

**MODELLING AND PREDICTION OF THE
ENVIRONMENTAL DEGRADATION OF FIBRE
REINFORCED PLASTICS**

Etienne Kolomoni Ngoy

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DECLARATION

I declare that this thesis is my own unaided work. It is being submitted for the Degree of Doctor of Philosophy to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

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ABSTRACT

In their service life, fibre reinforced plastics (FRP) face a variety of environmental conditions resulting from natural or artificial factors. These include variable temperature and humidity conditions, energetic radiations such as ultraviolet rays from the sun, and diverse chemical reactants such as liquid in storage tanks and pipes. These factors are always combined and negatively affect the material properties over the time.

Therefore, optimized utilization of FRP material requires reliable methods for quantifying, controlling, and predicting environmental effects. This allows for optimal handling of issues related to component design, economic assessment and safety considerations, as well as the technical problems relating to equipment maintenance.

Efforts worldwide are devoted to the modelling of FRP environmental degradation. However, modelling efforts have been hindered by the complexity of the process.

This analysis presents a comprehensive model of the environmental degradation of FRP and a prediction method. The modelling method consists of a theoretical demonstration based on material science theories. An analytical approach is proposed. It resolves the complexity of the process into only three components: the chemical degradation, the physical degradation, and the stress state modification. A method to represent the real service environment as a constant environment in laboratory is also introduced.

Then, the comprehensive model is expressed as a dynamic constitutive equation resulting from the combination of the historical variation in chemical link density and cohesive forces and the stress history of the material. It is shown that:

- The average of the chemical and physical degradation as well as its upper and lower limits can be determined in a laboratory, in a constant environment, as exponential functions of the degradation time.
- The environmental degradation can be comprehensively measured as a stress relaxation.
- Acceleration of the predictive test can be obtained from a modified time temperature shift principle.

RELATED PUBLICATION

Ngoy E.K., Campbell I.M.D., R. D. Reid, Paskaramoorthy R. “Modelling and prediction of the chemical and physical degradation of fibre reinforced plastics” *Journal of Materials Science* Vol. 44 (9), 2009, p. 2393, doi: 10.1007/s10853-009-3303-4.

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LIST OF SYMBOLS

Coefficient of chemical activity	γ (dimensionless number)
Coefficient of linear correlation	R^2 (dimensionless number)
Constants	$\alpha_i, \beta_i, a_i, b_i, c, \text{const}$
Density	ρ (kg/m ³)
Diffusion coefficient	D (m ² /s)
Diffusivity	J (l/m ² .s, moles/m ² .s)
Enthalpy	H (J, cal)
Ideal gas constant	R (J/ °K.mole, l.atm/°K.mole)
Kinetic constant	K
Mathematical divergence	∇
Natural logarithm	Ln
Power	P (W)
Pressure	P_r (Pa)
Relative humidity	Φ (%)
Sodium hydroxide	NaOH
Temperature	T (°C, °K)
Thermal flux	Φ_T (W/m ²)
Time	t (s)
Variation	Δ
Index of material rheology	Γ
Volume	V (m ³ , l)
Work and energy	W (J, cal)

LIST OF ABBREVIATIONS

Chop strand mat	CSM
Fibre Reinforced Plastics	FRP
Glass Reinforced Plastics	GRP
Woven roving	WR

1 INTRODUCTION

Fibre reinforced plastics (FRP) offer a number of advantages including light weight, better corrosion resistance, easy shaping, aesthetics, excellent mechanical properties and have found a wide variety of applications in modern industry. However, one limitation that is likely to slow down the use of FRP concerns the method for environmental degradation evaluation. The major unresolved issues involved concern the availability of a comprehensive model of the degradation process, capable of providing a quantitative basis for an acceptable predictive method of assessing the material performance in service, using short-term test results [1-3].

In their service life, FRP materials face a variety of environmental conditions resulting from natural or artificial factors. These include variable temperature and humidity conditions, energetic radiation such as ultraviolet (UV) rays from the sun or other artificial sources, and diverse chemical reactants such as liquid in storage tanks and pipes, or atmospheric oxygen and ozone.

FRP materials interact with environmental factors. This results in a change of the chemical and physical structure of the material and its composition. Effects of such changes are irreversible degeneration of the mechanical properties of the material for the most part. Aesthetic characteristics, such as colour and glow, undergo changes. The material may become brittle and cracks appear. In practice, any change affecting the material properties relative to the initial desirable properties is called degradation.

Environmental degradation factors are always combined and negatively affect the material properties over time. The top of a boat for instance is subjected to ultraviolet rays in combination with corrosive humidity and temperature cycles.

The inner surface of a pipe or a storage tank faces wet and corrosive conditions in combination with temperature cycles. The resulting degradation mechanism is complex. The degradability in service conditions varies from one polymer to another depending on the chemical structure and the presence of impurities that considerably contribute to the initiation of many degradation processes. For most of the cases, the environmental degradation is a slow process lasting up to several decades before effects be manifested. However, there are cases where effects are seen at short-term scale.

Therefore, optimized utilization of a fibre reinforced plastic material requires the availability of a reliable method for quantifying environmental effects and for predicting material lifetime. This allows for optimal handling of issues related to component design, economic assessment and safety considerations, as well as the technical problems relating to equipment maintenance. In this regard, efforts worldwide are devoted to the modelling of FRP environmental degradation. However, the high complexity of the process explains why no general model or viable corrosion resistance test method has been available so far [1, 2].

A great number of analyses have been published on the environmental degradation of fibre-reinforced plastics. In this regard, four predominant trends have been surveyed in the literature.

The first trend is supported by abundant literature and focuses on the characterization of effects and/or on the description of mechanisms [1-42]. The second trend in the literature deals with modelling and is also the focus of many published works [1, 16, 39, 43-50]. Modelling efforts, for the most part, are limited to partial models based on a single mechanism dominating the whole process. Such models are mostly based on moisture and/or on temperature effects and are empirical. Another modelling approach is that based on chemical reaction mechanisms especially in the case of hydrolysis and oxidation or photo-oxidation [23, 47-49]. The third trend in the literature goes beyond the characterization of effects and mechanisms and suggests prediction methods. These methods are

based on the assumption that the dominating mechanism is thermally activated and follows the Arrhenius law. The prediction relies on linear extrapolation based on temperature variation.

Due to the lack of predictive models, some researchers resort to exposure of the FRP material in typical service environments in order to assess the environmental resistance of the material. In this fourth trend, the method requires many years of exposure and tests must be conducted for each climatic area [1, 36]. Similarly, in industry, standards specify the material lifetime based on statistics resulting from many years of practice in the field. This implies that many years of experimentation are required prior to setting the lifetime standard for each new specification.

The lack of a reliable method of environmental effect prediction has been a hindrance for extended use of FRP material in fields such as construction [2, 17, 19] and is a cause of concern in the chemical industry where cases of catastrophic failure due to environmental degradation were reported [51].

Experimental methods show limitation with regards to the comprehensive description of FRP environmental degradation process. The work presented here suggests an analytical approach based on well-established material science laws. It is felt that, there is a need for a theoretical analysis of the environmental degradation of FRP. Such analysis should lead to a theoretical basis capable of providing a common frame where all the processes involved in the environmental degradation of FRP may be treated comprehensively. Without such a frame, direct experimental observation can only lead to partial and limited treatment of the problem.

This analysis is aimed at the development of a short-term test method for the prediction of the environmental degradation of mechanical strength of FRP composites. The method is based on a comprehensive mathematical model, involving all the factors that affect the degradation process. These factors include

the chemical degradation, the ultraviolet rays attack, the temperature and humidity effects, and the stress corrosion. In addition, this method must be practical, and relatively fast.

The suggested model is a mathematical function logically derived from material science theories and expresses a qualitative relation between the material degradation and environmental factors. The development of the model is based on a theoretical demonstration. The demonstration is based on a deductive argument using material science laws as premises. This means that, well established theories are applied to FRP environmental degradation process through a deductive reasoning in such a way that, results arrived at are logical and rigorous consequence of pre-existent material science theories. Therefore, the validation of the model is provided by the validity of the material science laws because the deductive reasoning shows that it would be self-contradictory to assert these laws and deny the model. Or, the negation of the model would be contradictory to the veracity of the material science laws. However, the deductive reasoning is further supported by experimental results obtained from a laboratory.

The suggested analytical approach resolves the complexity of FRP environmental degradation into only three processes: the chemical degradation, the physical degradation, and the modification of the stress state. The first step of the demonstration deals with the chemical and physical degradation. The method consists of deriving a qualitative mathematical relation between the degradation rate and the environmental factors including the chemical concentration, the moisture, the diffusion coefficient, UV rays, and the temperature.

In the second step, effects of mechanical stresses are introduced through a dynamic constitutive equation that takes account of the evolution of the material stiffness. In that equation, the material stiffness is expressed as a function of time arising from two contributions: the mechanical reaction due to the material viscoelasticity and the chemical and physical degradation. The resulting dynamic

constitutive equation provides the comprehensive model of FRP environmental degradation.

The analysis introduces also a method of reliably relating laboratory test results to the real service conditions. This method is based on the use of constant environment. From all the above, a short-term test method of FRP environmental degradation is deduced and is based on the test of stress relaxation.

Additionally, the modelling method suggested in this analysis is based on the environmental resistance of the matrix. This is because in industrial applications, the environmental resistance of a laminate is determined by that of its barrier coat, made of a resin rich layer. It is also observed, in general, that the degradation mechanism of FRP initiates in the matrix and primarily affects the matrix dominated properties [42, 46, 50]. Though the method can be applied to any thermoset matrix, experimental results are limited to those obtained from an orthophthalic polyester matrix. The laminate under investigation was designed to be comparable to a standard barrier coat and exposure of the material corresponds to that of a pipe or storage tank environment.

From the general introduction to the general conclusions that constitute respectively the first and the last chapter, the analysis goes over five other chapters to present successively a literature survey, a method for the determination of the laboratory test conditions, the chemical and the physical degradation, and the constitutive equation of environmental degradation in FRP.

The first chapter, this introduction, presents a description of the problem dealt with and the motivation of the research as resulting from unfulfilled need for a reliable method to predict FRP environmental degradation and the subsequent need for optimization of the design, economic assessment of the investment, safe use of GRP equipments, and optimization of maintenance operations.

The following two chapters are devoted to the literature survey. Focus is on two main topics as arising from the number of works published on these topics. These include environmental degradation mechanism and effects in chapter 2, and modelling efforts in chapter 3.

Prior to mathematical modelling of the environmental degradation process, the chapter 4 deals with a method to represent the real service environment into laboratory and a model of the environment that allow taking into account its complex variability when modelling the degradation process.

The chapter 5 constitutes the first step of the mathematical modelling of the environmental degradation process. It presents details of the modelling approach, and the chemical and physical degradation model. This part deals with case where no mechanical stress is involved in the degradation process. But, it provides the basis for the introduction of the chemical and physical degradation in the general case where mechanical stresses are combined with the remaining environmental factors. This general case is presented in chapter 6, which deals with the constitutive equation of environmental degradation in FRP and the resulting prediction methods. The constitutive equation provides the general model allowing a comprehensive test of environmental degradation of FRP.

The last chapter is the general conclusion where the analysis is summarized, and the main results presented. Of great importance, the short-term test method resulting from this work is presented. Some links to possible future works are also defined.

Appendix A is introduced to deal with the demonstration of some energy and mass transfer equations relating to the modelling process. Specials issues relating to the mathematical resolution of equations are dealt with in appendix B and C. Appendix D provides an illustration of the computation method relative to the prediction of the physical and chemical degradation of FRP.

2 ENVIRONMENTAL DEGRADATION MECHANISMS AND EFFECTS, A LITERATURE SURVEY

The literature describes the environmental degradation as a complex mechanism resulting from several factors. Moisture and temperature are viewed as the most common and deleterious environmental factors and many analyses focus on this. Ultraviolet irradiation and attack by chemical agents constitute also two of the most important aspects of the environmental degradation mechanism studied in the literature. This chapter presents four sections devoted to each of these environmental factors. Attention is also given to the stress corrosion aspect.

2.1 Moisture Diffusion

Moisture results from natural humidity, rainfall, industrial vapours or any liquid in contact with the material such as liquid circulating in pipes or stored in tanks. The relative humidity in the material service environment, can take values from moderate to fully moisture-saturated environment 100%. The humidity effects on FRP are chemical, physical, and mechanical.

Once humidity encounters the FRP laminate surface, it dissolves on the substrate surface and then migrates through the bulk of the material. The diffusion process is facilitated when the permeant molecules present compatibility with the polymeric structure in terms of polarity and cohesive energy. Plasticization occurs and this, subsequently, increases the diffusion rate. In the other side, when there is incompatibility, clustering occurs resulting in retardation of the penetration [24]. Many other factors, both internal and external, affect the diffusion process. However, depending on the environmental conditions and material characteristics, the diffusion results in a steady state concentration of the diffused humidity. The presence of moisture inside the FRP laminate structure as a foreign material,

negatively affects the cohesive characteristics of the laminate. The resulting effects are swelling, softening, and reduction of the glass transition temperature.

Moisture diffusion through FRP laminate has been extensively investigated throughout the last century. Main issues dealt with were firstly, the determination of the diffusion kinetic in terms of humidity distribution inside the laminate as a function of time. Secondly, the determination of humidity effects on the mechanical properties of the laminate. Thus, this section deals firstly with the kinetic of diffusion in the FRP laminate and secondly, with the effects of moisture diffusion on the mechanical properties of the laminate.

2.1.1 Kinetics of moisture diffusion through FRP laminates

The general kinetic law controlling the diffusion of liquid through a solid material is known as Fick's law [52]. According to this law, the mass of liquid entering a unit volume of a solid material per unit time is given by:

$$\frac{\partial C}{\partial t} = D \nabla^2 C \quad (2.1)$$

where C and t represent the liquid concentration and the time respectively. D is the diffusion coefficient that accounts for the material characteristics. Barrer [52] presents solutions of this equation for variable cases.

According to Springer [16], reporting on several researches conducted on environmental effects on composites materials, though for most of FRP materials encountered Fick's law constitutes a reasonable approximation of the diffusion kinetic, there are still many cases where this law remains inapplicable.

In the reported researches [16], the case of E-glass polyester composite, exposed to several kinds of liquid and humid air at variable temperature, shows that, under most conditions, Fick's law may be used to assess effectively the kinetic of diffusion. The same experiment shows also that the maximum value of moisture uptake is a function of the ambient relative humidity and does not depend on the

temperature for most of the times [6]. Shen and Springer [10] have studied the moisture absorption and desorption of composite material. They suggested the following relation between the ambient relative humidity Φ and the maximum moisture content M_m of laminate exposed to that environment:

$$M_m = a\Phi^b \quad (2.2)$$

In this relation a and b are constants depending on the material.

Based on Fick's law, the same authors suggested for the moisture content M (percentage weight gain) the following equation:

$$M = G(M_m - M_i) + M_i \quad (2.3)$$

In equation (2.3), M_i is the initial moisture content of the material, M_m is the maximum moisture content that can be attained under the given environmental conditions, and G is a time dependent parameter given by:

$$G = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp[-(2j+1)^2 \pi^2 (\frac{D_x t}{s^2})]}{(2j+1)} \quad (2.4)$$

G can be approximated by the following expression:

$$G = 1 - \exp[-7.3(\frac{D_x t}{s^2})^{0.75}] \quad (2.5)$$

where D_x is the material diffusivity in the direction normal to the surface and s is a parameter relative to the material thickness. This relation was developed for one-dimensional problems where the ambient moisture and temperature were assumed constants. The initial moisture and temperature distribution inside the material also must be uniform. The application of the proposed model to the case of a unidirectional graphite T-300 fiberite 1034 composite, fully immersed in water or exposed to humid air, has shown good correlation between experimental data and the theory.

Some investigators reported that moisture absorption level is history-dependent. Due to clustering, the diffusion proved to be a non-fickian two stage process. The

diffusion coefficient decreases with increasing permeation [18] and consequently, sorption behaviour under temperature cycles is not the same as under constant humidity and temperature level [19].

In material science, the diffusion mechanism through solid material is explained by the theory of vacant sites. According to this theory, solid polymers contain a steady-state distribution of molecular-size voids [24]. The diffused particles move through the solid network by interchange with the voids or vacant sites [21]. Though contested by some theorists who estimated, for the case of epoxies for instance, that the only mechanism governing the diffusion into solid material is the molecular interactions between the permeant and the polymeric solid [22], this theory allowed understanding successfully the kinetic of the diffusion for many cases. However, it is known that the diffused humidity interacts with the polymeric material and this leads to the transformation of the polymer. At least three types of transformation that mostly affect the permeation process have been surveyed by Gesner [23]: cross-linking, crystallization, and micro porosity. The cross linking reduces the material permeability likewise the crystallization. The micro porosity allows the convective diffusion to take place. This, subsequently, increases the total diffusion rate. All of the above explains the multiple behaviour of the diffusion coefficient that has been observed.

Srivastava [7] has reported a case where moisture affects the material rheology by increasing the viscosity. This was shown by the increased shear strength of a quasi-isotropic glass-fiber reinforced epoxy vinyl ester composite that was immersed in water with variable immersion time. This implies that the coefficient of diffusion decreases during the course of moisturization. Tang *et al* [8] mention a different behaviour. The plot of shear strength versus moisture content in a Fiberite 976 composite showed a decreasing trend of the shear strength corresponding to the increase in moisture content.

In fact, moisture diffusion through FRP appears to follow variable kinetic curves depending on the physical transformation occurring in the material or chemical

reactions between the permeant and the material [19]. This is illustrated in Figure 2.1:

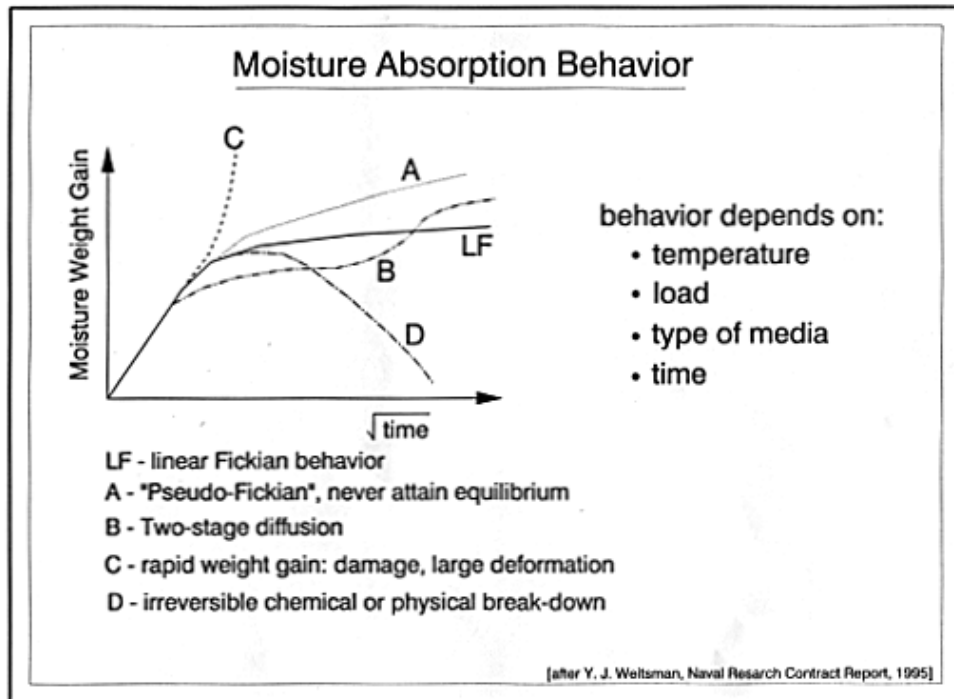


Figure 2.1 Moisture absorption trends in FRP [19]

- Curve LF represents linear Fickian behaviour where the moisture weight gain gradually attains equilibrium after a rapid initial take-off.
- Curve A represents the so-called pseudo-Fickian behaviour where the moisture weight gain never reaches equilibrium after the initial take-off. This depicts a transformation of the material structure accompanying the absorption.
- Curve B displays a two-stage diffusion denoting a change of environment such as temperature, applied load, relative humidity, or physical transformation occurred in the material.
- Curve C represents the case where large deformation or damage occurs in the material. Such large deformation may be fiber/matrix debonding or matrix cracking.

- e. Curve D shows the case where the gain in moisture weight presents a decreasing trend after the initial take-off. The process is irreversible as a result of leaching out of the material from the bulk following chemical or physical break-down. This, in fact, means that the weight variation measured does not represent the real humidity uptake but the loss of laminate mass due to leaching.

2.1.2 Factors affecting the diffusion process in FRP laminates

Many factors both internal and external to the material affect the kinetic of moisture diffusion in FRP.

Fibre volume fraction and orientation effect

Rao *et al* [25] showed that the equilibrium moisture content in a composite is a function of the fibre volume fraction and the fibre orientation to the diffusion path. These authors have studied the case of three-dimensional diffusion in a jute-epoxy laminate and in a glass-epoxy laminate. The moisture diffusion is as higher as the fibre orientation to the diffusion path α is increased. The fibre orientation effect is inversely proportional to the fibre permeability. The resulting diffusion coefficient D_c may be assessed as function of fibre and resin diffusion coefficient respectively denoted D_f and D_r , as follows:

$$D_c = V_f D_f \left(\cos 2\alpha + \frac{D_{22}}{D_{11}} \sin 2\alpha \right) \text{ if } D_f \gg D_r \quad (2.6)$$

$$D_c = D_r (1 - V_f) \left(\cos 2\alpha + \frac{D_{22}}{D_{11}} \sin 2\alpha \right) \text{ if } D_f \ll D_r \quad (2.7)$$

In equations (2.6) and (2.7), α , D_{11} and D_{22} respectively represent the fibre orientation angle, and the diffusivity in the directions parallel and normal to the fibre (longitudinal and transverse).

The equilibrium moisture content M_m is a linear function of the fibre volume fraction:

$$M_m = aV_f + b \quad (2.8)$$

In equation (2.8), a and b are constants.

