermal effects on the material.

3. EXPERIMENTS

3.1 Material

Two material plates were produced by mixing the araldite Ly113 epoxy and 33 wt% HY97 amine-hardener after degassing under vacuum conditions at room temperature. For the composite plate, the mixture of epoxy resin and hardener is injected through 6 layers of glass fibre fabrics (woven 8 H satin 0/90, 0.3 Kg/m²) using the Vacuum Infusion Method at room temperature. Afterwards and in order to accelerate the process of curing of the matrix, the two plates were heated using the post curing: 2 hours at 80°C, 2 hours at 100°C and 1 hour at 120°C, successively.

Specimens were cut from plates and cleaned with ethanol. After pre-conditioning at 30°C, the specimens were immersed, under fixed conditions, in distilled water at 70°C for 6 months. Specimens were removed at fixed time-intervals, weighted and measured in thickness. The fibre volume fraction V_f , was derived by burn off of the matrix and presents 43% of the total volume fraction.

3.2 Dielectric spectroscopy

Capacitance and dielectric loss factor in the frequency range [10K-20M] Hz were measured using dielectric spectroscopy based on the impedance method (ASTM 150D). Square specimens of 20x20mm² were used for the dielectric spectroscopy. The relative real part of the complex permittivity, ϵ' , was determined through the measured capacitance C

$$\epsilon' = \frac{C}{A\epsilon_0}h \quad (11)$$

where h denotes the thickness of the tested specimen, A presents the area of the measured specimen and ϵ_0 denotes the vacuum permittivity ($8.85 \cdot 10^{-12}$ Farads /m).

3.3 Dynamic mechanical analysis

According to the analogy proposed in the section 2.1, dynamic mechanical compression testing should be the appropriate method to evaluate the out-of-plane properties of the test material. Unfortunately, it is difficult to measure the mechanical loss factor by means of dynamic compression, due the relatively small thickness of the specimens. Instead, we used torsional-dynamic mechanical analysis (torsional-DMA) with a Myrenne pendulum is to measure the in-plane shear properties (storage, loss modulus and loss factor) and glass transition temperature of the tested material. However this technique measures the in-plane shear properties. By choosing a (0/90) orientation of the fabric, the properties measured are matrix dominated and equal to the shear properties of one lamina.

Rectangular specimens of 74x8.5mm² were used for the torsional-DMA in the temperature range [20-150] °C at a frequency of 1Hz. In this experiment, the response of the tested specimen to a twisting moment is measured. The twisting motion involved fixing one end of the coupon in all degrees of freedom and imposing a rotation angle, θ , at the opposite end. The measured values are the storage shear modulus G' , the loss modulus G'' and the loss factor, given by, respectively

$$G' = 4p^2 \cdot q \cdot F \cdot (f^2 - f_0^2) \quad (12)$$

$$G'' = 4p \cdot q \cdot \Lambda \cdot F \cdot f^2 \quad (13)$$

$$\tan d_M = \frac{G''}{G'} \quad (14)$$

where A is the damping energy, f is the frequency of the system including the specimen and f_0 is the frequency of the system without specimen. F is called the dimensional factor of the specimen, equation 15.

$$F = \frac{3.L}{h^3.w.(1-0.63\frac{h}{w})} \quad (15)$$

Here L is the length of the structure, w is the width and h is thickness of the tested specimen. The glass transition, T_g , is measured by means of the loss factor peak.

4. RESULTS AND DISCUSSION

4.1 Water uptake

Figure 2 shows the percent weight changes $M\%$ (equation 7) of the composite and epoxy matrix specimens used in the dielectric measurements. Specimens were immersed in the 70°C-distilled water during 6 months. The fitted model (equation 6) is as well shown in figure 2.