Effect of solvent molecules

The molecule size of the permeant liquid, likewise the molecule polarity, significantly affects the permeation. Larger molecules diffuse more slowly and polar molecules diffuse more easily in polar thermosetting structure. The analysis conducted by Sonawala and Spontak [27] showed, for example, that the isophthalicpolyester offers a high solubility to aqueous solutions due to the high concentration of ester-linkages available for hydrogen bonding with permeated water. The analysis of Bellenger *et al* quoted by Sonawala [27] showed that the equilibrium moisture content does not depend on the temperature and the packing density. Instead, it is correlated to the concentration of hydroxyl, ether, and ester groups. It was shown that the solubility of water into the vinyl ester laminate increases with the number of carbonyl groups. Verleg and Van der Wal [53] studied the absorption of several types of solvents in thermosetting unsaturated polyester and vinyl ester. Their results showed that the penetration time as well as the penetration flux, increases from the lowest solvent to the heaviest one.

Temperature effects

Throughout the literature, it is generally observed that temperature affects the diffusion coefficient and effects on the equilibrium moisture content depend on the material type. Loos *et al* [5-6], reporting on a case of fiberglass polyester composites, showed that the diffusion followed Fick's law and the equilibrium moisture content does not depend on the temperature. However, in the case of epoxy composites reported by Marsh *et al* [18], the solubilization followed Henry's Law given by the equation (2.9). According to this law, the equilibrium moisture content is a function of the humidity pressure P_r and depends on the temperature T as follows:

$$M_m = \gamma P_r e^{\frac{-H}{RT}} \quad (2.9)$$

In equation (2.9), γ is the coefficient of chemical activity. H , and R respectively represent the solubilization enthalpy, and the ideal gas constant.

The temperature dependence function of the diffusion coefficient for permeable and impermeable material can be represented by an Arrhenius type relationship.

$$D = D_0 e^{\frac{-W_D}{RT}} \quad (2.10)$$

Where W_D is the activation energy of diffusion and the subscript 0 refers to the initial temperature conditions. This relation has been successfully used by several researchers [8, 21, 54]. However, it is reported that this holds only over a limited range of temperature below the temperature of glassy transition [2].

Applied load and hydrostatic pressure effects

The load applied on the material also affects the moisture uptake. Maron *et al* [29] observed the moisture penetration into both glass fibre and carbon fibre epoxies composite under stressed and unstressed conditions at 95°C. From their observation, they concluded that the diffusion rate as well as the equilibrium moisture content is increased under external load. The same behaviour was observed in the course of studies conducted in the composite facility of the school of mechanical engineering at the University of the Witwatersrand on the polyester, vinyl ester resin, and a corrosion barrier coat material, all of them subjected to tensile load [55-57].

It is reported [2] that the hydrostatic pressure does not influence the diffusion coefficient but affects equilibrium percentage moisture in the material. Avena *et al* [4] observed that high pressure is susceptible to reduce moisture uptake as it tends to compress the matrix and close the micro voids or defects.

2.1.3 Humidity effects on FRP laminates

Major concerns about moisture uptake in FRP laminate are related to the deterioration of the material performance. As said earlier, the moisture diffusion

into FRP laminate induces swelling, plasticization, clustering, and reduction of glass transition temperature. Some liquids are susceptible to react chemically with the polymeric matrix as well as with the reinforcing fibres. For instance, water, likewise the remaining polar solvent such as alcohols, hydrazine, and ammonia, attacks the polymeric material by a solvolytic reaction whereby the hydroxyl reacts with the polymeric chain. This leads to a chain scission and the formation of alcohol and carboxylic acid. The solvolytic reaction is catalyzed by acidic or basic environment. Moisture attacks the fibre material as well as the interface fibre-matrix by hydrolysis.

Another known effect of moisture on FRP is related to the cycling humidification. The material exposed to the natural environment is often subjected to cycle effects of moisturization during rainy time followed by drying during sunny time. The cyclic moisturization induces residual stresses inside the material leading to cracks apparition.

Hygroscopic expansion resulting from the absorption of moisture by a FRP composite is also a well-known effect. The material is subjected to a strain assumed to be proportional to moisture content expressed as weight percentage. The constant of proportionality is called the coefficient of the hygroscopic expansion. The hygroscopic expansion effect is generally associated with the thermal strain resulting from the thermal expansion. When the material is constrained, as are the individual layers of fibres and matrix in a laminate, the thermal or hygroscopic strain cannot develop freely. This leads to the hygrothermal stresses [58] of which effects on the FRP material has been recognized as one of the most deleterious. For example, in construction, Sachin *et al* [59] have observed that the main cause of environmental damage into the FRP wrapped concrete cylinders is the combined effects of moisture and elevated temperature on the tensile strength of E-glass fiber.

Thus, the humidity negatively affects the internal structure of FRP material and accelerates the failure of the laminate under load.

Many reported works in the literature show that moisture affects both the tensile strength and the elastic modulus of the composite material. For example, the degradation of material properties can reach 20 to 25% decrease in modulus, for 3 to 4% moisture content, depending on the material characteristics, the temperature and the degree of moisturization. This is illustrated by the case of brittle epoxies studied by Tang *and al* [8]. In a survey into durability of fluid containment vessels marine structures and aircrafts with up to nineteen years of service, Lieblein [60] suggested that, over a period of twenty years, in addition to the reduction in strength as result of exposure to moisture, the reduction in modulus is of the order of 10 %.

Moisture effects are often associated with temperature. Shen and Springer [10] have assessed the change in the ultimate tensile strength of composite materials exposed to air in which humidity varied from 0 to 100% and temperature ranges from 200°K to 450°K. The material used was the Thornel 300/fiberite 1034 graphite epoxy composite with 0°, 45°, and 90° lay-ups. For 90° lay-up, they observed 60 to 90% reduction in tensile strength for about 1% to 1.5% moisture content combined with temperature. For 0° and 45° lay-up, in the same conditions, effects were negligible. The same authors, Shen and Springer [11], investigated also the change in elastic modulus for the same material in the same conditions than that used for the ultimate tensile strength. The results were similar where the deterioration was about 60 to 90% for 90° lay-up while no more than 20% reduction was noted for the 0° and 45° lay-up.

2.2 Temperature Effects

The temperature is part of all environments the FRP materials usually encounter. In the natural environment, FRP materials may be subjected to temperature raging from -30°C to 60°C depending on the geographical region, the climatic season, and the moment of the day. More elevated temperatures may be encountered in industrial environments. They result from industrial vapours and hot media

transported in pipes or stored in tanks. High temperatures over the range of 150°C are associated only with particular circumstances such as fire. Long-term exposure to moderate temperature accounts for the failure of many FRP materials. The absorption of thermal energy leads to a set of deleterious effects on the matrix. The thermal energy attacks also the bonding region between the matrix and the fibre as well as the overall composite laminate. These effects are chemical as well as physical and irreversibly affect the material mechanical properties for most of the time. These effects are well known. In the literature, authors dealing with the temperature effects on the fibre reinforced plastics focus mainly on the mechanism whereby the temperature affects the mechanical properties of the material.

2.2.1 Thermolysis and Thermoxidation

In an inert atmosphere, the temperature induces the thermolysis of polymeric materials. The thermolysis is an energetic action where chemical bonds are broken by imparting to electrons sufficient energy to pull them out of the bond. This leads to the scission of the molecular chain. Three mechanisms at least have been recognized for the thermolysis process [61]:

- The depolymerization in which reduction of macromolecular size occurs without change in chemical composition or alteration of the monomer unit structure. The cleavage occurs by random chain scission to yield either the monomer or the lower molecular weight product
- The elimination whereby small molecules are eliminated without main chain scission, giving an alternated double bond chain responsible for the coloration of the material.
- The cyclization whereby a macromolecular chain presents potential reactant groups located in close proximity. At elevated temperature, these groups react and the intramolecular cyclization occurs with or no elimination of small molecules.

Thermolysis is restricted to some particular cases where high temperatures are encountered in the absence of oxygen. The thermoxidation, however, is a more common degradation mode polymeric materials face in normal service conditions. Reid Shelton [30] comments that even relatively stable polymers undergo significant deterioration on long-term exposure at ordinary temperature in air. The thermoxidation is an autocatalytic process in which the major product is a hydroperoxide that decomposes under appropriate conditions to give free radicals capable of initiating a free-radical chain reaction. The decomposition of hydro peroxide is accelerated by heat [29]. Peroxide molecules in many plastics material are originated from the manufacturing process and play the role of catalysis that contribute in large part to the initiation of the degradation process. It is also mentioned that the kinetics of this process is oxygen diffusion dependant [12].

2.2.2 Residual stresses due the Temperature

The temperature is also responsible for residual stresses in the FRP laminate. One of the well-known deleterious effects results from the cycling temperature. A long exposure to the sun increases the material temperature. Following such exposure, a sudden cooling resulting for example from the rain or due to night conditions, yields transient stresses on the material surface. Such stresses are known to be the cause of cracks initiation [12] and cause the material to become brittle.

The residual stresses due to the temperature in the composite material result also from the mismatch of the coefficient of thermal expansion between the laminate components. This causes the laminate deformation and leads also to cracks apparition [13]. Residual stresses resulting from post-curing can approach or exceed the design load and acceptable material limits. The magnitude can be sufficient to promote environmentally assisted cracking [31]. A simple experiment was conducted in the RP/Composite facility at the University of the Witwaterstrand. During this experiment, a post-cured specimen along with a non post-cured specimen were allowed to stand for five days with a content of 75% of sulphuric acid. It was observed that the post-cured sample experienced

environmental cracking while the non post-cured sample remained undamaged [62].

2.2.3 The Arrhenius Law

The most important temperature effects are related to the temperature dependence functions of the remaining environmental agents. It is known that the temperature affects both the moisture diffusion and the chemical reaction of degradation according to an Arrhenius type dependence function. According to Arrhenius law, each temperature increase of about 10°C results in doubling the reaction rate. This shows the high impact of temperature variation on chemical reactions such as the oxidation of the polymeric material due to UV rays and the hydrolysis in humid environment.

2.3 Ultraviolet Radiations Effects and Mechanism.

UV rays are the part of the solar radiation spectrum covering the wavelength range from 100 nm to 400 nm and constitute about 5 to 7% of the total energy emitted by the sun. Only a fraction of this radiation reaches the earth's surface as most of the radiation is absorbed by the atmosphere.

The UV-B range (280 nm – 315 nm) is known to be the most destructive part of the ultraviolet light spectrum [20]. Its effects on polymeric materials have been discussed in the literature for many years [12, 20, 32, 33, 47]. UV rays interact with the matrix material of the FRP laminate by a mechanism that includes photolysis and photo-oxidation.

Photolysis induces a molecular chain breakage process. The chain scission results from an energetic action initiated by light energy that the electrons of the chemical bond absorb. Photolysis produces free radicals that react with oxygen to initiate photo-oxidation. In the natural environment, atmospheric oxygen is always present and so photo-oxidation proceeds from photolysis.

2.3.1 Photooxidation

In the course of photo-oxidation, photons attack the organic chain and produce free peroxide-radicals. These radicals subsequently react with the organic molecular chain to produce hydro-peroxides that can be decomposed by UV rays of wavelength below 360 nm. Photo-oxidation is thus a complex free-radical chain reaction involving several steps in its mechanism [12, 20, 32, 33, 47].

The reaction is catalyzed by the hydro-peroxide and carbonyl molecules commonly found in the polymer as products of thermal oxidation during polymerization or processing. Likewise, transition metal ions are important catalysts for the photo-oxidation process. Traces of these ions are present in the polymer as residue of Ziegler-Natta catalysts used during the polymerization reaction [33].

Effects of photo-oxidation on FRP include chemical as well as physical changes. The chemical changes include cross-linking and chain scission [20, 35] associated with the formation of double bonds and oxygen-containing structures such as carboxylic acids, alcohols, ketones, and peroxides. The changes are physically manifested by the discoloration of the polymer (Figure 2.2), which changes from white to yellow, red, or reddish black as degradation occurs.



Figure 2.2 Degradation due to UV rays identified as discoloration or flaking of the surface on the topside of a pipe (with the permission of SASOL)

Surface cracking and embrittlement often accompany photochemical discoloration [33]. Observations of FRP exposed to UV rays [34, 35] show evidence of morphological changes on the degraded surface including formation of crazes and cracks due to chain scission, formation of holes and voids by the venting of volatile degradation products, and gelation processes associated with cross-linking.

2.3.2 Photo-degradation mechanism

Efforts worldwide are devoted to the elucidation of the physical and chemical mechanisms that lead to the deterioration of the mechanical properties of the material [42, 46, 50, 53, 63, 64]. Most of the analyses of the photo-degradation reported in the literature are based on the description of complex chemical kinetics [1, 32, 47].

It is generally observed that the photo-degradation process affects primarily the composite matrix and subsequently the matrix dominated properties [42, 46, 50]. It has been shown that effects of UV irradiation are strongly dependant on mechanical stresses [46, 65-67] and other environmental factors. These factors include moisture [36, 42, 63, 64, 67] and temperature [36, 68]. These effects can be described by a thickness profile showing the moisture and oxygen diffusion dependency [66, 69].

Startsev *et al* [36] observed that the mechanical properties of polymer composite materials used in aviation vary in a layered way after exposure to a natural environment. A gradient is generated through the laminate thickness. Because of such a gradient, effects on the mechanical strength depend strongly on the laminate thickness. This is consistent with the results reported by Larsson [9] who exposed Kevlar 49–epoxy composites with various thicknesses (0.13 mm, 0.25 mm, and 0.50 mm) to UV rays from a xenon source over 1000 and 2000 hours. He noted that no perceptible effect of exposure was observed on the 0.25 mm and 0.50 mm thickness laminate, while the loss in strength on the 0.13 mm thickness

laminate was about 40%. The latter observation provided the basis for a model proposed by Sevostianov *et al* [50] whereby the degradation process is considered to be a progressing damaged front that moves through the laminate.

The literature report on many other approaches based on the characterization of the mechanical, physical, and chemical degradation mechanism. Hartly and Guillet [70] investigated the chemical mechanism of the ketone polymers photochemistry. They showed that the degradation occurs according to Norrish type II and I, and that the type II is predominant at ordinary temperature.

2.4 Chemical Agents Effects

Apart from water and atmospheric gasses such as oxygen and ozone, which are the most important chemical reactants in the natural environment, FRP material face also a variety of chemical attacks (Figure 2.3). These result from air pollutants, industrial smog, and liquid circulating in pipes or stored in tanks made of FRP.

Industrial smog content includes dyes, solvents, detergents, metals, and many others, while air pollutants resulting also from industrial smog includes acidic and basic gasses such as dioxide sulphur and oxide of nitrogen.

Chemical reactions of degradation are facilitated by the thermal or light energy encountered in the usual FRP environment. The degradation mechanism is particular to each kind of chemical agent. However, the common characteristics are the diffusion dependence and the Arrhenius type temperature dependence of chemical attack processes.



a)



b)

Figure 2.3 Chemical attacks on industrial pipes (with the permission of SASOL)

- a) Inner of a pipe attacked by chemical: The glass surface tissue hanging from the walls where the resin has been removed by chemicals.
- b) Advanced corrosion on the surface of a pipe: The structural laminate becomes exposed, which looks like dry glass, with no resin bonding it together.

Authors dealing with the chemical degradation of FRP materials focus mainly on water caused hydrolysis. Very little information has been presented on the remaining known chemical agents. Polymers containing ester or amide links are susceptible to hydrolytic attack. Fibreglass also can be hydrolyzed at the siloxy bond. Bonds formed by silane groups and constituting the interface matrix–fibre are also subjected to hydrolysis by water as already mentioned in section 2.1.3. Effects of hydrolysis include molecular chain length reduction resulting into the embrittlement of the material and the deterioration of tensile strength, shear strength, and module.

Springer *et al* [46] have surveyed results of researches conducted on glass-reinforced polyester and vinyl ester, at two temperatures, in a variety of environments relevant to civil applications including humid air, saturated solution of NaCl in water, diesel fuel, lubricant oil, antifreeze, and gasoline. It is shown the significant reduction in tensile strength and in shear strength while the modulus was only slightly affected. It is also emphasized the fact that high effects are related to the presence of water humidity and that high or low pH humid environment is highly detrimental to fibres.

Comparing the degradation of two GRP laminates namely pultruded isophthalic polyester and a hand moulded vinyl ester, in 5% brine solution and 10% NaOH solution, Sonawala and Spontak [27] demonstrated a case where the degradation kinetic is determined by the diffusion or by the solubility of the chemical solution into the laminate. They noticed that polyesters undergo dramatic tensile strength deterioration while vinyl esters present higher properties retention. This was explained by the fact that polyesters offer higher solubility to aqueous solutions due to a higher concentration of esters linkage available for hydrogen bonding with permeated water, while vinyl esters present higher resistance to permeation [27, 28].

Prian and Barkatt [40] investigated the degradation mechanism in the case of fibreglass plastic composites exposed to aqueous media. They showed that the

leaching of alkaline components out of the fibre and the resulting increase in pH at the interface matrix-fibre determine the fundamental mechanism that explains the drastic increase in degradation rate during long-term exposure. The increase in pH leads to the acceleration of the hydrolytic attack at the interface. The degradation and opening up of the interface allows further penetration of moisture. This subsequently accelerates the hydrolytic attack. The degradation occurring mainly at the fibre–matrix interface was also noticed earlier by Harper and Naeem [71] who studied the moisture absorption of glass reinforced vinylester and polyester composites.

2.5 Stress Corrosion

The stress corrosion constitutes an important aspect of environmental degradation the literature deals with. It has been observed that environmental factors affect consistently the stress-rupture time of stressed material exposed also to environmental factors [45] or inversely the severity of the environmental degradation increases when the material is also subjected to mechanical stresses [1].

Pritchard and Speake [45] carried out an experience on a glass-polyester composite laminate immersed in water under load at three different temperatures. The experiment allowed them to observe that the combination of water and temperature effects could plasticize the material or increase the fracture toughness of the resin and the stress-rupture time was affected accordingly. Many works have been devoted to stress corrosion throughout the literature and effects vary according to particular conditions of experimentations.

Barkatt [2] reports a relation that was found between the crack velocity and the stress intensity in an environmentally assisted cracking:

$$V = \frac{A(X_0)^n \exp(bK)}{n} \quad (2.11)$$

In this equation, V is the velocity of crack propagation, X_0 is the partial pressure of water, n is the order of the chemical reaction, and K is the stress intensity factor. A and b are constants. This formula describes the process kinetic in the initial and most important stage controlled by the stress corrosion rate. The mechanism includes a second stage controlled by the moisture diffusion rate where the crack propagation velocity is given by:

$$V = \frac{CD_w X_0}{\delta n} \quad (2.12)$$

In the above equation, D_w is the moisture diffusivity, δ is the boundary layer thickness, and C is a constant.

A quite different approach has been suggested by White and Turnbull [1] whereby the problem is presented as a stress-aided chemical reaction. It is stated that the most highly stressed bonds will be the most likely to react. Experimentation carried out on a polypropylene specimen showed that the rate of oxidation increases with the load at high loads. It was explained that the stress alters the activation energy of oxidation by reducing it and according to Arrhenius law, the rate of oxidation r as suggested by Zhurkov, quoted by White and Turnbull [1] can be given as follows:

$$r = A \exp\left(\frac{-(\Delta G - B\delta)}{RT}\right) \quad (2.13)$$

In equation (2.13), A is the frequency factor. ΔG and δ respectively represent the energy barrier and the stress magnitude. B is a constant that has the dimension of a volume.

White and Turnbull [1] reported some other results found by Popov *et al* (1991) showing that the tensile stresses accelerate the degradation while compressive stresses retard it.

2.6 Conclusion

Mechanisms and effects studied in the literature include moisture diffusion, temperature, ultraviolet irradiation, chemical attack and the stress corrosion. Attack by moisture involves a diffusion step, followed by hydrolysis or hydration. Though, most of diffusion occurring in FRP laminate follow Fick's law, variable kinetics have been observed depending on the type of transformation occurring in the material and the type of physical and chemical interaction between the permeant and the material. Factors influencing the moisture diffusion include fibre volume fraction and orientation, size and polarity of solvent molecules, temperature, the applied load and the hydrostatic pressure. Humidity affects the material properties and accelerates failure. Cycling humidity, as well as cycling temperature results in hygrothermal residual stresses that can approach or exceed the design load. The synergic effect resulting from the combined action of temperature and humidity is known to be very deleterious. The temperature influences considerably ultraviolet irradiation and chemical action through Arrhenius law. Temperature effects include also thermolysis and thermo-oxidation.

Ultraviolet irradiation is one of the most important natural degradation factors for FRP and one of the most studied in the literature. The UV-B range (280 – 315 nm) is known to be the most destructive for FRP. The chemical mechanism is complex, and the process includes photolysis and photo-oxidation. In natural atmosphere, due to oxygen, the photo-oxidation is the most common. The process is strongly dependent on mechanical stresses, humidity and temperature. Ultraviolet irradiation causes the material discoloration, the surface cracking, embrittlement, and reduction in mechanical properties.

FRP encounter several kinds of chemicals in their service environment. The literature provides only limited information on chemical attacks. The most known effects are the hydrolytic or solvolytic attack that results in mechanical strength deterioration. The process is boosted in acidic or alkaline medium. The combined

action of chemical and mechanical stresses produces a synergic action known as stress corrosion that result in the acceleration of the material failure.

In general, environmental degradation primarily affects the composite matrix and subsequently the matrix dominated properties. The effects can be described by a thickness profile showing the moisture and oxygen diffusion dependency.

3 MODELLING AND PREDICTION METHODS OF ENVIRONMENTAL DEGRADATION, A LITERATURE SURVEY

Optimal utilization of FRP material requires a good understanding of the environmental degradation effects and the availability of reliable method for quantifying and predicting these effects. The previous chapter presented an overview of the degradation mechanism and effects reported in the literature. Those investigations were aimed at the development of models allowing to set assessment and prediction methods of environmental effects. The present chapter presents an overview of modelling issues including limitations to global modelling, and predictive methods based on partial models. Attention will be given also to analytical methods used.

3.1 Modelling and Limitations

White and Turnbull [1] presented a comprehensive review of the modelling and prediction issues relative to the environmental degradation of polymers. They underlined the necessity to develop models that allow short-term laboratory data to be used to give an accurate forecast of the lifetime of the component, to assist in material selection and to permit economic planned replacement.

Their review, however, noted that no general or accurate model was available at the time. They pointed out that the main difficulty was the great number of chemical and physical processes involved in the environmental degradation, and their interactions. White and Turnbull [1] explained that the problem was as complex as identifying the various reaction's pathways, then measuring the rate constants, including the effects of intermediate reactions products, determining the diffusion coefficient for main

chemical agents as well for intermediate reactions, and this should take account of effects resulting from the variation of the matrix morphology during the degradation. These observations were consistent with the conclusions from a review by Schutte [3] who reported that the major unresolved issues are firstly, the difficulty to take into account all the processes involved and their interactions in a comprehensive model and secondly, the uncertainty related to the translatability of laboratory tests conditions to the real service environment [3].

A more recent review of the subject by Barkatt [2] in 2001 restated the same conclusion. Barkatt recognized that considerable efforts had been made to model the degradation of FRP, but unfortunately, no comprehensive models were yet available to provide a quantitative basis for evaluating the performance of FRP.

A great number of published works focus on the characterization of effects and/or on the description of mechanisms [1- 43]. A large range of material properties have been observed for a large range of materials in a variety of environments. It has been observed that environmental factors negatively affect the material properties over time. Concerns have arisen regarding the degradation mechanism since this is understood as a prerequisite to any modelling effort. For most of the cases, the mechanisms deduced were applicable only to some particular processes.

In this regard, considerable progress was made in understanding the diffusion mechanism as well as some specific processes like oxidation, and hydrolysis as already presented in the previous chapter. Such analysis allowed mainly the development of stabilizing systems applied in polymeric materials against environmental agents attack. The use of stabilizer allows reducing the acuity of problems related to the environmental degradation. Stabilizers have sometimes produced spectacular improvement in the lifetime of polymeric material [1]. However, in some cases, they may not be effective, or their effect may wear off over

the time. Predictive models would then be useful at least for the assessment of the stabilizer effectiveness.

Modelling efforts, for the most part, are limited to partial models based on a single mechanism dominating the whole process [1, 16, 39, 43-50]. Such models are mostly based on moisture and/or on temperature effects and are empirical.

An example is the model based on hygrothermal stress distributions reported by Springer [44]. This model is based on a three-step method for effects evaluation. Firstly, analyses are conducted to determine the temperature and moisture distribution inside the material. Secondly, hygrothermal stresses and strains are calculated based on the distribution of temperature and moisture. In the third step, the change in material performance is evaluated based on calculated hygrothermal stresses. However, this method is subject to limiting hypotheses, such as that the diffusion should obey Fick's law.

A second example is the empirical model based on moisture effects proposed by Prichart *et al.* [45]. They reported on a case where the kinetic equation was deduced empirically by mathematical regression of experimental data. The changes in tensile strength and modulus of a fibreglass–polyester resin composite were plotted versus the moisture content in the course of an exposure. Two temperatures were used with several fibreglass orientations. It was reported that the predicted behaviour based on that model was good for up to three years. Unfortunately, no information on longer time scales is provided.

Nakamura *et al.* [46] suggested an empirical model that allowed for quantification of the combined effect of UV rays, humidity, and cyclic load on the flexural strength of cross-ply laminates of carbon fibre reinforced epoxy.

Another modelling approach is based on chemical reaction mechanisms especially in the case of hydrolysis and oxidation or photo-oxidation [23, 47-49]. This approach leads to complex mathematical formulae and parameters in these formulae cannot always be measured.

Some models of photo-oxidation have been surveyed from the literature. Generally, these models relate the degradation time to UV rays absorption and the time is only indirectly related to the material properties. Parameters in these models are not easily measurable from a practical point of view and the applicability of any model proposed is limited to specific polymers. Illustration of the above is given by the following cases:

Reich and Stivala [47] have described a kinetic model based on the reaction mechanism proposed by Ershov *et al* [47]. This model was successfully applied to the photo-degradation of polystyrene. In that model the degradation rate is measured by the rate of oxygen absorption as follows:

$$-\frac{d[O_2]}{dt} = \frac{k_1 k_2 k_3}{k_4 (k_5 + k_6)} [O_2] [S] I_0 \quad (3.1)$$

In equation (3.1), $[O_2]$, $[S]$, I_0 are respectively the oxygen concentration, the polymer concentration and the UV radiation intensity; while k_1 , k_2 , k_3 , k_4 , k_5 , and k_6 are respective kinetic constants associated with chemical steps in the mechanism.

A review by White and Turnbull [1] has reported some alternative mechanisms that have been described in the literature. For example, polyethylene oxidation under ultraviolet radiation was determined by Karpukhin to follow the following rate equation:

$$\frac{dc}{dt} = aI + bI^{\frac{1}{2}} \quad (3.2)$$

In the above equation c is the carbonyl concentration, I is the ultraviolet intensity and a , and b are constants. A kinetic model proposed by Minsker *et al.* applicable to Polyvinyl Chloride was also reported in the review. In the model, the humidity and UV rays effects are correlated to determine the degradation time τ as follows:

$$\tau = \tau_0 e^{\frac{U}{T}} W^{-\alpha} H^{-1} \quad (3.3)$$

In equation (3.3), T , W and H represent the temperature, the relative percentage humidity and the UV rays dose respectively. U is a thermodynamic parameter proportional to the activation energy. In the report, no description of the parameter α was given.

Beak-Su Lee *et al* [38] presented an approach in which they correlated the chemical transformation on a UV-treated surface of an epoxy/glass composite with electrostatic changes and suggested a control model based on the electrostatic behaviour.

Based on the observation that the degradation process can be considered as a progressing damage front that moves through the laminate, Sevostianov *et al* [50] proposed a mathematical model. They suggested a mathematical relation that calculates the overall modulus as a function of time arising from the contributions of the modulus of both damaged and undamaged layers. However, this model is affected by several limiting hypotheses and by the omission of the effects of moisture diffusion.

3.2 Accelerated Test Methods

One important trend in the literature goes beyond the characterization of effects and mechanisms and suggests prediction methods. These methods are based on partial models where a single mechanism dominates the whole degradation process.

Assumption is made that the dominating mechanism is thermally activated and follows Arrhenius law. The prediction relies on linear extrapolation based on temperature variation. The material is subjected to an accelerated degradation in a laboratory and results are extrapolated to real services conditions using acceleration factors based on the partial model. Acceleration factors are based not only on temperature increase, but also on media that are more corrosive or the application of mechanical loads [2, 16]. Examples of these are given below.

3.2.1 Acceleration using higher temperature based on Arrhenius law

This method is reported by Mill [12]. It is assumed that there is a single process that is thermally activated. Then according to Arrhenius law the degradation rate is proportional to $A \exp(-W/RT)$ which implies that the degradation time is proportional to $A \exp(W/RT)$. Then the plot of $\log(\text{time})$ versus $1/T$ that should be a straight line allows extrapolating the lifetime from one temperature to a different temperature. Mill [12] reported that the application of this model to the hydrolysis of polycarbonate showed good results. But caution is given concerning the applicable range of temperature. Rana *et al* (1961) and Holland (1996) quoted by Barkatt [2] reported as well the case of silicate glasses hydrolysis for which the method was applied successfully. For these materials, the Arrhenius behavior was observed over a broad range of temperature up to 90°C.

3.2.2 General method using extrapolation based on the temperature

The procedure in this method consists of performing tests in accelerated conditions as well as in real service condition for a short time. The extrapolation factor F is experimentally deduced by comparing the rates in accelerated and real service conditions respectively represented by K_a and K_r .

$$F = \frac{K_a}{K_r} \quad (3.4)$$

The lifetime in real service conditions represented by T_r is now calculated from the lifetime in accelerated conditions represented by T_a :

$$T_r = T_a F = T_a \left(\frac{K_a}{K_r} \right) \quad (3.5)$$

However, precaution should be taken to assure that the acceleration does not cause the change of the controlling degradation mechanism. Collin *et al* [72] reported that this method was used to predict moisture and temperature effect, within the range of expected service environment for FRP used for structural applications in the aircraft industry. It was also demonstrated that elevated temperature could be used to reproduce the same reduction in T_g obtained by the moisture and consequently the same effects on the mechanical properties of the material.

3.2.3 Accelerated or artificial humidification

The accelerated humidification allows the moisture content in the material to reach, within a shortened time, the level it would normally reach after a long-term exposure. This is achieved by exposing the material to higher percentage humidity. The reduction of the exposure time is approximately 50% [43].

Artificial humidification consists of using physical models whereby the real exposure conditions are physically simulated in a laboratory so that to obtain the same moisture content as in real service conditions. This method was also used to predict the moisture distribution over time. Springer [73] reported on the simulation of the environmental humidity and temperature cycle allowing to calculate the moisture content and distribution of a FRP for twenty years service life of an aircraft.

Physical model are extensively used nowadays through environmental chambers. This is applied not only for humidity but also for all the remaining environmental agents.

3.2.4 Limitation of accelerated methods

According to Rana *et al* (1961) and Holland (1966) quoted by Barkatt [2], extrapolation based on Arrhenius law holds only over a limited range of temperatures. A recent review by Celina [74] shows the considerable limitation of this law in many cases due to two competing processes. Similarly, studies reported by Prian and Barkat [40] show the non applicability of this method in many cases due to supra or sublinear kinetics arising during the degradation. The most important limitation faced is the incontrollable deviation of the kinetic curve after a certain period of exposure due to accelerated conditions. This occurs when the material reaches its glass transition temperature T_g and at the swelling point during moisture diffusion.

Moderate temperature increase causes also the material post-curing. The extent of cross-linking caused by the post-curing affects the diffusion process and consequently the degradation kinetic also. Another complication noted is related to the chemical reaction products in course of degradation. These products modify the environment composition affecting variables such as pH and chemical media reactivity.

An important aspect is that related to the translatability of laboratory test conditions to real services environment [3]. White and Turnbull [1] underlined the difficulty to correlate accelerated conditions used in the laboratory with the real service environment conditions. From their survey of the literature, they stated that there was a general agreement that no correlation exists between natural and artificial weathering, and these views were even expressed in some standards. However, an interesting view is this one expressed by David and Sims quoted by White and Turnbull [1]. They said: “ Accelerated tests should only be considered therefore as

giving a rough indication of the relationship between natural and artificial weathering ...[Artificial weathering] is neither as perfect as its disciples claim nor as useless as its detractors state...The degree of correlation between natural and artificial ageing seems to be inversely related to the degree of acceleration”.

Obviously as one can conclude, there was controversy denoting that the subject was not yet correctly elucidated and that much investigation still was needed.

3.3 Standard Test Methods

In industry, some practical methods have been standardized and allow providing qualitative indications to serve only as practical guide for the assessment of material corrosion resistance. The ASTM C581-74 provides the standard method of assessing the chemical resistance of thermosetting resin used in glass-reinforced structures. The test procedure includes immersion of samples into the corrosive liquid, visual inspection of the sample surface for colour change, pits, cracking, loss of gloss, etching, and mechanical test for hardness, flexural strength, and modulus. The inspection is conducted in regular intervals during the exposure that may last up to 180 days or a year. The obtained results may be plotted to check for kinetic trends. Such evaluation, as said previously, provides a rough qualitative indication of the material chemical resistance as “no attempt is made to incorporate into the method all the various factors which may enter into the serviceability of a glass fiber reinforced resin structure when subjected to chemical environment.” (ASTM C581-74).

3.4 Analytical Methods

A major aspect of the problem concerns analytical methods for environmental degradation effects quantification. The ASTM Standard Test Methods for Chemical resistance of Thermosetting Resin used in glass fiber reinforced structures, ASTM C581-74 for instance, resorts to mechanicals properties measurement for effects quantification. Maier *et al* [75] has demonstrated that utilization of mechanical

properties for effect quantification, requires a drying step during which the material undergoes supplemental transformations in such a way that the results are subject to considerable uncertainty.

In fact, a number of methods are found in the literature. Apart from methods using the direct measurement of the mechanical material properties, the alternate way consists of monitoring chemical or physical transformation occurring in the material because of the degradation. Some example are provided by vibrational methods such as Raman spectrometry, Infrared spectrometry [76, 77] and Nuclear Magnetic Resonance (NMR). Likewise, these analytical methods like electron-scanning microscopy (ESM), thermo gravimetric analysis (TGA) or differential scanning calorimetry (DSC) have been abundantly used for monitoring of chemical structure changes. But the use of these methods is validated only by the existence of known good correlation between the monitored change and the material mechanical properties.

3.5 Conclusion

The design, selection and economic evaluation of FRP material require the availability of a reliable method for long-term environmental effects quantification. Modelling of environmental degradation have been hindered by the complexity of the process and the resulting difficulty to take into account all the processes involved and their interactions in a comprehensive model. Modelling efforts, for the most part, are limited to partial models based on a single mechanism dominating the whole process. Such models are mostly based on moisture and/or on temperature effects and are empirical. No comprehensive models or viable prediction method is yet available. The prediction methods used are based on the assumption that dominating mechanism is thermally activated. However, application of this method has been hindered by irregular kinetics caused by transformations occurring in the material in the course of acceleration. Irregular kinetics were observed because no method was

yet defined to take comprehensively into account all the processes involved in the degradation. The literature shows also that another unresolved issue is related to the translation of laboratory test results into the real service conditions.

4 METHODS TO REPRESENT THE REAL SERVICE ENVIRONMENT IN LABORATORY

One major unresolved issue in predicting FRP environmental degradation is that related to the translation of real service conditions into laboratory. The main problem results from the difficulty to reproduce the complex variability of the real service environment in laboratory. It also results from the difficulty to correlate accelerated test conditions to the real conditions. In addition, an effective modelling of the degradation process requires a reliable method to take into account the complex variability of the environment that causes the degradation.

This chapter demonstrates a simplified method to represent the variability of the real service conditions into laboratory to allow for an effective modelling of the degradation process and accelerated predictive tests.

4.1 Constant Environment Models

4.1.1 The model based on statistical control charts

The concept suggested in this subsection is based on the fact that the variability of a parameter is generally represented by an average value with a variation range determined by an absolute error. Alternatively, the variability of a process is expressed in terms of a statistical control chart determined by constant control limits [78].

Therefore, the variability of any process or variable is expressed in terms of constant limits that fix the variation range.

This implies that, if a defined relation exists between the variable and its effects, then the variation limits or the statistical control limits of the effects can also be exactly determined.

Therefore, effects can be determined in a range that corresponds exactly to the variability of the variable.

Let f_j be an environmental factor. j is an integer such that $1 \leq j \leq n$ and n represents the number of environmental factors in the service environment. The service environment may comprise various environmental factors such as temperature, moisture, chemicals (oxygen, ozone, acids, etc...), energetic radiations (UV rays, nuclear radiations or other artificial radiations), and different types of environmental stresses. Environmental stresses are of several kinds: the hygrothermal stresses from humidity and temperature cycles, erosive stresses from friction with circulating liquid in pipes or tanks or friction with wind and dust, stresses from rainfall impact, and vibration stresses in the vicinity of industrial engines. However, in this analysis all of these environmental variables will be represented into only five categories including: environmental chemical (C_0), temperature (T), ultraviolet rays (I_{UV}), moisture (Δm) and hygrothermal stresses (σ_{env_n}).

The environmental factor f_j is a continuous function of time (except for special cases such as explosion or fire). Its variation over the time can be represented by a statistical control chart determined by the upper control limits $f_{j_{UCL}}$ and the lower control limits $f_{j_{LCL}}$.

Let $E_d(f_j)$ be the environmental degradation resulting from f_j . If $E_d(f_j)$ is a defined function of f_j , then the control limits of the degradation correspond respectively to $E_d(f_{j_{UCL}})$ and $E_d(f_{j_{LCL}})$. Therefore, the control limits of the degradation can be determined in laboratory in a constant environment defined by

$$f_{j_{UCL}} \text{ and } f_{j_{LCL}}.$$

The above means that the real service environment can be reliably reproduced in laboratory in terms of constant environment that express exactly the variability of environmental factors.

However, when substituting a variable environment by a constant one, care must be taken to compensate the fatigue effect caused by temperature and humidity cycles. To this end, the material exposed to a constant environment must additionally and in the same time, be subjected to cyclic stresses equivalent to those caused by the temperature and humidity cycles. The amplitude of the cyclic stress in laboratory is also determined by the upper and lower control limits of the cyclic stress in the real service environment.

4.1.2 Model based on the mean value

The present concept stems from the need to manage the complex variability of the service environment when modelling the degradation process. The idea consists of replacing a variable environment by a constant one that produces the same effect on the material for the same exposure duration. To this end, environmental effect is treated in terms of mass and energy transfer. The constant environment is required to produce identical amount of work implying the same amount of transferred mass and energy, at a comparable rate (power) during the same exposure time.

The total work an environmental factor achieves in transforming the material during degradation depends on the amount of transferred mass and energy. The latter is a function of the environmental factor magnitude and the exposure duration. Effect of the environmental factor magnitude over the exposure time is expressed as an integrated value of f_j over the time. So, if $W_{env}(f_j)$ represents the transferred mass and energy under the environmental factor f_j , then:

$$W_{env}(f_j) = k_0 \int_{t_1}^{t_2} f_j(t) dt \quad (4.1)$$

where k_0 represents a constant and t is the time.

Equation (4.1) is actually a common expression of well-established laws that govern energy and mass transfer in materials [79, 80]. It corresponds respectively to the Newton's law for calorific flux, Fick's law for moisture or chemical solution flux and the definition of UV ray intensity (see Appendix A).

If f_j is a continuous function over the time interval $\Delta t = t_2 - t_1$, then it can be represented by a constant value denoted f_{jc} and determined by the theorem of mean values for integration [81]. Resulting from that theorem, the mass or energy transferred by f_j over the time interval $\Delta t = t_2 - t_1$ is equivalent to that transferred by the constant f_{jc} over the same time interval. This is shown here below.

The theorem of mean value for integration is expressed as [81]:

$$\exists f_{jc} = f_j(t_c) = \text{constant, such that } t_1 < t_c < t_2 \text{ and } \int_{t_1}^{t_2} f_j(t) dt = f_{jc} \Delta t$$

Taking account of equation (4.1), this implies that

$$W_{env}(f_{jc}) = k_0 \int_{t_1}^{t_2} f_{jc} dt = k_0 f_{jc} \Delta t = k_0 \int_{t_1}^{t_2} f_j(t) dt = W_{env}(f_j) \quad (4.2)$$

An experimental illustration of equation (4.2) is provided in section 4.2 for the case of storage tanks or pipes exposure conditions. This equation implies that all environmental histories can be modelled as a continuous sequence of constant environmental states comprising constant environmental factors. A useful application of this conclusion is shown in the next chapter (section 5.9.2)

4.2 Experiment

Samples of polyester composite laminate were exposed to an environment comparable to a pipe or storage tank service conditions. The experiment was based on thermal energy and mass transfer. The thermal energy and mass transferred under a variable source of temperature was compared to that transferred under an equivalent constant temperature source. It was considered that, the humid environment in a storage tank or pipe, is constant (laminate entirely wet in a liquid). Thus, only the temperature variation was considered. The material used is shown in Table 4.1.

Table 4.1: Materials

LAMINATE		RESIN FORMULATION	
Composition	Resin/fibre/resin	Resin	Orthophthalic polyester Crystic 196
Glass fibre	WR 400 g / m ²	Resin (phr)	100
V _f (%)	AVG	Catalyst (phr)	2
	StD	Accelerator (phr)	0.6
Thickness (mm)	3.0 ± 0.1	Curing cycle	24h/ 25°C, 3h/ 80°C
Void (visual)	No voids		

4.2.1 Experimental procedure and results

Experiment 1: heat flow across a reference point

1. The laminate sample was exposed to a variable temperature source. The variation in temperature at a reference point inside the laminate was measured by mean of a thermocouple. In the first experiment, the thermal energy was allowed to flow across the reference point (Figure 4.1) and the transferred heat was measured as an integrated heat flow across the reference point over the exposure time.

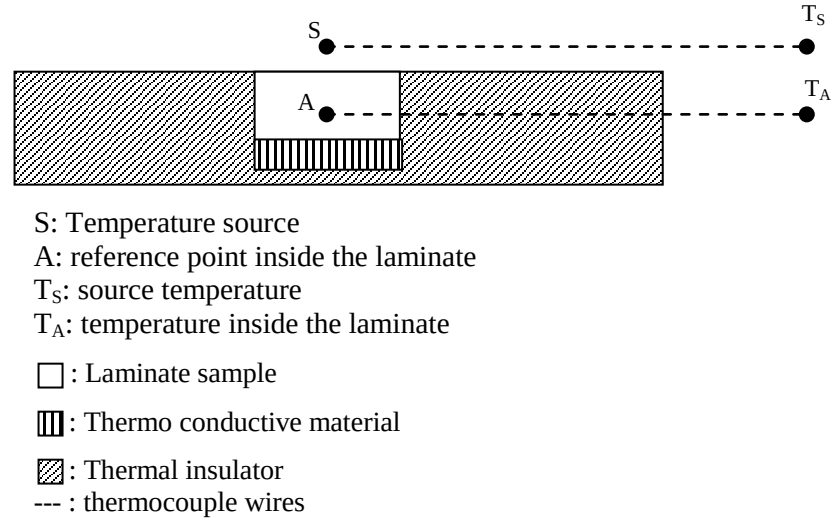


Figure 4.1 Test specimen for heat flow

2. The source temperature and the temperature inside the laminate were recorded respectively as $T_S V$ and $T_A V$ where V stands for variable conditions. Results are presented in Figure 4.2.

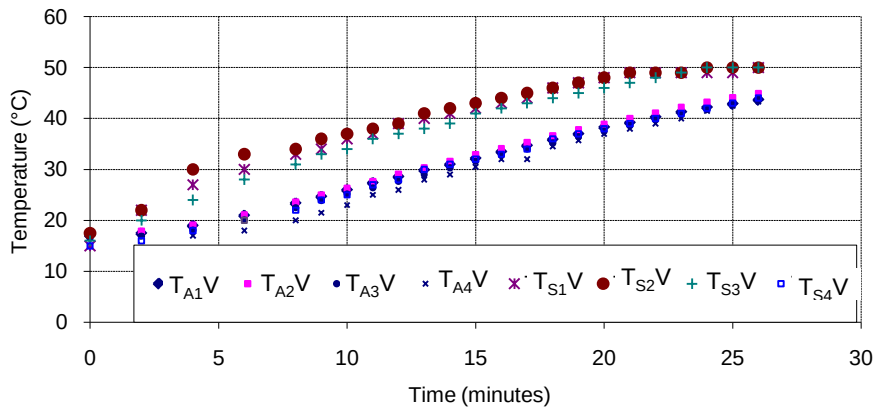


Figure 4.2 Temperature variations under variable source

3. An interval of time was chosen from zero to 20 minutes and the equivalent constant temperature was determined for that interval according to the theorem of mean value (Figure 4.3).