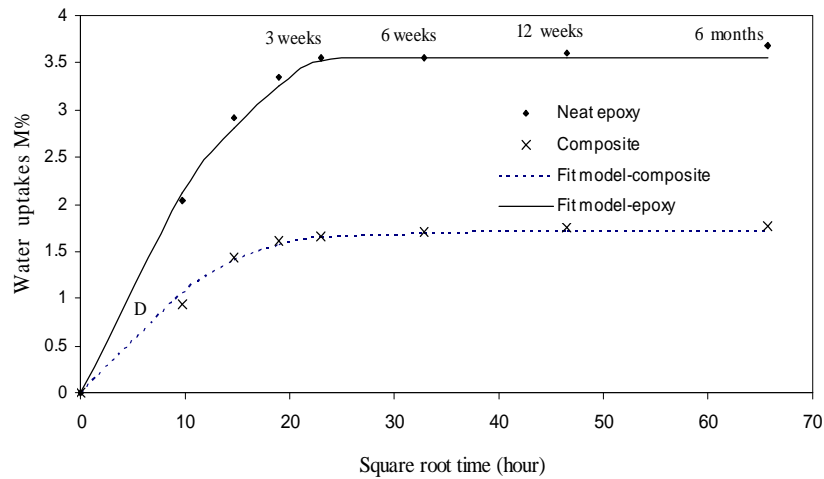


Figure 2: Percent weight uptakes of composite and epoxy matrix.

As shown in figure 2, the proposed model (equation 6) values are fitting those of the measurements for both epoxy and composite specimens. The thickness of the specimens, coefficient of diffusion and the transition time are given in table 1.

Table1: Properties of the composite and epoxy.

Material	h (mm)	M_{∞} (%)	D_z (x 10 ⁻³ mm ² /h)	t_t (hour)
Composite, $V_f=43\%$	1.68	1.68	1.80	308
Epoxy matrix	2.02	3.56	3.51	225

4.2 Dielectric response

The dielectric loss factor measurement as a function of frequency is shown in the figure 3, in the dry state and after 6 weeks of immersion. The results show two kinds of relaxation mechanisms at the saturation phase of the water diffusion in glass reinforced epoxy material.

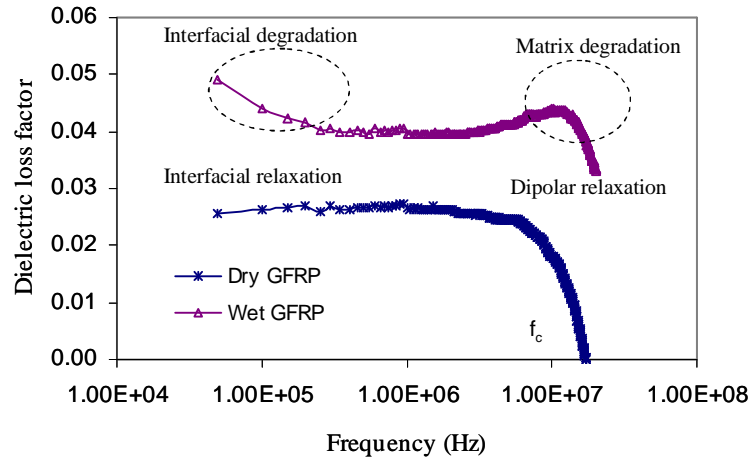


Figure 3: Dielectric loss factor of the glass reinforced epoxy laminate dry and immersed.

The increases in the characteristic frequency (f_c) in the high frequency range and in the dipolar relaxation peak are attributed to the hydrolysis of the epoxy matrix. However, at low frequency, the increase in the loss factor, which is known to be ionic relaxation (compromise of ionic conductivity and interfacial relaxation) [9] is reflecting the deterioration of the interface fibre/matrix and matrix cracking.

Within six months of immersion, the change in the relative dielectric permittivity and the loss factor as a function of time are shown in figure 4.

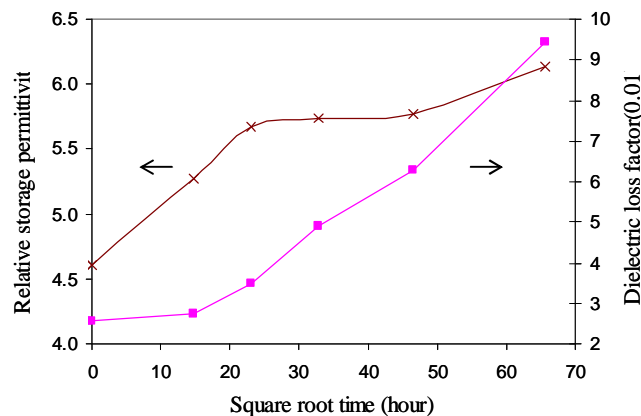


Figure 4: Variation of the relative dielectric permittivity and the dielectric loss factor at 0.5MHz.