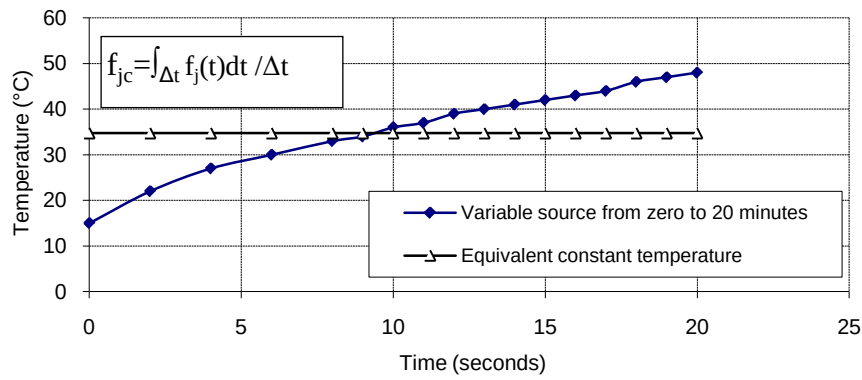


Figure 4.3 Determination of the equivalent constant temperature

4. The laminate was conditioned in such a way as to obtain the same initial temperature as under the variable source and then exposed to the constant temperature source. The temperature inside the laminate was recorded for the same time interval and the very same reference point as for the variable temperature source. Source and reference point temperatures are respectively denoted T_{SC} and T_{AC} where C refers to constant conditions (Figure 4.4).

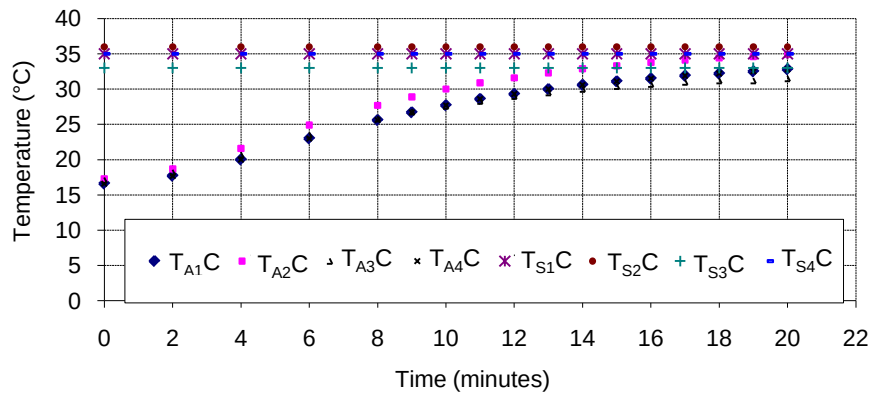


Figure 4.4 Temperature variations under constant source

5. The integrated heat flow under variable temperature source was compared to that obtained under the equivalent constant temperature source (Figures 4.5 and 4.6, Table 4.3). It is shown that, comparatively to the variable source, the constant source creates exactly the same integrated heat flow at the reference point in the material, over the same time interval.

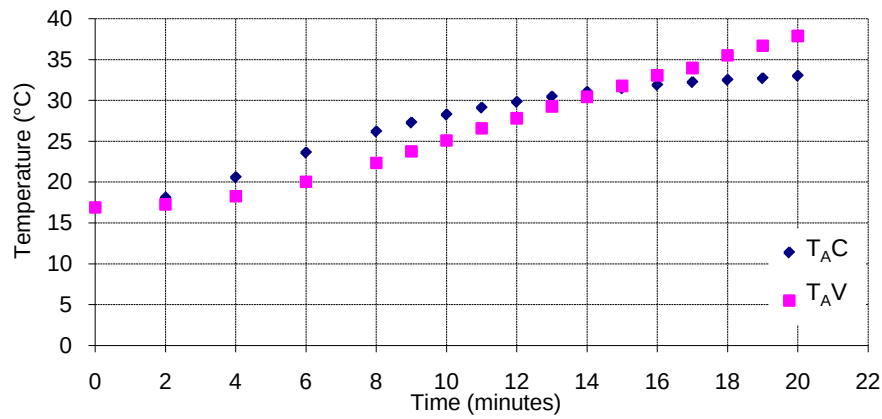


Figure 4.5 Comparing average variations in temperature at the reference point

Table 4.2: Integrated heat flow ¹

Test	1	2	3	4	AVG	Std
Variable source (°C.S)	26.3	28.1	24.0	24.3	25.7	1.9
Constant source (°C.S)	25.5	26.6	25.7	26.3	26.1	0.5

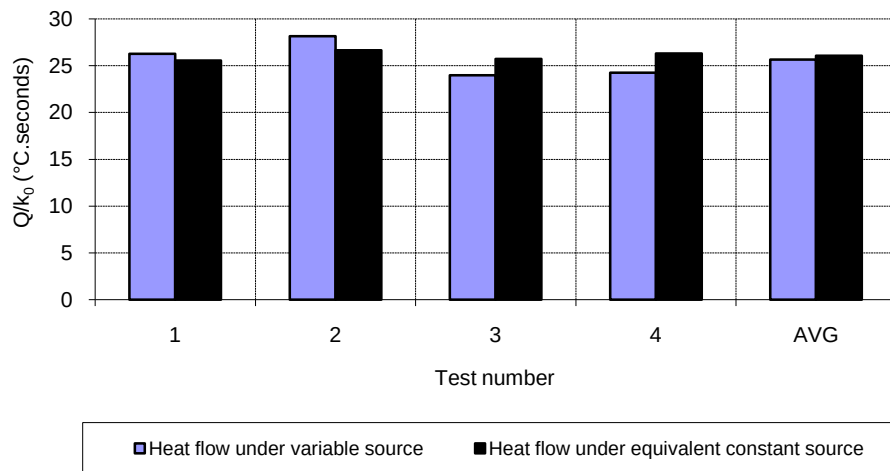


Figure 4.6 Comparing integrated heat flows at the reference point

¹Integrated heat flow was measured as $Q/k_0 = \int_0^{20} \Delta T dt$ according to Fourier law for heat conduction.

$k_0 = A_r \cdot h / l$ where A_r , h , and l respectively stand for the transmission surface area, the coefficient of thermal conductivity, and the laminate thickness.

Experiment 2: Variation in temperature at the reference point

1. The laminate sample was exposed to a variable temperature source. The variation in temperature at a reference point inside the laminate was measured by mean of a thermocouple as in the first experiment. In this experiment, the heat flow was stopped at the reference point by mean of a thermal insulator (Figure 4.7). The transferred thermal energy was measured by the accumulated heat at the reference point. Following the calorimetric equation $\Delta Q = M.s.\Delta T$, where Q , M , and s respectively stand for the heat, mass heated, and specific heat of the sample [82], the accumulated heat is expressed as a variation in temperature denoted ΔT .

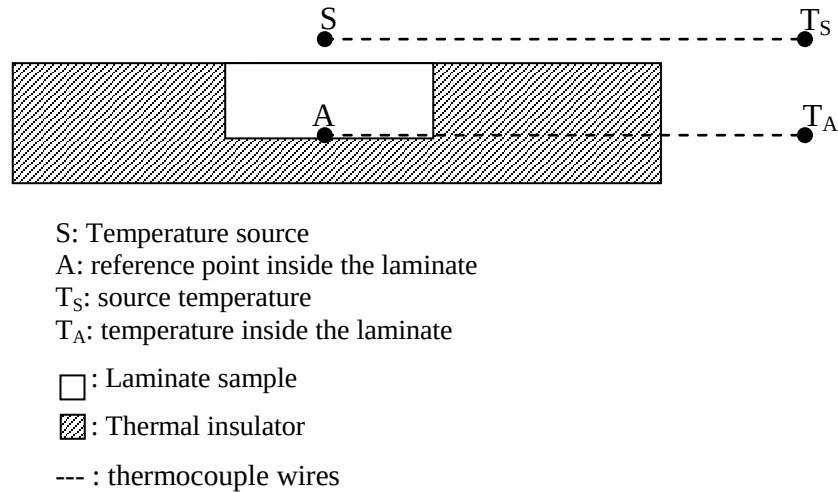


Figure 4.7 Test specimen for the change in temperature at the reference point in the material

2. The same steps 2 to 4 as in the first experiment were repeated. The working time interval was chosen from 5 to 15 minutes. The Figures 4.8 and 4.9 show respectively the variation in temperature under variable source and under equivalent constant source.

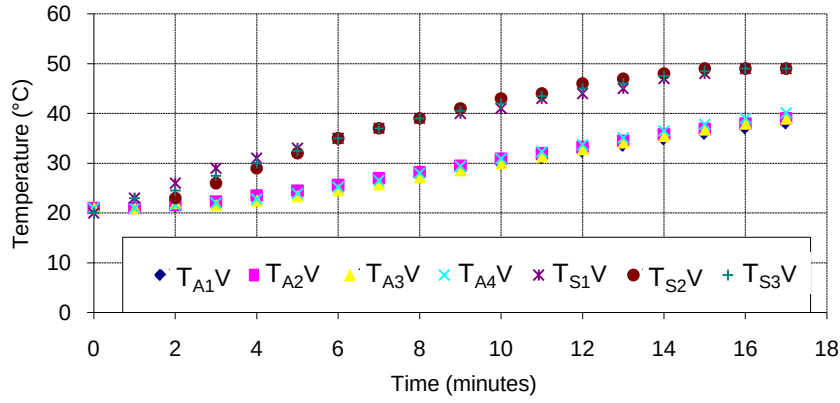


Figure 4.8 Temperature variations under the variable source

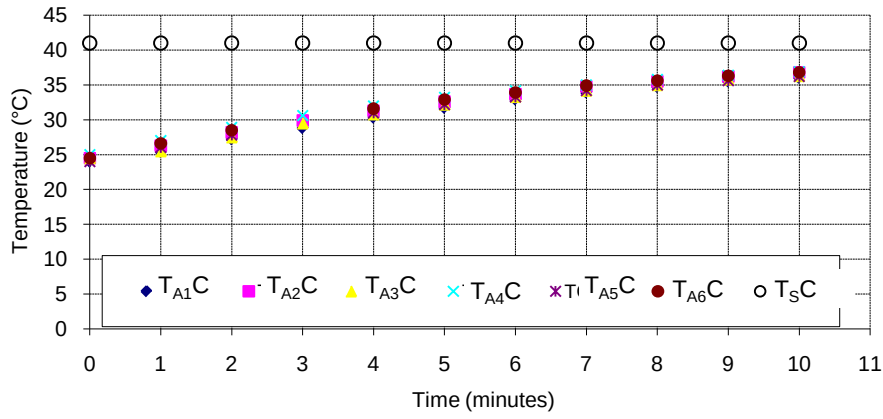


Figure 4.9 Temperature variations under the equivalent constant source

3. The change in temperature at the reference point under variable temperature source was compared to that obtained under equivalent constant temperature source, for the same time interval (Figure 4.10). It is shown that, under the equivalent constant source, the change in temperature at the reference point is the same as under the variable source. This denotes that the amount of transmitted energy is preserved.

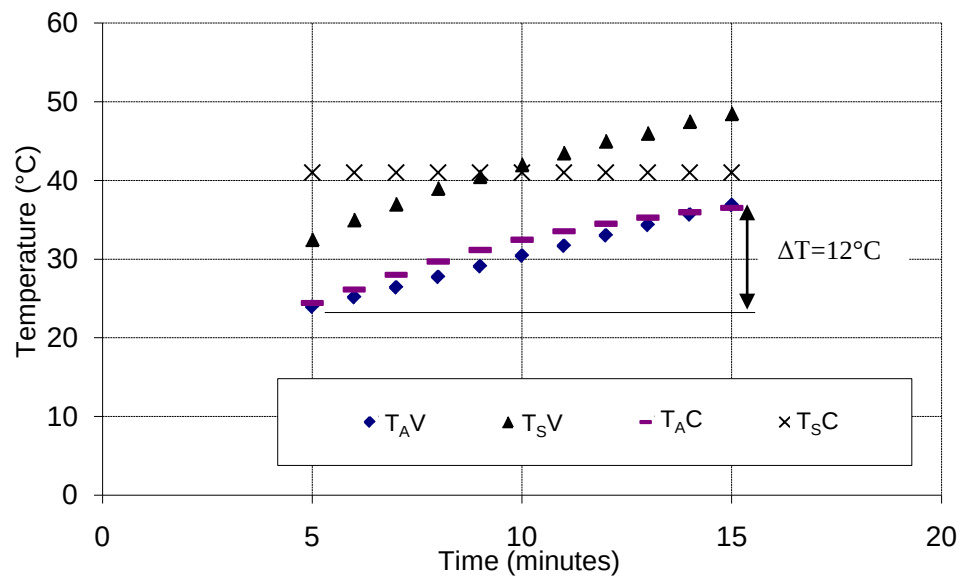


Figure 4.10 Comparing the change in temperature under variable and constant temperature source

Experiment 3

1. A dozen of polyester laminate samples were moisturized in distilled water under variable temperature source and one other dozen of the very same polyester laminate were moisturized under an equivalent constant temperature source (Figure 4.11).

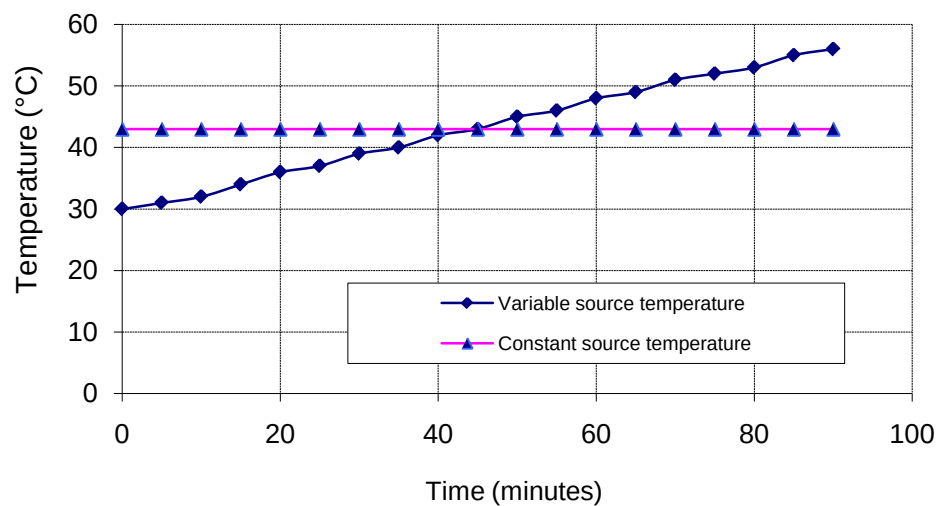


Figure 4.11 Variation of temperature during moisturization

2. Moisture diffusion under the two different temperature sources was compared (Figure 4.12 and 4.13)

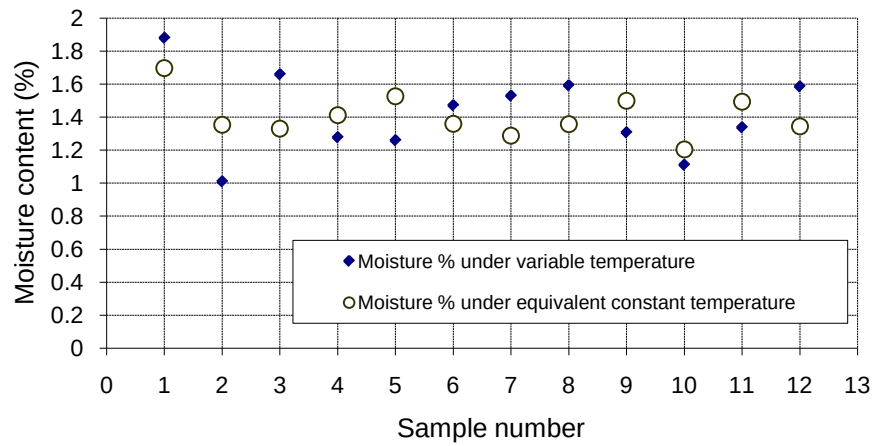


Figure 4.12 Scattering of moisture content after exposure under variable and constant temperature sources

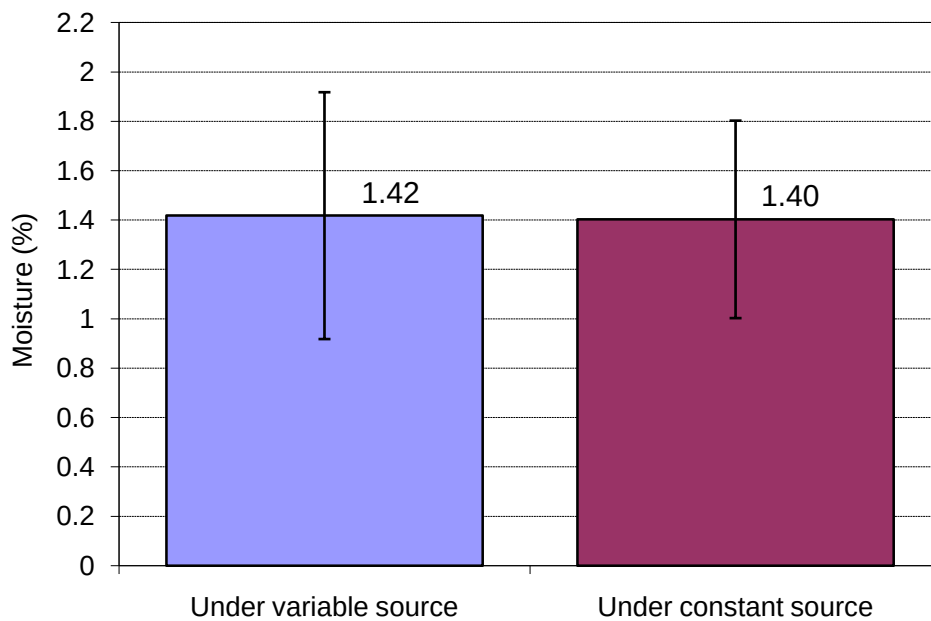


Figure 4.13 Comparing moisture content after exposure

The above results (Figures 4.12 and 4.13) indicate that the change from the variable source to the equivalent constant one does not affect moisture diffusion.

4.2.2 Discussion

Experimental results show that it is possible, for suitably chosen time interval, to replace a variable source of temperature by an equivalent constant source that transmits exactly the same amount of energy. It is also shown that such transformation from the variable source to the constant one does not affect the diffusion results. Therefore, the amount of transmitted mass and energy is conserved.

However, in order to insure comparable transformation or degradation of the material, the transmission rate or power under the constant source is also required to be in the same range than that generated under the variable source. This means, their difference should be negligible.

In the above experiment, the transformation from the variable source to the constant one modifies the distribution of the difference in temperature between the material and the environment (Figure 4.14).

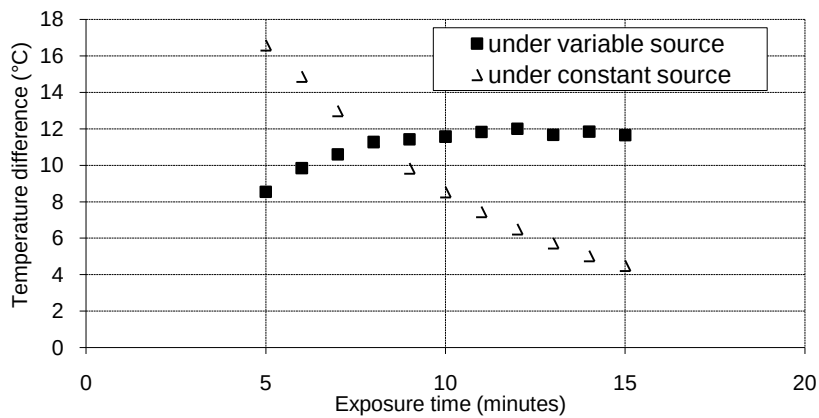


Figure 4.14 Temperature difference between the material and the environment in the course of exposure

Subsequently, the distribution of transmission rate or transmission power is also modified as the latter depends proportionally on the temperature difference according to Fourier law for heat conduction [80] (Figure 4.15).

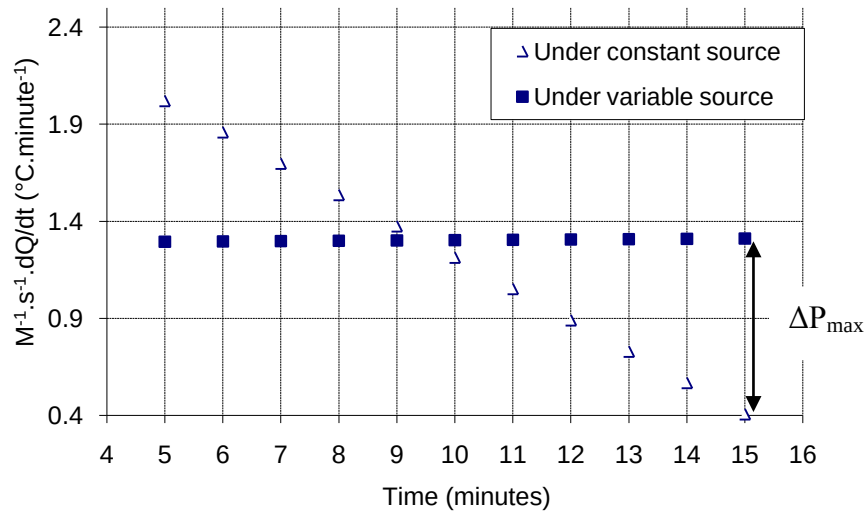


Figure 4.15 Transmission power in the course of exposure²

In Figure 4.15, the maximal difference in transmission power is represented by $\Delta P_{\max}$. The figure shows that $\Delta P_{\max}$ is proportional to the length of the time interval. Then, it is trivial that $\Delta P_{\max}$ can get negligible if the time interval is sufficiently reduced.