In figure 4 and until three months of immersion, the change of the dielectric permittivity takes a similar behaviour as the water uptakes, see figure 2. The verification of the fitted

model (equation 9 and 10) values and the measured values of the dielectric loss factor change is shown in figure 5 where the factor α is given by: $\alpha(M_{\%}) = 1 + 0.05M_{\%}(t)$.

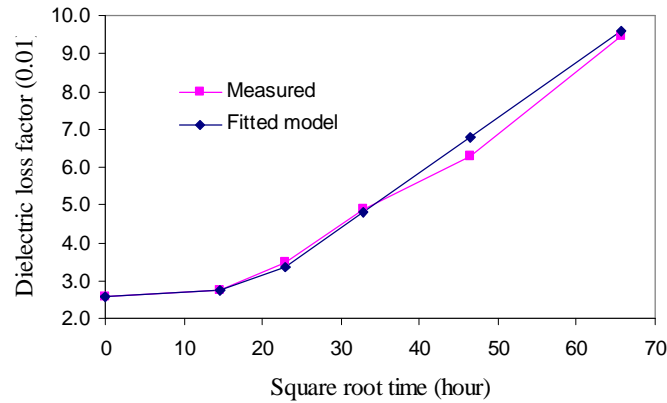


Figure 5: Comparison of the measured and fit model values of the dielectric loss factor.

As shown in figure 5, after the transition time (308 hours) the dielectric loss factor is suddenly increasing, in agreement with earlier results [8] mentioned in section 2.3.

4.3 Mechanic response

At 6 weeks of immersion, the DMA measured values with temperature dependence of the loss factor show a plasticisation of the composite material; a negative shift of the transition region and a broadening of the loss factor curve due to the water diffusion, see figure 6.

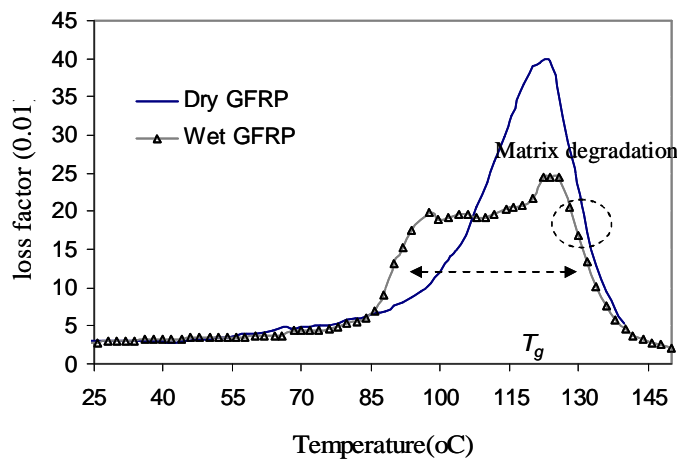


Figure 6: Mechanical loss factor of dry and immersed composite in distilled water at 70°C.

These changes are happening in the rubbery region where the matrix behaviour is dominant; in which it is difficult to conclude whether the effect is due to the degradation of the fibre/matrix adhesion. Generally, the glass transition region is referred to as an α -glass transition [3] when measured by mechanical means. There would be the additional

complication of the Poisson's ratio change [3]. However the transition temperature of γ -transition ($T < 0^\circ\text{C}$) is shown to be sensitive to the effects of the addition of fibre in the epoxy matrix with a constant Poisson's ratio [3]. Consequently, a measurement of loss factor in the γ -transition region of the immersed composite may show a considerable change due to water uptake.

Figure 7 shows the hygrothermal effects on the loss factor and the elastic modulus of the composite specimen around 21°C and at 1Hz. The storage modulus is slightly decreasing, while the loss factor is increased compared to the loss factor of the dry composite.

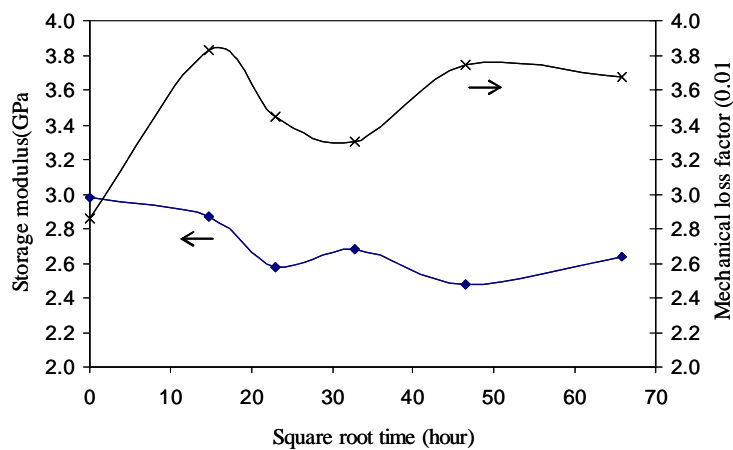


Figure 7: Change of the shear modulus and loss factor with the time of immersion measured around 21°C .

Around six weeks of immersion, the storage modulus has slightly increased with respect to three weeks of immersion. This behaviour is certainly due to the rectangular area of the specimen, which affects the water uptake behaviour.

The storage modulus of the composite decreased linearly with the water uptake, at $T \ll T_g$. By respect to the storage modulus change of the unreinforced matrix in the glassy region, the elastic region of the composite material appears to be far more sensitive to the degradation of the matrix/fibre adhesion and the related stress transfer of fibre-to-matrix than the rubbery phase.

4.3 Comparison of dielectric to mechanical changes

Figures 4 and 7 show qualitative agreement with the analogy between the dielectric and mechanical properties changes proposed in section 2.1.

Quantitatively, and comparing to the dielectric loss factor change at ambient temperature, the mechanical loss factor is less sensitive to the hygrothermal conditioning (water and temperature). However there is a correlation between the characteristic time ($1/f_c$) and the glass transition temperature T_g ; both of them are decreasing, reflecting the softening of the matrix due to water uptake.

5. CONCLUSION

Both dielectric and mechanical loss factors are efficient parameters to characterise the properties changes of degraded composite materials, yet the dielectric loss factor is much more sensitive to the microcracking and the phase separation of composite constituents.

A proper choosing of the temperature and frequency ranges of the mechanical measurement may provide considerable conclusions on the dielectric-mechanical analogy and especially on the detection of the fibre/matrix interface degradation.

REFERENCES

- 1- Weitsman Y.J. Effects of fluids on polymeric composites-a review. Talreja R., Manson J.A.B. In: Kelly A, Zweben C. Comprehensive composite materials, Vol.2. UK: Elsevier Science Ltd, 2000; 369-401.
- 2- Mallick P.K. Fiber-reinforced composites, materials, manufacturing, and design. Marcel Dekker, Inc 1993.
- 3- Ishida H. Characterization of composite materials. Butterworth-Heinemann USA, 1994.
- 4- Havrilliak S., Havrilliak S.J. Dielectric and mechanical relaxation in materials: analysis, interpretation, and application to polymers, Germany: Hanser publishers, 1997.
- 5- BS EN ISO 62: 1999, Plastics - Determination of Water Absorption.
- 6- Springer S.G. Environmental effects on composite materials. PA: technomic publishing Co., Inc. 1981, pp. 1-6.
- 7- Shen C.H., Springer G.S. *Moisture Absorption and Desorption of Composite Materials*. Journal of Composite Materials, 10, pp 2-20, 1976.
- 8- Kelly A. Concise encyclopedia of Composite materials. CBE, FRS page: 165-173. Pergamon Press plc 1989.
- 9- Anderson J.C. Dielectrics. London 1964.