Therefore, a variable temperature source over a determined time interval can theoretically be represented as constant temperature that produces comparable degradation over the same time interval.

² Expression of transmission power is obtained from the calorimetric law: $\Delta Q = M.s.\Delta T$ by differentiation, as the value of k_0 in the Fourier equation is not determined. s and M respectively stand for the specific heat and the mass of the heated material

The above, directly results from equation (4.1) and therefore, can be extended to the remaining environmental factors. This means that the real service environment history can be determined as a theoretical succession of constant environmental states based on the theorem of the mean value. The time intervals can sufficiently be minimized in such a way as to obtain a discrete pattern as the one represented in Figure 4.16b. In such a pattern, the difference in transmission power is minimized and effect of cycling temperature or humidity over the overall time interval is preserved. A useful application of this concept is presented in the next chapter.

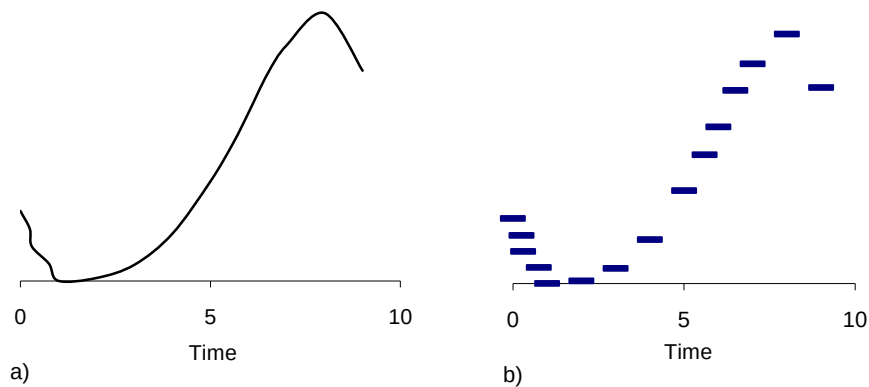


Figure 4.16 Schematic representation of a transformation from a continuous variable environment (a) to a succession of constant environments (b)

Transformation time intervals are sufficiently reduced to minimize the difference in transmission power and preserve the cycling effect over the overall exposure time

4.3 Conclusion

A simplified method to represent the variability of the real service environment into laboratory has been demonstrated. The method is based on the statistical control chart and the use of a mean value. It is shown that, the real service environment can be reliably reproduced in laboratory in terms of constant environment that expresses exactly its variability. The constant environment is provided by the statistical control limits of the real service conditions.

It is also shown that, the environment history can be modelled as a sequence of constant environments by replacing variable factors by constant values over a determined time interval. Experimental observation based on the storage tank model indicates that the amount of transmitted mass and energy is preserved. The transmission power also is preserved if the time interval is sufficiently reduced. The above models provide a method to manage the complexity relating to the variability of real service conditions. This constitutes a solution to issues relating to the translatability of laboratory test results to real service conditions.

5 THE CHEMICAL AND PHYSICAL DEGRADATION MODEL

Modelling and prediction of the environmental degradation of fibre reinforced plastics has been hindered by the complexity of the process. Published works are limited to effects and mechanism characterization or partial models, most of the time empirical.

In this chapter an analytical approach is presented which resolves the degradation process into only three components: the chemical link density variation, the cohesion force variation, and the stress state modification. The first two are referred to as chemical and physical degradation.

The present chapter demonstrates that in a constant environment an exponential function correlates the chemical and physical degradation of the material to the environmental factors. It is also shown that the chemical and physical degradation rates in a real service environment can be determined in a laboratory in a constant environment based only on the variation of the chemical link density. The suggested model is a mathematical function logically derived from material science theories and expresses a qualitative relation between the material degradation and environmental factors.

5.1 The modelling approach

In order to resolve the complexity of the environmental degradation process, the analysis relies on the fact that, irrespective of its cause, all environmental degradation results only from one of the following three sub-processes:

- Chemical degradation, corresponding to the modification of the density of chemical links caused either by chemical attack, thermal attack or ultra violet rays.

- Physical degradation, corresponding to the deterioration of cohesive forces or plasticization caused by either moisture absorption or temperature increase.
- Mechanical degradation, corresponding to the modification of the stress state caused by temperature cycles or humidity.

The effects of these three sub-processes are only of two kinds. Firstly, the material stiffness is altered. This results from the modification of chemical link density and from the variation of cohesive forces. These effects will be referred to as “chemical and physical degradation”. Cases where environmental factors cause crosslinking (post-cure by UV rays or temperature) or stiffen the material are not seen as degradation. This is because the mechanical strength of the material is not negatively affected. These cases are consequently not considered in the following development. Secondly, the stress state is modified as a result of hygrothermal stresses. The ultimate effect of these two processes is the transformation of the material rheology. Therefore, material rheology provides the common parameter allowing the integration of the two processes into a common mathematical relation which provides the mathematical model. The analysis focuses therefore on the rheological changes in the material. This view is schematically presented in Figure 5.1.

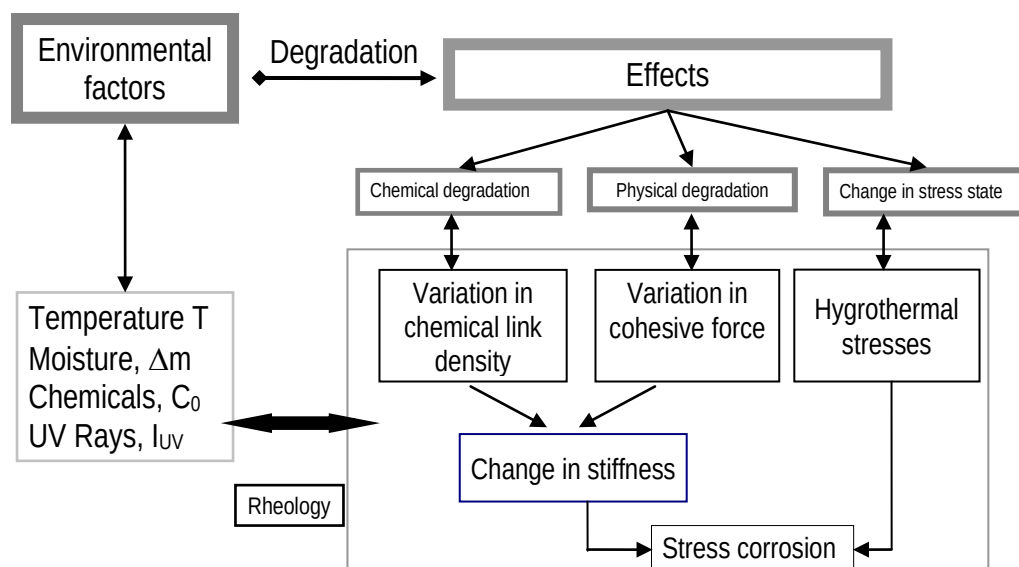


Figure 5.1 Environmental degradation process

For the sake of methodology, this chapter deals only with the chemical and physical degradation. The method consists of deriving a qualitative mathematical relation between the degradation rate and the environmental factors including the chemical concentration, the moisture, the diffusion coefficient, the temperature, and the UV rays. The qualitative mathematical relation contains theoretical parameters that can be determined experimentally. At first, based on material science theories, the environmental factors are mathematically correlated to the material rheology. Secondly, the chemical and physical degradation is expressed as a function of the material rheology. Then, based on the mathematical relation between the material rheology and the environmental factors, the chemical and physical degradation is expressed as a mathematical function of the environmental factors to derive the mathematical model. The validity of the mathematical model is measured by the degree of correlation between the variation of the degradation index calculated from the model and the variation of the mechanical strength of the material measured experimentally over the course of the degradation.

5.2 Definitions

Following the above description, the alteration of the material stiffness during the chemical and physical degradation is caused by the variation in chemical link density and the variation in cohesive forces. Indices L_d , C_f , E_d , are now introduced and are respectively the chemical link degradation index, the cohesion force deterioration index, and the stiffness degradation index.

5.2.1 Degradation index of the chemical link density: L_d

It is assumed that for a given material, if the cohesive forces are held constant, only the modification of chemical link density determines the degradation. The variation in mechanical properties is then directly related to the variation in chemical link density and thereby the variation in diffusivity. Theoretically, the mechanical resistance of a given material may therefore be expressed as a given critical chemical link density that should assure the material structure will hold

against breaking stresses. The index of the degradation of the chemical link density L_d defines the material degradation due only to chemical link breakage and is an increasing value over the course of the degradation.

The chemical link density index L_d is modified only by attack from chemicals, UV rays and temperature, respectively, represented by symbols ch , UV and Th . Mathematically the total variation of L_d is the sum of its variation due to the effects of chemical agents, UV rays and thermal attack, expressed as follows:

$$dL_d = dL_{d\ ch} + dL_{d\ UV} + dL_{d\ Th} \quad (5.1)$$

Variation in the rate of L_d is obtained by derivation of equation (5.1) as follows:

$$\frac{dL_d}{dt} = \frac{\partial L_d}{\partial(ch)} \frac{d(ch)}{dt} + \frac{\partial L_d}{\partial(UV)} \frac{d(UV)}{dt} + \frac{\partial L_d}{\partial(Th)} \frac{d(Th)}{dt} \quad (5.2)$$

5.2.2 Degradation index of the cohesive forces: C_f

For a given material, assuming that the chemical link density is held constant, the degradation is directly related to the decrease of cohesive forces and consequently the reduction in the mechanical strength. So, theoretically, the mechanical resistance of a given material may be expressed as a given critical cohesive forces level that should assure the material structure will hold against breaking stresses. The cohesive force degradation index defines the material environmental degradation resulting only from the variation of cohesive forces. The index C_f increases when the cohesive forces decrease.

The variation of the cohesive force results only from diffused moisture and from temperature variation. On this basis, the degradation rate of the cohesive forces can be mathematically expressed as the sum of only two contributions arising from the variation in the rates of the diffused moisture and temperature:

$$\frac{dC_f}{dt} = \frac{\partial C_f}{\partial(\Delta m)} \frac{d(\Delta m)}{dt} + \frac{\partial C_f}{\partial(Th)} \frac{d(Th)}{dt} \quad (5.3)$$

where Δm represents the diffused moisture.

5.2.3 The degradation index of the material stiffness: E_d

The index E_d represents the degradation of any material property such as tensile strength, modulus, etc. The chemical and physical degradation of the material stiffness is the sum of two contributions including chemical link degradation and cohesive force degradation. This can be mathematically expressed as follows:

$$E_d = p_1 L_d + p_2 C_f \quad (5.4)$$

The factors p_1 and p_2 are weighting factors relating the contribution of the chemical link density and cohesive forces to the degree of degradation. The stiffness degradation rate can then be deduced from equation (5.4) by differentiation as follows:

$$\frac{dE_d}{dt} = p_1 \frac{dL_d}{dt} + p_2 \frac{dC_f}{dt} \quad (5.5)$$

The next step in this analysis is aimed at the determination of each of the terms in the second part of the equation (5.5). It is intended to express these terms as a function of environmental factors. To this end, the following section introduces theoretical assumptions based on material science theories.

5.3 Material Rheology as a Function of Chemical Link Density

It is assumed that the material rheological state is linearly correlated to a power of the chemical link density. This is mathematically expressed as follows:

$$\left(\frac{1}{\Gamma} \right)_{L_d} = k_1 (L_d)^a \quad (5.6)$$

In equation (5.6), Γ represents a material rheology index such as the viscosity or stiffness; in which case its inverse expresses the material compliance and a is an empirical positive constant. In the rest of this text, the symbol k_i represents a positive constant and subscripts following parentheses mean “due to”. Thus,

equation (5.6) gives the material rheological state due to the degradation state of the chemical link density.

The equation (5.6) is a logical assumption asserting that the stiffness of a solid polymer is proportional to its chemical link density or is inversely proportional to the index of chemical link degradation. This means that a specific reduction of the chemical link density results in a corresponding specific reduction of the material stiffness and that the reduction is affected by factors such as molecular chain length and molecular spatial configuration. This kind of correlation provides the basis of rheometric measures. For instance, in rubber vulcanization, the crosslink level or molecular weight distribution is linearly correlated to the shear torque resistance [83]. A similar principle was also used in the equation of Mark-Houwink [84] for the determination of polymer molecular weight in dilute solution. The study of the melt viscosity of polymers has also established the same kind of correlation between the molecular weight and the polymer melt viscosity. In this case, the exponent of the molecular weight varies from 1.5 to 3.5 [85]. The experimental verification of this relation for the polyester resin shows that the value of a in equation (5.6) is 1.0 (see subsection 5.4.3).

5.4 Material Rheology as a Function of Moisture Content

It is assumed that the material stiffness is inversely proportional to a power of the moisture content and this assumption may be mathematically expressed as follows:

$$\left(\frac{1}{\Delta\Gamma} \right)_{moist} = k_2 \left(\frac{\Delta m}{\rho} \right)^b \quad (5.7)$$

In this equation Δm is the mass of the diffused moisture measured by the variation in the sample weight over time and ρ is the specific mass of the diffused liquid. This assumption results from the consideration that the diffused moisture creates additional separation space between the polymer molecules. The intermolecular distance r as well as the dielectric parameter and consequently the intermolecular

attraction forces, F_{cf} , are thus modified. The additional separation space can be expressed as a volume determined by the moisture content as follows:

$$\Delta V = \frac{\Delta m}{\rho} \quad (5.8)$$

Considering Van der Waal's law for cohesive forces, one can deduce the following equation and hence equation (5.7') where b is a constant depending on the material:

$$\Delta F_{cf} = \frac{k_3}{(\Delta r)^d} = \frac{k_4}{(\Delta V)^{d/3}} = k_4 \left(\frac{\Delta m}{\rho} \right)^{-d/3} \quad (5.9)$$

$$\left(\frac{1}{\Delta \Gamma} \right)_{moist} = \left(\frac{k_5}{\Delta F_{cf}} \right)_{moist} = k_6 \left(\frac{\Delta m}{\rho} \right)^b \quad (5.7')$$

The equation (5.7) assumes that the laminate has been plasticized by the diffused liquid but it can also be applied to the case where the penetrating moisture forms clusters as noted by Marsh *et al* [18]. In this case, the resistance to the diffusion process is proportional to the interaction area between the diffused mass and the laminate. This area is equal to the external surface area of the diffused volume and it can also be expressed as a power of the volume.

5.5 Material Rheology as a Function of Temperature

It is assumed that the material stiffness is inversely proportional to a power of the temperature variation and this assumption may be mathematically expressed by the following equation where ΔT is the temperature variation and c is a constant.

$$\left(\frac{1}{\Delta \Gamma} \right)_T = k_7 (\Delta T)^c \quad (5.10)$$

The temperature variation affects the material rheology by modifying the thermal kinetic energy of molecules and consequently the level of segmental motions along with the activation energy for flow. This effect is manifested by variation of the material free volume. Common experimental measurement of this effect shows a linear correlation between the temperature and the free volume with a

slope change at the glass transition temperature [85, 86]. This can be expressed as follows:

$$\Delta v = k_8 \Delta T \quad (5.11)$$

In this equation Δv is the free volume that can also be expressed in terms of intermolecular radius, r , as shown in equation (5.9). Then Van der Waal law of cohesive forces can be written in terms of free volume and in terms of temperature as follows:

$$\Delta F_{cf} = \frac{k_3}{(\Delta r)^d} = \frac{k_9}{(\Delta v)^{d/3}} = \frac{k_{10}}{(\Delta T)^{d/3}} \quad (5.12)$$

Equation (5.12) can also be written in terms of material rheology as follows:

$$\left(\frac{k_5}{\Delta F_{cf}} \right)_T = \left(\frac{1}{\Delta \Gamma} \right)_T = k_{11} (\Delta T)^c \quad (5.13)$$

where c is a positive constant depending on the material. This equation accounts only for the physical degradation. Chemical degradation including thermolysis and post-curing is already considered in equation (5.6).

5.6 Chemical Concentration as a Function of Material Rheology and Diffusion Effect

A portion of a pipe or storage tank wall is shown in Figure 5.2. The wall laminate is exposed to a chemical denoted ch , and to moisture at a temperature T . l is the laminate thickness. C_0 and C_l are respectively the chemical concentrations at the internal and external surfaces of the laminate.

According to Fick's law, the concentration C_{ch} is a function of the diffusive rate J which can be expressed as

$$J = -D \frac{\partial C_{ch}}{\partial l} \quad (5.14)$$

Integration of equation (5.14) (see Appendix B) leads to

$$C_{ch} = k_{12} D \frac{C_0 - C_l}{l} \quad (5.15)$$

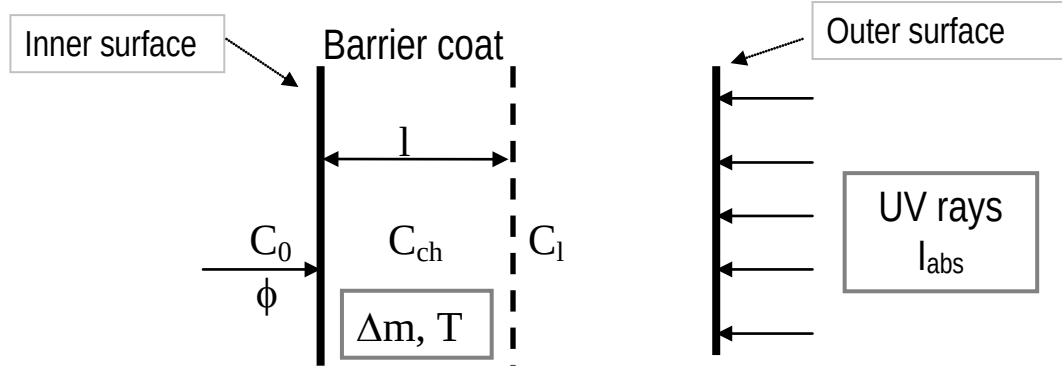


Figure 5.2 Portion of pipe wall

Since $C_0 \gg C_l$, one can assume that $C_0 - C_l \approx C_0$. Equation (5.15) can therefore be written as

$$C_{ch} = k_{12} D \frac{C_0}{l} \quad (5.16)$$

Analogously to the Stokes-Einstein equation [87, 88], it is assumed that the diffusion coefficient and the material rheology are correlated in the following manner:

$$D_0 = k_{13} \frac{T}{\Gamma} \quad (5.17)$$

Equation (5.17) represents the effect of material rheology on diffusion and expresses the obvious fact that in a solid material moisture diffusion increases with temperature and decreases with an increase in viscosity. However, the diffusion coefficient is also related to the variation in the thermal kinetic energy of the diffusing molecules according to the Arrhenius law [8, 21, 26] as follows:

$$D = D_0 e^{\frac{-W_D}{RT}} = k_{13} \frac{T}{\Gamma} e^{\frac{-W_D}{RT}} \quad (5.18)$$

In equation (5.18) W_D is the activation energy of diffusion. The relation between the concentration C_{ch} and the material rheology is obtained by combining equations (5.16) and (5.18):

$$C_{ch} = k_{14} \frac{T}{\Gamma} \frac{C_0}{l} e^{\frac{-W_D}{RT}} \quad (5.19)$$

This relation shows that the concentration of the diffused material inside the laminate depends on its concentration at the laminate surface, on the temperature, on the material viscosity at the given temperature and on the laminate thickness.

However, the material rheology is modified over the course of degradation. The variation of material rheology arises from the variation of chemical link density, L_d , and from the variation of cohesive forces due to moisture and temperature. In order to account for this effect, let the total differential of the material rheology be given as a function of these three variables as follows:

$$d\left(\frac{1}{\Gamma}\right) = \frac{\partial\left(\frac{1}{\Gamma}\right)}{\partial L_d} dL_d + \frac{\partial\left(\frac{1}{\Gamma}\right)}{\partial(\Delta m)} d(\Delta m) + \frac{\partial\left(\frac{1}{\Gamma}\right)}{\partial T} dT \quad (5.20)$$

Integration of equation (5.20) gives the expression of the material rheology as follows:

$$\frac{1}{\Gamma} = \left(\frac{1}{\Gamma}\right)_{L_d} + \left(\frac{1}{\Gamma}\right)_{moist} + \left(\frac{1}{\Gamma}\right)_T \quad (5.21)$$

Equation (5.21) is now substituted into equation (5.19). The chemical concentration is then given as a function of the material rheology as follows:

$$C_{ch} = k_{14} \frac{C_0}{l} \left\{ \left(\frac{T}{\Gamma}\right)_{L_d} + \left(\frac{T}{\Gamma}\right)_{moist} + \left(\frac{T}{\Gamma}\right)_T \right\} e^{\frac{-W_D}{RT}} \quad (5.22)$$

Equations (5.6), (5.7), (5.10), and (5.22) provide qualitative relations between the material rheology and the environmental factors. These relations provide the basis for combining effects of these environmental factors into a single mathematical relation. To this end, in the next section, the material rheology is related to the

degradation rate. The degradation rate is subsequently related to environmental factors, based on the material rheology.

5.7 Rheology Dependant Function of Degradation Rates

5.7.1 Chemical degradation rate as a function of material rheology

Considering again a portion of the pipe wall as represented in Figure 5.2, the chemical reaction occurs between the polymeric matrix and the chemical reagent. As the polymeric material constitutes the reaction medium, only the chemical reagent concentration C_{ch} will determine the chemical reaction rate and the law of chemical reaction rates can be expressed as

$$\left(\frac{\partial L_d}{\partial t} \right)_{ch} = k_{ch} C_{ch} \quad (5.23)$$

In equation (5.23) k_{ch} is the kinetic constant given by the Arrhenius law

$$k_{ch} = A_0 e^{\frac{-W_{ch}}{RT}} \quad (5.24)$$

In equation (5.24), W_{ch} is the activation energy of the chemical reaction, R is the ideal gas constant and A_0 the frequency factor. There are two cases to be considered. Firstly, the reaction at the material surface which is not influenced by diffusion and the chemical degradation rate does not depend on the material rheology. According to equation (5.23), the reaction kinetic can be expressed as

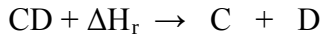
$$\left(\frac{\partial L_d}{\partial t} \right)_{ch}^0 = k_{ch} C_0 \quad (5.25)$$

where the superscript 0 refers to the laminate surface. Secondly, the reaction inside the laminate where the chemical concentration, and consequently the chemical degradation rate, is a function of the material rheology, which can be obtained by substituting equation (5.22) into equation (5.23):

$$\left(\frac{\partial L_d}{\partial t} \right)_{ch} = k_{14} k_{ch} \frac{C_0}{l} \left\{ \left(\frac{T}{\Gamma} \right)_{Ld} + \left(\frac{T}{\Gamma} \right)_{moist} + \left(\frac{T}{\Gamma} \right)_T \right\} e^{\frac{-W_D}{RT}} \quad (5.26)$$

This equation covers in general all types of chemical attack where the process comprises a diffusion step. These also include thermo-oxidation and photo-oxidation. However, the thermal attack and the UV irradiation comprise also thermolysis and photolysis respectively. These are energetic actions where bonds are broken by imparting sufficient energy to electrons to pull them out of the bond.

The thermolysis reaction can be schematized as follows:

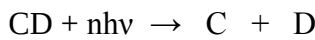


The rate of reaction is proportional to the thermal flux in the material [47]:

$$\left(\frac{\partial L_d}{\partial t} \right)_{Th} = \alpha_3 \frac{\Phi_T}{\Delta H_r} \quad (5.27)$$

In equation (5.27), Φ_T is the thermal flux, ΔH_r is the thermal energy yield per chain scission, and α_3 is a constant. For a given material at constant temperature, the expression $\alpha_3 \Phi_T / \Delta H_r$ is a constant. The case where temperature is variable is irrelevant in this analysis as shown later in subsection 5.9.2.

Taking $nh\nu$ as the photon energy yield per chain scission, the photolysis reaction can similarly be schematized as



The reaction rate is proportional to absorbed UV intensity I_{abs} :

$$\left(\frac{\partial L_d}{\partial t} \right)_{UV} = \alpha_4 \frac{I_{abs}}{nh\nu} \quad (5.28)$$

Equations (5.27) and (5.28) express the chemical degradation rate as function of environmental factors. No further transformation will be operated on these equations because the goal is to express the degradation rate as function of environmental factors. Now equations (5.25), (5.26), (5.27), and (5.28) are substituted into equation (5.2) and the chemical degradation rate is expressed as a function of materiel rheology as follows:

$$\begin{aligned} \frac{\partial L_d}{\partial t} = & k_{ch} C_0 + k_{14} k_{ch} \frac{C_0}{l} \left\{ \left(\frac{T}{\Gamma} \right)_{Ld} + \left(\frac{T}{\Gamma} \right)_{moist} + \left(\frac{T}{\Gamma} \right)_T \right\} e^{\frac{-W_D}{RT}} \\ & + \alpha_3 \frac{\Phi_T}{\Delta H_r} + \alpha_4 \frac{I_{abs}}{nh\nu} \end{aligned} \quad (5.29)$$

5.7.2 Physical degradation rate as a function of the material rheology

The determination of the physical degradation rate as a function of the rheology is based on the fact that variation in the material rheology resulting from the change in temperature and moisture, is proportional to the cohesive force:

$$F_{cf} = k_{15} (\Gamma)_{moist,T} \quad (5.30)$$

According to the definition given in subsection 5.2.2, C_f increases when the cohesive forces are reduced. This means that a positive variation in C_f corresponds to a negative variation in the cohesive forces as expressed in the following equation:

$$dC_f = d(-F_{cf}) = k_{15} d(-\Gamma) \quad (5.31)$$

The physical degradation rate as function of the material rheology is obtained by derivation of equation (5.31) as follows:

$$\frac{dC_f}{dt} = k_{15} \frac{d(-\Gamma)}{dt} = k_{15} \left(\frac{\partial(-\Gamma)}{\partial(\Delta m)} \frac{d(\Delta m)}{dt} + \frac{\partial(-\Gamma)}{\partial T} \frac{dT}{dt} \right) \quad (5.32)$$

5.8 Degradation as a Function of Environmental Factors

The material rheology has been correlated to environmental factors (subsection 5.1.3). Equations (5.6), (5.7) and (5.10) are qualitative relations resulting from materials science laws. Based on materials science laws, it has also been shown that the variation of material rheology is a function of the chemical and physical degradation rates (subsection 5.1.4). In the following subsection, the chemical and

physical degradation rates are related to environmental factors, based on the material rheology.

5.8.1 The chemical degradation rate as a function of environmental factors

The chemical degradation rate can be expressed as a function of environmental factors by substituting equations (5.6), (5.7) and (5.10) into equation (5.29). This leads to

$$\begin{aligned} \frac{dL_d}{dt} = & k_{ch}C_0 + \left[\alpha_0 L_d + \alpha_1 (\Delta m)^b + \alpha_2 T^c \right] C_0 Te^{\frac{-(W_{ch}+W_D)}{RT}} \\ & + \alpha_3 \frac{\Phi_T}{\Delta H_r} + \alpha_4 \frac{I_{abs}}{nh\nu} \end{aligned} \quad (5.33)$$

In equation (5.33) $\alpha_0 = k_1 k_{14} / l$; $\alpha_1 = k_2 k_{14} / l \rho^b$; and $\alpha_2 = k_7 / l$. These three parameters α_0 , α_1 , α_2 and generally the symbol α_i in the rest of the description, are positive constants depending on the material type and environmental conditions. All terms of equation (5.33) are positive and increasing functions of environmental factors. This shows that the chemical degradation rate is an increasing monotonic function of the environment.

5.8.2 Physical degradation rate as a function of environmental factors

In order to determine the physical degradation rate as a function of environmental factors, equations (5.7) and (5.10) are substituted in equation (5.32) which gives:

$$\frac{dC_f}{dt} = k_{15} \left(\frac{d(-\Gamma)}{dt} \right) = k_{15} \left(\frac{d \left(\frac{\rho}{-\Delta m} \right)^b}{dt} \right) + k_{15} \left(\frac{d(-T^{-c})}{dt} \right) \quad (5.34)$$

By applying the chain rule of differentiation to the terms on the right side of equation (5.34), one obtains

$$\frac{dC_f}{dt} = \alpha_5 \frac{\rho^b}{(\Delta m)^{b+1}} \frac{d(\Delta m)}{dt} + \alpha_6 \frac{1}{T^{c+1}} \frac{dT}{dt} \quad (5.35)$$

5.9 The Model of Chemical and Physical Degradation

5.9.1 The mathematical model

In this section, the rate of chemical and physical degradation is determined as a function of environmental factors to derive the mathematical model. To this end, equations (5.33) and equations (5.35) are substituted into equation (5.5) as follows:

$$\begin{aligned} \frac{dE_d}{dt} = & k_{ch}C_0 + \left[\alpha_0 C_0 L_d + \alpha_1 C_0 (\Delta m)^b + \alpha_2 C_0 T^C \right] e^{\frac{-(W_{ch}+W_D)}{RT}} + \alpha_3 \frac{\Phi_T}{\Delta H_r} \\ & + \alpha_4 \frac{I_{abs}}{nh\nu} + \alpha_4 \frac{\rho^b}{(\Delta m)^{b+1}} \frac{d(\Delta m)}{dt} + \alpha_5 \frac{1}{T^{C+1}} \frac{dT}{dt} \end{aligned} \quad (5.36)$$

In equation (5.36), the environmental factors C_0 , T , and Δm vary with time in a way that is not always controllable. The exact solution of equation (5.36) requires the determination of the time dependence function of each of the environmental factors. It is not obvious that such a task may be achieved successfully and the solution of the equation would be quite complex. Nevertheless, the problem can be resolved by treating the environmental history as a sequence of constant environments as explained in the next section.

5.9.2 The Physical and Chemical degradation in a constant environment

In chapter 4, it was shown that, the real service environment could be modelled as a continuous succession of constant environmental states (section 4.2). Now considering that concept, the above equation (5.36) is applied in one of the constant environments and this leads to the following:

Exponential equation of the chemical and physical degradation

In a constant environment, equation (5.36) can be rewritten in a simple form as

$$\frac{dE_d}{dt} = \alpha_0 k T C_0 E_d + \alpha \quad (5.37)$$

where k and α are constants defined by the following equations:

$$k = \frac{1}{p_1} e^{\frac{-(W_D + W_{ch})}{RT}} \quad (5.38)$$

$$\begin{aligned} \alpha = & \left[\alpha_1 C_0 (\Delta m)^b + \alpha_2 C_0 T^c \right] T e^{\frac{-(W_{ch} + W_D)}{RT}} + \alpha_3 \frac{\Phi_T}{\Delta H_r} + \alpha_4 \frac{I_{abs}}{nh\nu} + \alpha_5 \frac{\rho^b}{(\Delta m)^{b+1}} \frac{d(\Delta m)}{dt} \\ & + \alpha_6 \frac{1}{T^{c+1}} \frac{dT}{dt} - T \alpha_0 k C_0 p_2 \left[\alpha_7 \left(\frac{\rho}{\Delta m} \right)^b + \alpha_8 \frac{1}{T^c} \right] \end{aligned} \quad (5.39)$$

Equation (5.37) was obtained by rewriting equation (5.4) as:

$$L_d = \frac{1}{p_1} (E_d - p_2 C_f) \quad (5.40)$$

and then by substituting equation (5.40) in equation (5.36), taking into account that the environment is constant.

The rate of change of E_d can be obtained from the solution of equation (5.37). The former is given by the exponential function below, correlating the chemical and physical degradation to time t (see Appendix C):

$$\frac{dE_d}{dt} = \alpha e^{\alpha_0 k T C_0 t} \quad (5.41)$$

Equivalence between indices L_d and E_d

In a constant environment, according to equation (5.5) and equation (5.35), the degradation rate of the material stiffness is linearly correlated to the degradation of the chemical link density as shown here below:

$$\frac{dE_d}{dt} = p_1 \frac{dL_d}{dt} \quad (5.42)$$

This implies that index L_d is equivalent to index E_d . Practically, this means that in a constant environment, the degradation rate of the material stiffness is determined by the degradation rate of the chemical link density.

Statistical control limits of the degradation rate

Since the degradation rate of the chemical link density is a monotonic ascending function of the environment (see subsection 5.8.1), equation (5.42) implies that the degradation rate of the material stiffness is also a monotonic ascending function of the environment:

$$(f_{j2} \geq f_{j1}) \Rightarrow \left[\frac{dE_d}{dt}(f_{j2}) \geq \frac{dE_d}{dt}(f_{j1}) \right] \quad (5.43)$$

Subsequently, as explained in chapter four, degradation rates measured at the control limits of the environment correspond to the control limits of the degradation rate. In the same way, the degradation rate obtained at the average value of f_j , corresponds to the average degradation rate.

This means that the control limits of the degradation rate and its average value can be determined as simple exponential functions in constant environmental conditions respectively determined by the control limits of the real service environment and its average conditions.

5.10 Experimentation

The above analysis has provided a theoretical demonstration of the assertion that, in a constant environment, the chemical and physical degradation of a polymeric material follows an exponential law. Experimental evidence given in the present section provides further validation. Experiments were designed in such a way as to simulate storage tank or pipe exposure conditions and a range of measurement methods were used. These include Raman spectrometry for chemical structure changes, rheometry for storage modulus, and mechanical testing of tensile and shear strength evolution during degradation. The material used was a polyester laminate formulated in such a way as to be comparable to a standards barrier coat.

5.10.1 Material

The materials are selected in such a way as to represent a significant choice for the local composite industry. The laminate formulation is presented in Table 5.1.

Table 5.1: Materials

RESIN				
		Experiment 1	Experiment 2	Experiment 3
Material		Orthophtalic polyester Crystic 196	Orthophtalic polyester NCS 901 PA	Orthophtalic polyester NCS 901 PA
Resin phr		100	100	100
Catalyst(Butanox M50) phr		2	2	2
Accelerator (Crystic E) phr		0.6	-	-
Curing cycle		24h/ 25°C, 3h/ 80°C	24h/ 25°C, 3h/ 80°C	24h/ 25°C, 3h/ 80°C
LAMINATE				
Composition		Resin/fiber/resin	Res/fib/res/fib/res/fib/res	Res/fib/res/fib/ res
Glass fiber		WR 27.4 g /m ²	CSM 300 g /m ²	CSM 300 g /m ²
V _f (%)	AVG	14	41	14
	StD	1.16	1.52	3.1
Thickness (mm)	AVG	0.21	2.89	2.00
	StD	0.02	0.06	-
Void(visual)		No voids	No voids	No voids

5.10.2 Lamination method

The method for making samples was chosen so as to reduce optimally all kinds of variation between samples: minimal variation in thickness and weight, minimal void content, and constant volume fraction. To this end, three methods were experimented: Vacuum bag, hand lay up followed by short vacuum bag, and hand lay up followed by compression in the mould.

In the first case, the procedure was as follows:

- Cut the fibre in such a way as it fits exactly into the mould and according to the number of layers.
- Clean the mould carefully and apply the releasing wax.
- Lay down the fibre material in the mould and close the mould firmly.

- Then the resin is sucked into the mould by means of a vacuum bag.

This required preparing the resin in such way as to get a long enough gelling time to allow for a good spread of the resin. However, results were not good due to air bulbs. The resin used was so thick that air bulbs retained during the mixing could not be released before the gelling. The laminate contained too much voids. A different procedure was then applied so that to evacuate air bulbs. Hand lay up followed by a strong rolling, then by the laminate compression under a mould or in the vacuum bag (Figure 5.3). This should allow an even resin flow throughout the laminate and thus, a uniform thickness. Obtained laminates presented good properties as shown in Table 5.1



Figure 5.3 Mould compressed under vacuum bag for even resin spread

5.10.3 Experimental procedure

Experiment 1

Ten sets of five material samples were exposed to a corrosive environment. The expository chamber (Figures 5.4 and 5.5) was set in such a way as to simulate the service environment of a pipe or storage tank where samples were simultaneously exposed to the chemical and physical degradation. The chamber comprised two compartments thermally and optically isolated. Each compartment comprised the following:

- a. A set of UV-B lamps. The light spectrum emitted by the fluorescent lamp comprised peaks around 313 nm at about 500 microWatt/cm²/30Å. The emitted energy was very low for higher wavelength (less than 100 microWatt/cm²/30Å between 350 nm and 400nm), while the sun spectrum put out more than 1000 microWatt/cm²/30Å in the same region.
- b. Heating device 900 Watts
- c. Digital temperature controller
- d. 24 expository cells
- e. A grill with a capacity of 25 expository cells. The laminate was exposed to ultraviolet rays at one face and entirely wet with a chemical solution to the second face while the temperature inside the expository chamber is maintained constant.

Exposure conditions were determined from a table of chemical resistance (Crystic resin) in such a way as to obtain notable degradation in relatively short time (Table 5.2)

Table 5.2: Exposure conditions

Temperature	Constant at 40°C
UV rays from outside cell	450 μWatt /cm ²
Humidity from inside cell	100% sample entirely wet
Chemical reagent from inside	5% sodium hydroxide
Maximal duration	10 days



Figure 5.4 External view of the expository chamber

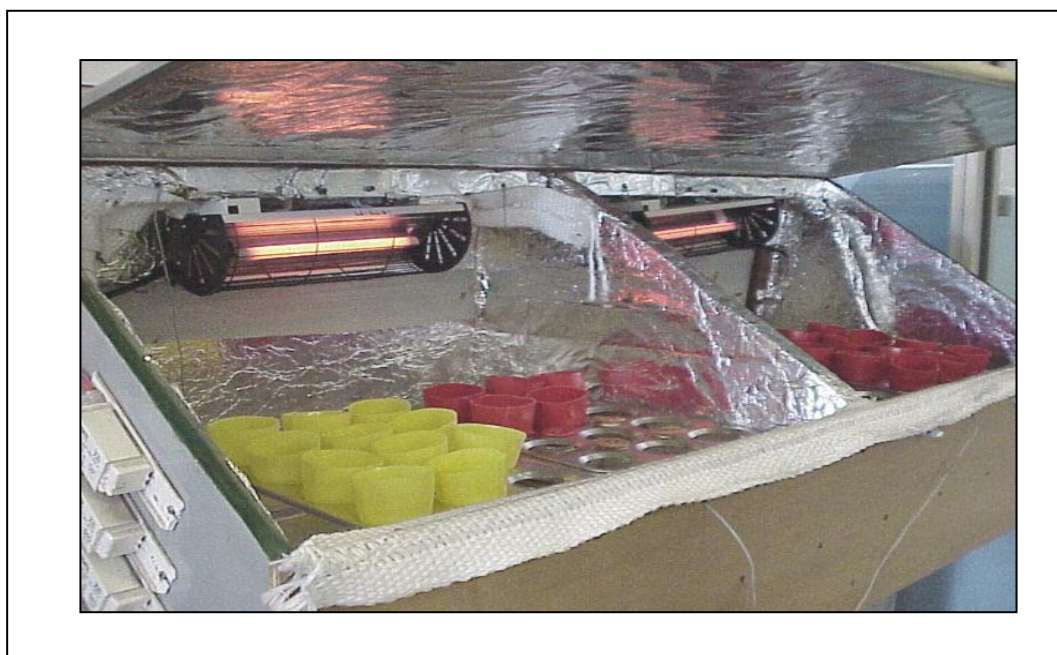


Figure 5.5 Internal view of the expository chamber

The experimental procedures are as follows:

- a. Ten samples of material 1 (Table 5.1) were cut in such a way as they fit in the expository cells and the fibre directions were marked (Figure 5.6).
- b. The samples were initially post cured for three hours at 80°C according to the manufacturer's recommendations for optimal mechanical strength. The samples were then carefully checked for voids or cracks prior to being mounted in the cells of exposure chamber.
- c. A fixed volume of 5% sodium hydroxide solution was injected into each cell.
- d. All the cells were then immediately mounted on the tray in the exposure chamber where the temperature was already set at 40°C.
- e. Five samples were simultaneously exposed to ultraviolet rays, in order to assess the effects of post curing due to ultra violet rays only. Five others were put into an entirely closed aluminium container which stopped ultraviolet rays and the container was then placed in the exposure chamber at the same time in order to determine the post curing effects due to temperature only.
- f. Samples were unloaded one by one from the chamber at 24 hour intervals. Unloaded samples were immediately tested for tensile strength and moisture content (Figures 5.7 and 5.8).
- g. All the samples were then scanned using a Raman spectrometer (Figure 5.9) for changes in chemical structure. Three parameters were used to monitor the chemical change: the ester group reduction, the carbonyl variation, and the orthophthalicbenzene ring variation peaks

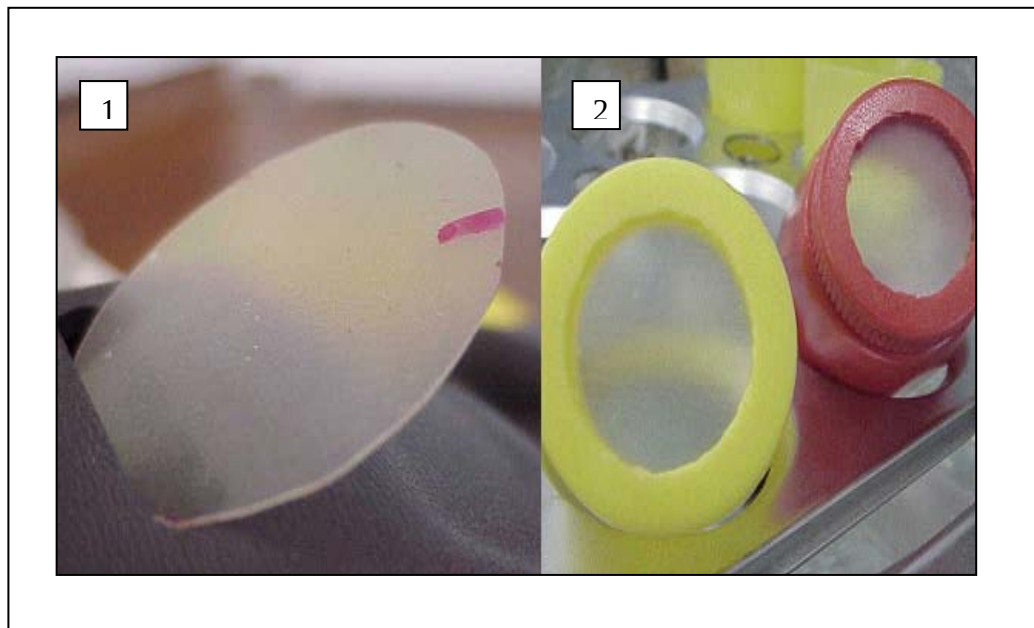


Figure 5.6 Sample cut in circular shape, the fibre direction marked, (1) and ready to be fitted to the expository cell (2)

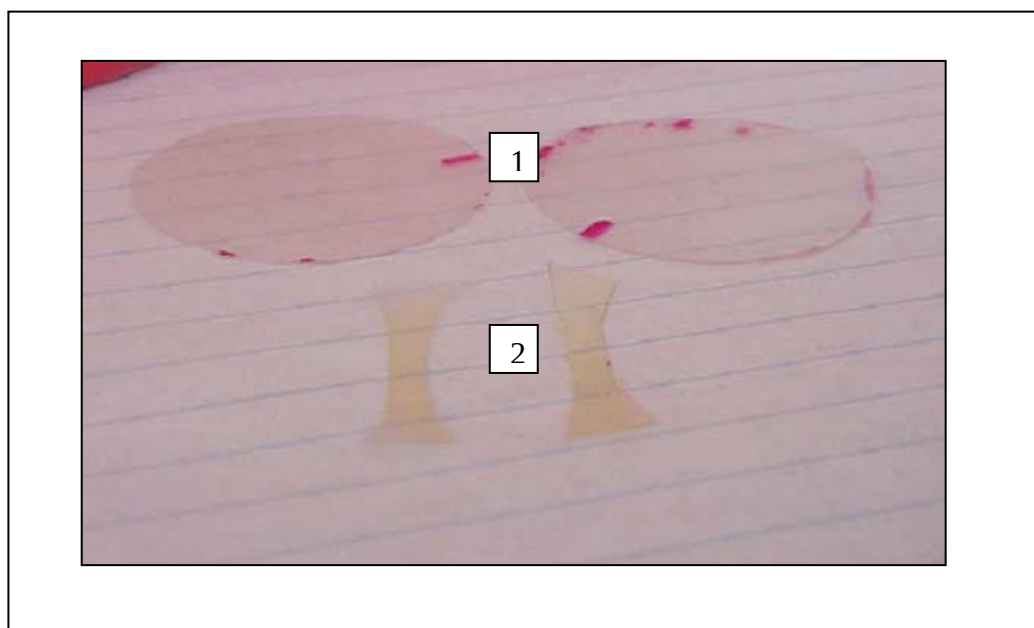


Figure 5.7 Sample from the expository chamber (1) and cut for tensile strength test (2)



Figure 5.8 Tensile test on dog bone samples of 3mm width, 15mm long

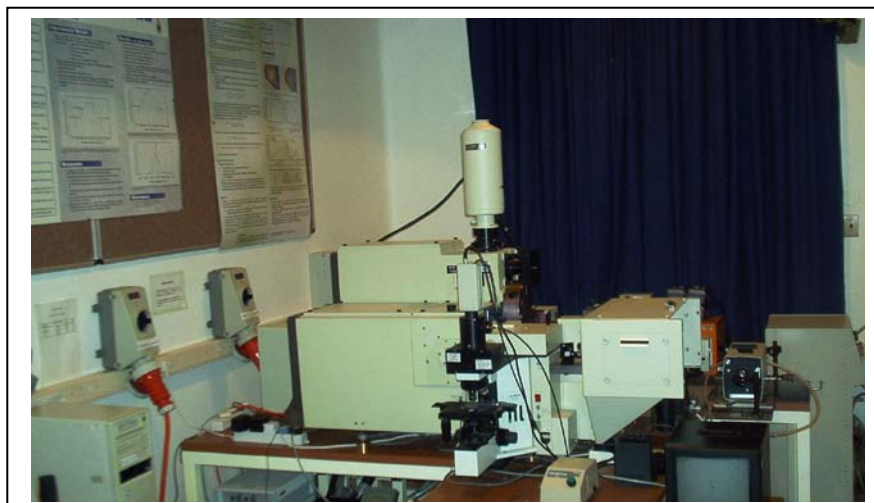


Figure 5.9 Raman spectrometer

Raman spectra were acquired using the micro-Raman attachment of a Jobin-Yvon T64000 Raman spectrometer operated in single spectrograph mode with a 600 grooves/mm grating and the 647.1nm line of a krypton ion laser as excitation source. Laser plasma lines were removed using a narrow band interference filter, and the dispersed signal was detected using a cooled CCD detector. So that to not modify the analysis spot through localized heating the laser power at the sample was kept low. The diameter of the laser spot with the 20x objective was $\sim 2\mu\text{m}$.

Experiment 2

Ten sets of 5 samples from material 2 (Table 5.1) were exposed to 10% sodium hydroxide aqueous solution for a maximum of eight hours at 80°C (Figure 5.10). Sets were unloaded consecutively at 60 minute intervals. Unloaded samples were immediately rinsed in abundant distilled water in order to stop further reaction. Samples were then dried in desiccators for twenty four hours and then tested in shear strength.

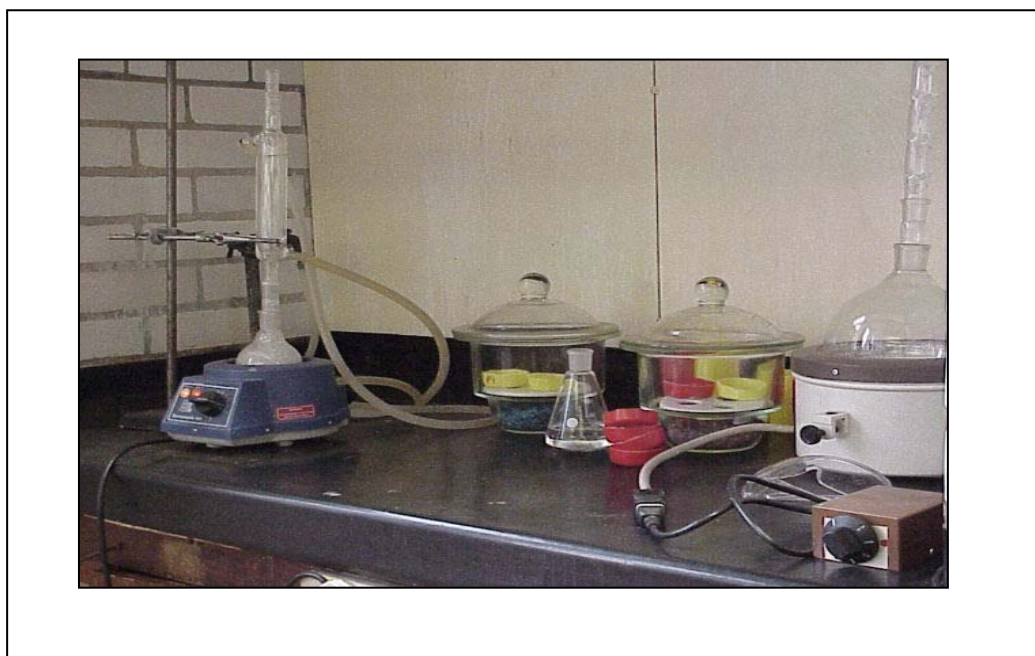


Figure 5.10 Hydrolysis apparatus

The hydrolysis apparatus was mounted and allowed for an accelerated chemical degradation at constant temperature (80°C). It comprised two identical compartments; each made of a temperature controlled heating device, a 500 ml glass flask, and a condensing tube.

Experiment 3

The same procedure as for experiment 2 was followed with ten sets of 3 samples of polyester composite laminates (see table 5.1) over nine hours. The samples were then tested for shear modulus on an Anton Paar Physica MCR rheometer.

5.10.4 Experimental results and discussion

Tensile strength

The tensile strength was measured for samples subjected only to the temperature, for samples exposed to UV rays and temperature only, and for samples exposed to UV rays, temperature and chemical attack. Results are presented in Table 5.3. The plot in Figure 5.11 shows that the laminate strength is not affected by the post cure and that the degradation of the tensile strength occurs according an exponential law (Figure 5.12).

Table 5.3 Tensile Strength of exposed samples

Duration (Days)	Tensile strength (MPa)					
	Degraded samples		Post-curing effect			
			UV rays		Temperature	
	AVG	StD	AVG	StD	AVG	StD
1	89	0.019	95	0.016	95	0.016
2	68	0.001				
3	-		91	0.009	86	0.004
4	36	0.008				
5	39	0.000	89	0.015	138	0.011
6	19	0.002				
7	17	0.003	121	0.031	90	0.008
8	19	0.002	99	0.042	90	0.008

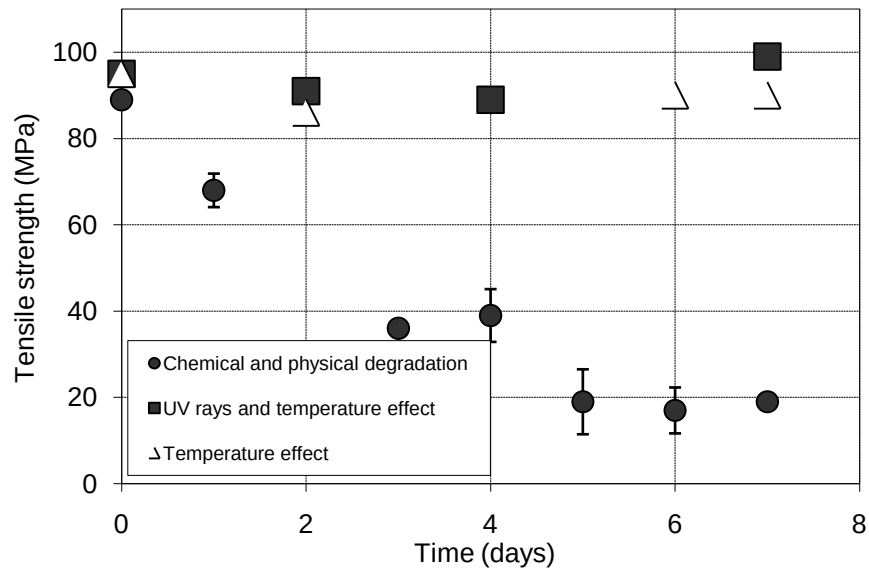


Figure 5.11 UV and temperature post-curing effect on tensile strength

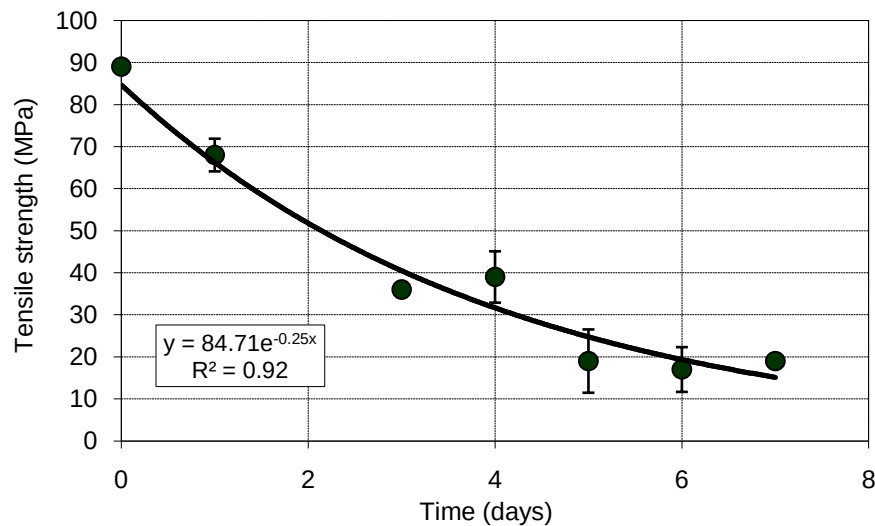


Figure 5.12 Variation of tensile strength during degradation

Moisture curve

Figure 5.13 shows that the moisture percentage increases during degradation, denoting that the more the material structure is degraded the more the moisture penetrates inside the laminate. This explains the dramatic increase in absorbed moisture from the sixth day where the laminate has reached a high disintegration

level corresponding to the lowest value of tensile strength recorded in Figure 5.12. This shows that the moisture recorded inside the laminate is related to material disintegration from chemical attack and not due to Fickian diffusion. The curve shows an exponential trend corresponding to the suggested theoretical degradation model.

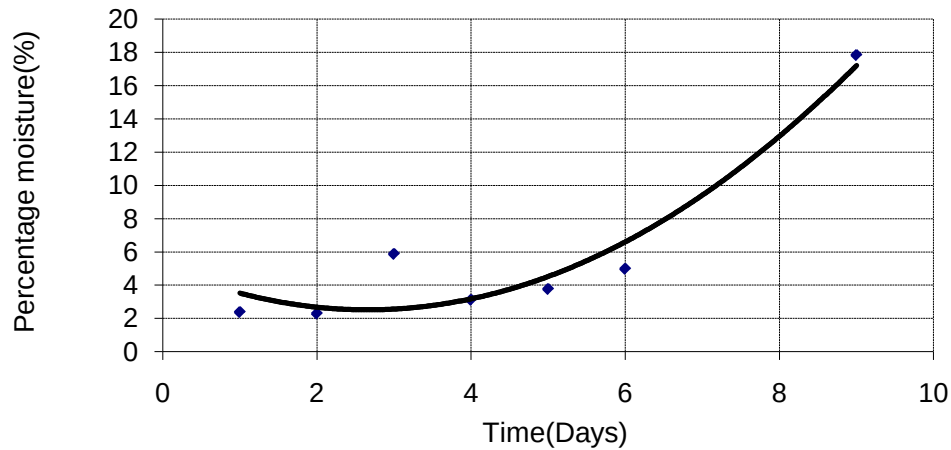


Figure 5.13 Moisture variation during degradation

Micrograph

SEM pictures, showed broken fibres following resin depletion (figure 5.14).

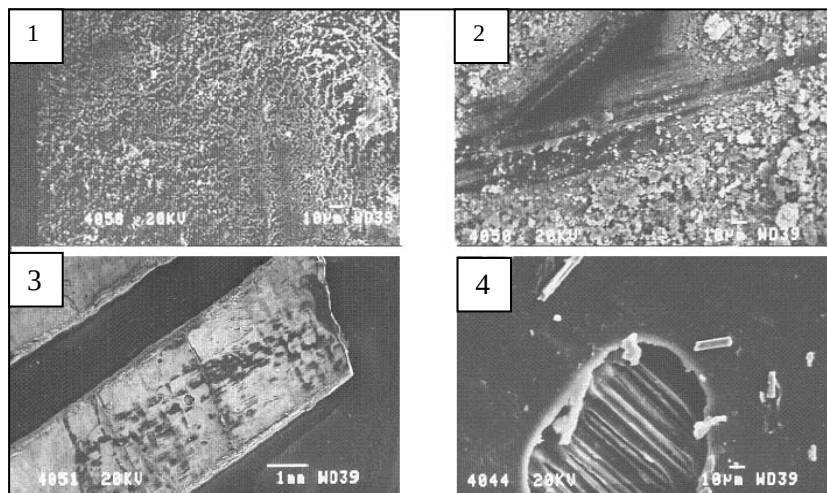


Figure 5.14 Micrograph

(1) Non attacked area, (2) progressive depletion of resin and fibre denudation, (3) attacked area showing pits and resin depletion, (4) inside of pits showing broken fibres

Raman spectra

Raman spectra were acquired both for non-degraded and degraded samples. The spectra were compared to show the change in chemical structures as below.

Spectrum of non-degraded samples

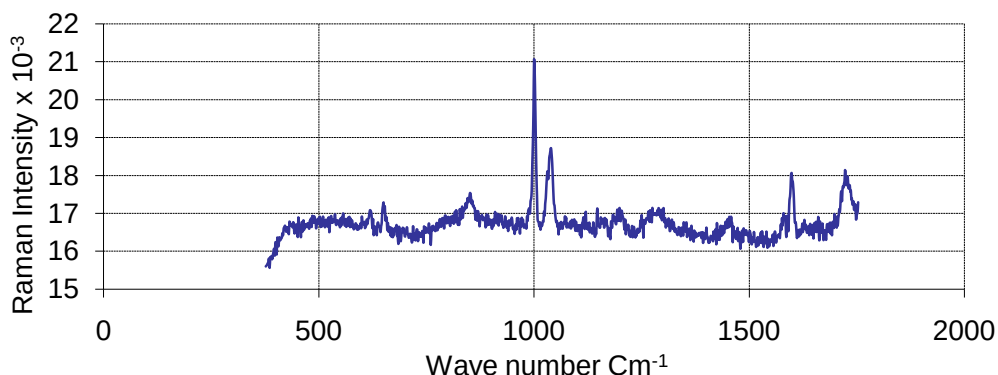


Figure 5.15 Spectrum of non-degraded samples from 370 cm^{-1} to 2000 cm^{-1}

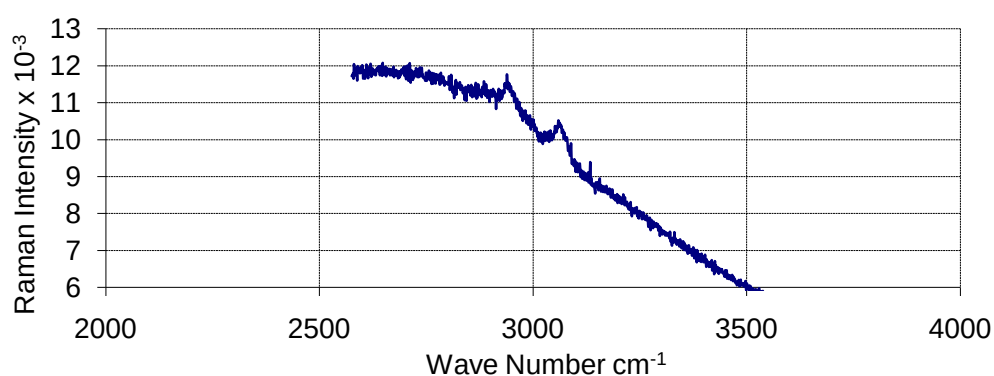


Figure 5.16 Spectrum of non-degraded sample from 2000 cm^{-1} to 3600 cm^{-1}

The spectrum shows peaks at the following bands (Figures 5.15 & 5.16)

- | | |
|------------------------------|-----------------------------|
| - 3060 cm^{-1} | - 1200 cm^{-1} |
| - 2939 cm^{-1} | - 1040 cm^{-1} |
| - 1729 cm^{-1} | - 1001 cm^{-1} |
| - 1600 cm^{-1} | - 850 cm^{-1} |
| - 1450 cm^{-1} | - 650 cm^{-1} |
| - 1280-1300 cm^{-1} | - 620 –625 cm^{-1} |

Figures 5.15 and 5.16 show typical spectra of ortho-para-phthalic polyesters. Peaks at 1729 cm^{-1} band denote the stretching of an ester carbonyl conjugated with a C=C bond or with an aromatic ring. The peak at 1280 cm^{-1} indicates that such aromatic ring may be a phthalate or benzoate. The ester groups conjugated with an aromatic ring are normally characterized by a strong absorption band due to the carbonyl C=O stretching between 1740 and 1715 cm^{-1} and involving the stretch of C-O near 1200 cm^{-1} [89]. The presence of aromatic rings is confirmed by peaks at 1001 cm^{-1} for the mono-substituted rings and 1040 cm^{-1} for the ortho substituted aromatic rings. These peaks are usually strong in Raman and normally expected to arise respectively at $1000 \pm 5\text{ cm}^{-1}$ and $1033 \pm 11\text{ cm}^{-1}$ bands. The aromatics rings are possibly also responsible for the absorption at 650 cm^{-1} for the para substituted and 625 cm^{-1} for the mono substituted. These peaks are usually medium strong in Raman.

The resin structure comprises carbonyl group in 1,3 Diketone. The enol form of the 1,3 Diketone is shown by the absorption at 1600 cm^{-1} . The 1500 cm^{-1} , 1450 cm^{-1} , and 1260 cm^{-1} peaks confirm this. The absorption around 1450 cm^{-1} may possibly also represent the C-H bending in alkane branches of the polymeric chain.

The spectra show another absorption band around 3060 cm^{-1} and 2930 cm^{-1} . This may be related to the bonded OH groups in the enol form of 1,3 Diketone structures which usually absorbs around 3000 to 2700 cm^{-1} . It may also be related to the methylene group -CH₂- in a 6 membered ring that may absorb at 2930 cm^{-1} or also to the diene bonds C=C which peaks arises above 3000 cm^{-1} .

Change in chemical structure showed by Raman spectra

Raman spectrometry shows the change in chemical structure resulting from the hydrolysis of ester groups and photo-oxidation. The spectra show increasing peaks at 1001 cm^{-1} after an earlier decreasing period (Figure 5.17), a decrease of peaks at 1040 cm^{-1} (Figures 5.18 and 5.19), and a shift of peaks from 1040 cm^{-1} to 1032 cm^{-1} over the course of the degradation (Figures 5.20).

The peaks at 1001 cm^{-1} and at 1040 cm^{-1} represent the mono-substituted and the ortho-substituted aromatic rings respectively. These peaks are usually strong in Raman and are normally expected to arise at $1000 \pm 5\text{ cm}^{-1}$ and $1033 \pm 11\text{ cm}^{-1}$ bands respectively [89].

Therefore, the observed decrease and shift may denote the modification of the initial structure (substituents sensitive bands) resulting from environmental attack followed by the production of alcohol structures that normally absorb between 1075 cm^{-1} and 1000 cm^{-1} for aromatic secondary alcohol, and between 1036 and 970 cm^{-1} for axial cyclic secondary alcohol [89]. This occurs as well around 1600 cm^{-1} (figure 5.21) denoting the production of carbonyl structure due to ultraviolet rays attack and around 3060 denoting the arise of diene bond also due to ultraviolet rays attacks.

Figure 5.22 shows the gradual hydrolysis of ester groups that absorb at 1729 cm^{-1} . The peaks decrease according to an exponential law.

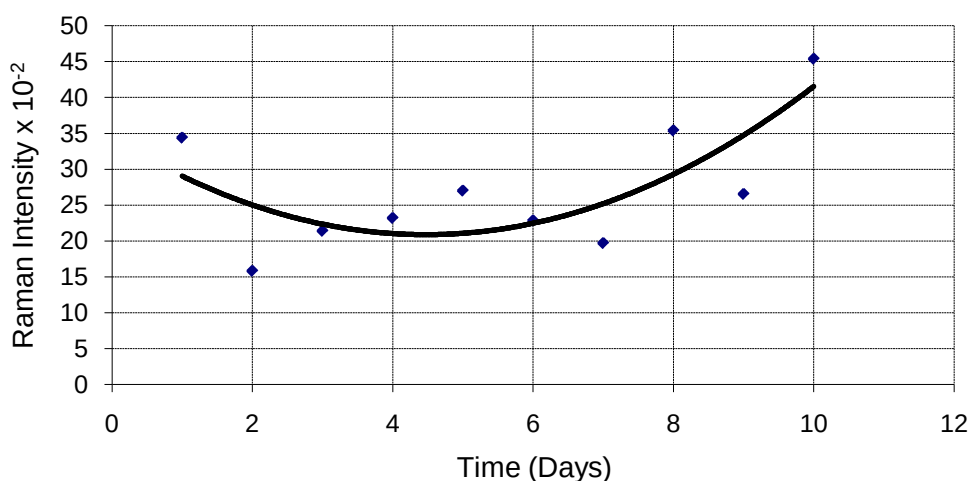


Figure 5.17 Variation of monosubstituted aromatic ring peaks (1001 cm^{-1})

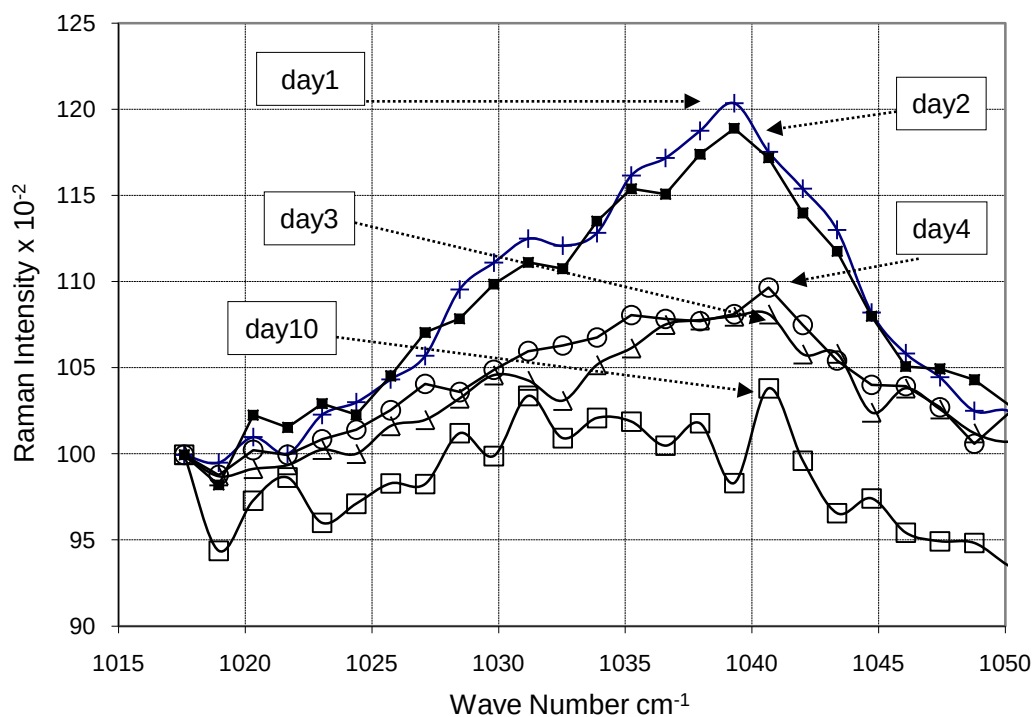


Figure 5.18 Decreasing of ortho substituted aromatic ring peaks (1040 cm⁻¹)

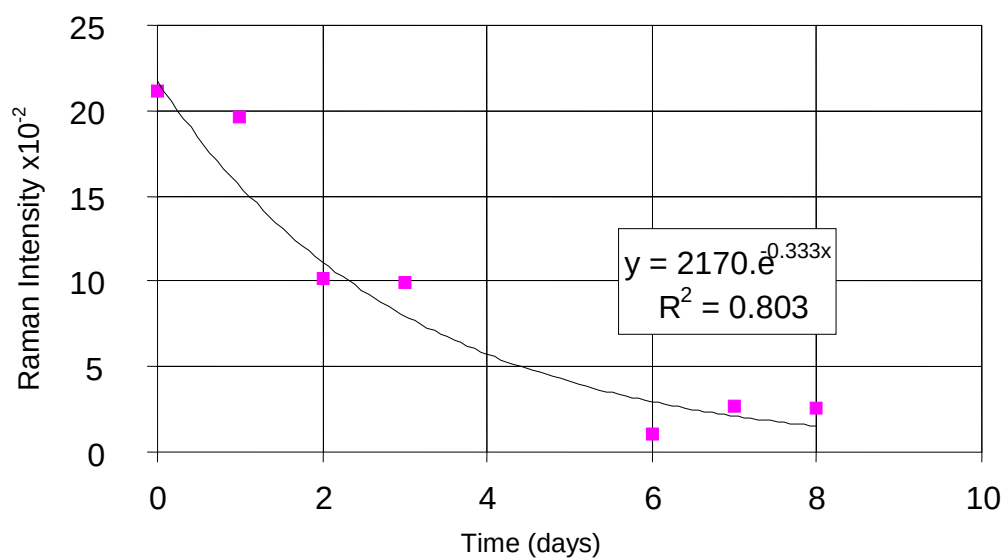


Figure 5.19 Decreasing peaks at 1040 cm⁻¹

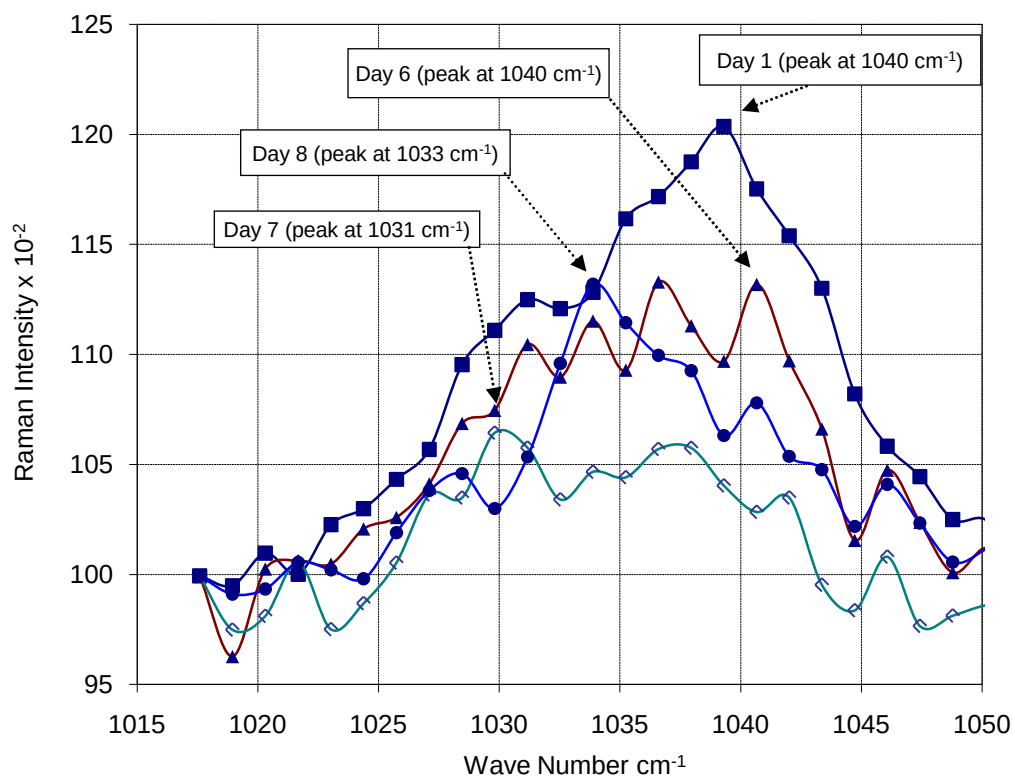


Figure 5.20 Peaks shifting from 1040 cm⁻¹ (days1, 6, 7) to 1032 cm⁻¹

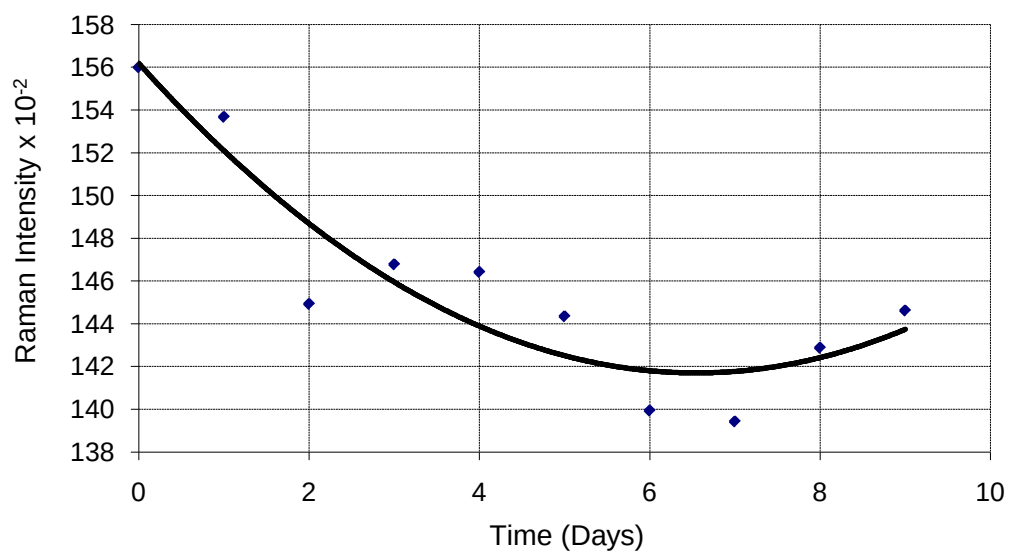


Figure 5.21 Variation of 1600 cm⁻¹ (Carbonyl) Raman peaks during degradation

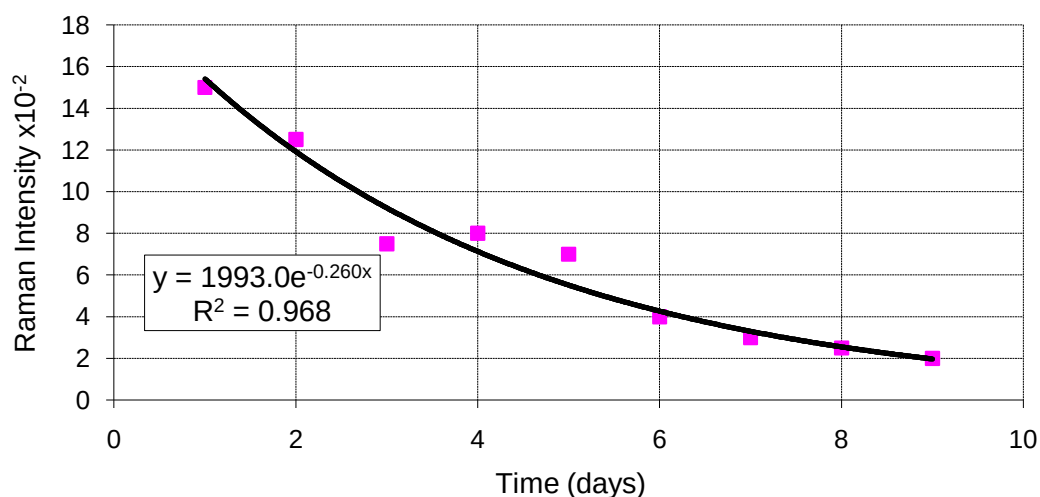


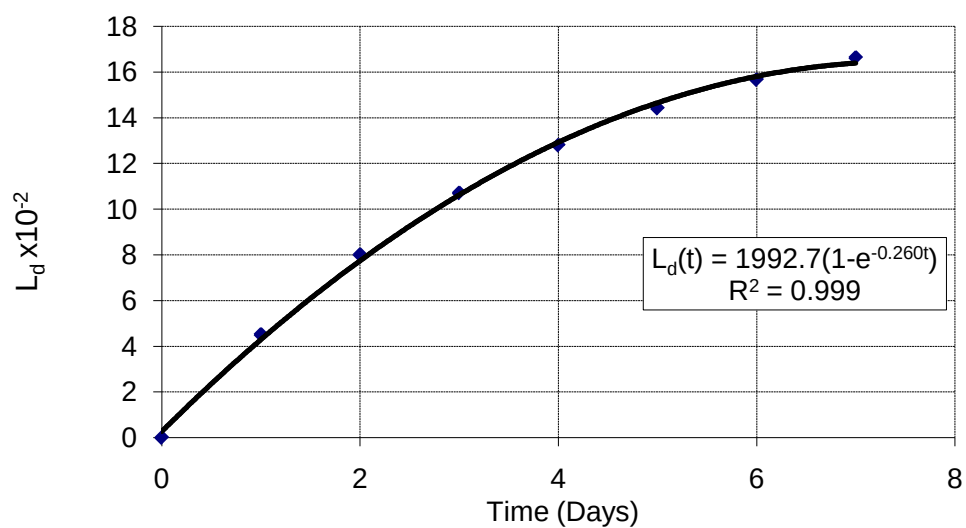
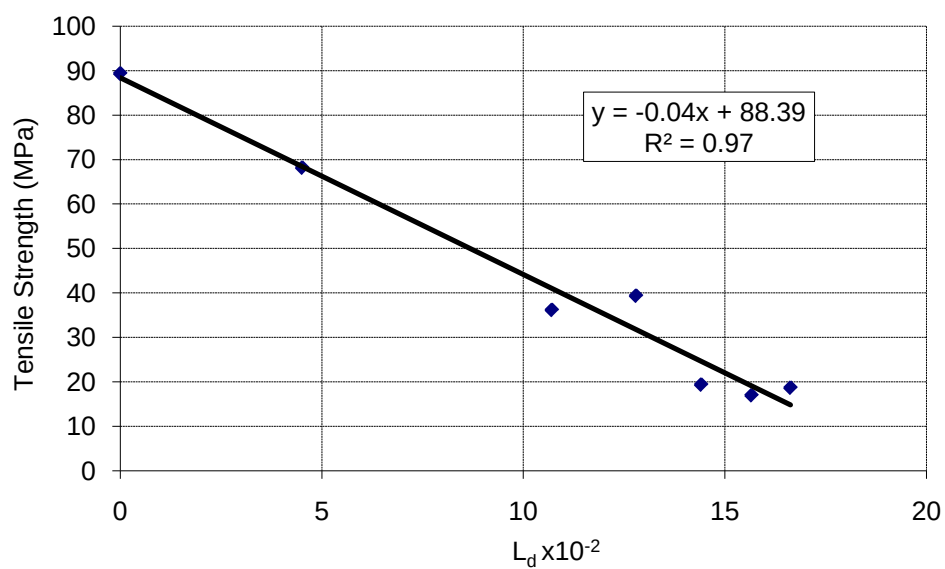
Figure 5.22 Decrease of ester peaks (1729 cm^{-1}) during degradation

Correlation between the model and experimental results

According to the model suggested in this analysis, in a constant environment the degradation of the material stiffness is linearly correlated to the variation in chemical link density and this variation rate is an exponential function of time. In order to experimentally assess the validity of this theoretical assertion, the degree of correlation between L_d and the material strength was numerically measured. The numerical regression of Raman peaks provided the degradation model (Figures 5.22) corresponding to the variation in chemical structure. Values of L_d were obtained from the Raman peaks of ester groups. The index L_d corresponds to the degree of degradation. As Raman peaks decreases, the degradation increases. Thus, the variation rate of L_d is taken by the opposite of variation rate of Raman peaks. The degradation model corresponding to L_d was subsequently determined by integration of L_d variation rate (see Appendix D), and represented in figure 5.23. The material strength was taken by the tensile strength (Table 5.4 and Figure 5.12). The correlation coefficient R^2 is 0.97 (Figure 5.24) indicating very good correlation between the model and experimental values.

Table 5.4: Calculated value of index L_d and experimental tensile strength

Days	0	1	3	4	5	6	7
Calculated L_d	0	451.5	800.6	1070.7	1279.6	1441.1	1566.1
Experimental Tensile Strength (MPa)	89	68	36	39	19	17	19

**Figure 5.23** Index of chemical links degradation deduced from ester groups reduction**Figure 5.24** Correlation between the model and experimental values

This good linear correlation also provides the experimental verification of equation (5.6) showing a linear correlation between the material stiffness and the degree of chemical links degradation.

Comparing calculated and experimental material lifetime based on tensile strength evolution

In order to perform the experimental comparison, the problem was set as follows: “what is the material lifetime if the minimal admissible value for its tensile strength is determined as a given percentage of the initial value?”

From the degradation model of chemical structure in Figure 5.22, the theoretical degradation rate for the material strength was determined by derivation (see Appendix D):

$$\frac{dL_d}{dt} = 511.9e^{-0.260t} \quad (5.44)$$

Based on equation (5.44), the lifetimes were predicted for a range of property retention values (see Appendix D). The predicted values are compared to experimental values determined from table 5.4. The comparison is presented in Figure 5.25.

Table 5.5: Predicted and experimental lifetime

Percentage reduction (%)	Tensile strength value (MPa)	Predicted Life-time (Days)		Experimental Life-time (Days)
		Calculated	Interpretation	
80	17.9	6.3	6 minimal	5 to 6
70	26.8	4.7	4.5 minimal	4 to 5
60	35.7	3.6	3.5 minimal	3
50	44.7	2.7	2.5 minimal	2
40	53.6	2.0	2 minimal	1 to 3
30	62.5	1.4	1 minimal	1
20	71.5	0.9	Less than 1	Less than 1

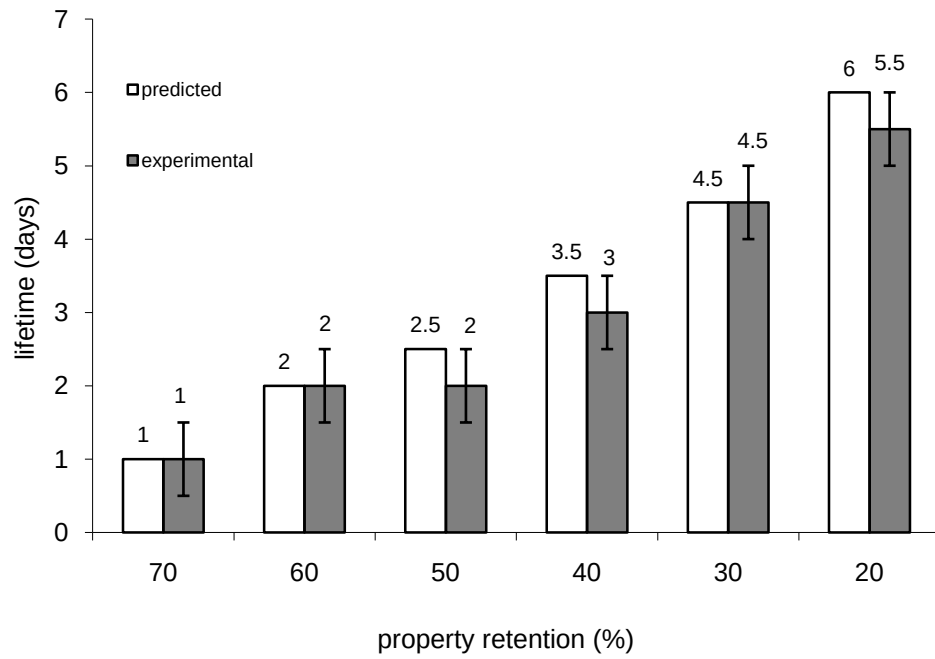


Figure 5.25 Predicted lifetimes compared to experimental lifetimes

Variation of shear strength under physical and chemical degradation

Test results are presented in Figure 5.26. The figure shows that the variation of shear strength resulting from the degradation follows an exponential trend.

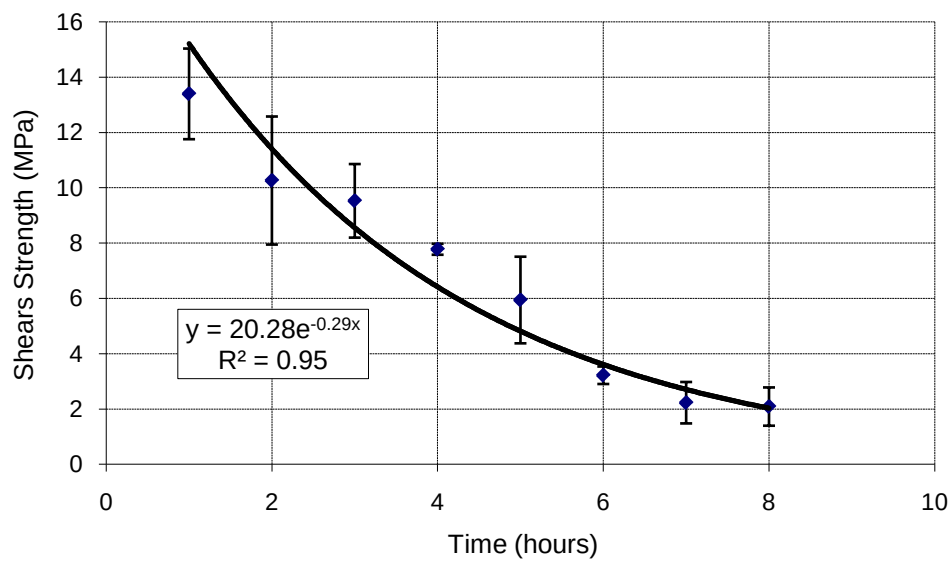


Figure 5.26 Shear strength variation of samples subjected to chemical degradation

Variation of storage modulus under physical and chemical degradation

Figure 5.27 presents the storage modulus variation for attacked samples at several temperatures below T_G . The variation follows an exponential trend.

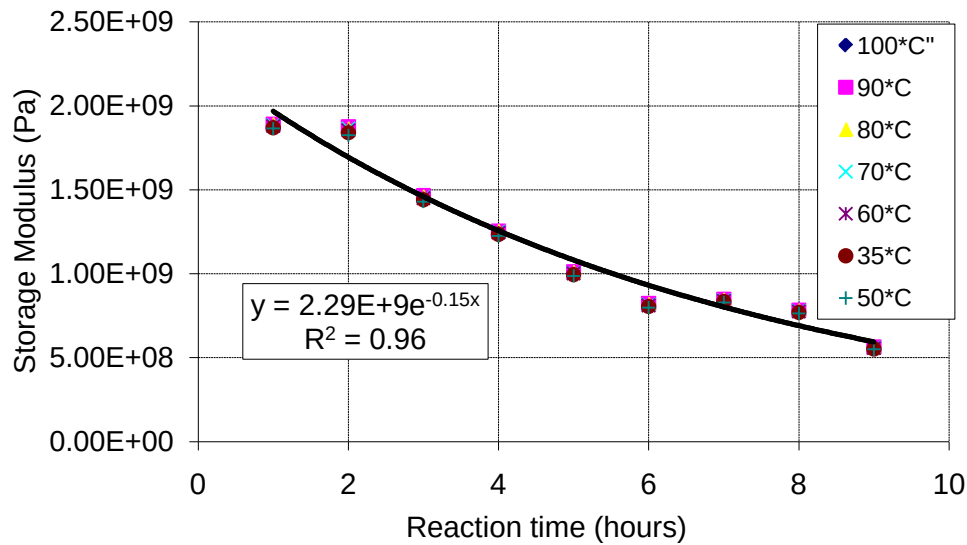


Figure 5.27 Variation of storage modulus during the course of degradation

5.11 Conclusion

Throughout the literature, the environmental degradation of FRP is described as a complex process. Modelling efforts are limited to partial models, most of the time empirical. No viable prediction method is yet available for the environmental degradation of the material mechanical strength. The analytical framework presented in this chapter relies on resolving the degradation process into only three components consisting of chemical degradation, physical degradation, and mechanical degradation. Based on material science theories, the analysis has demonstrated that, in a constant environment, the chemical and physical degradation of a polymeric matrix follows an exponential law. This results from the effect of the material rheology transformation on the diffusion process. The resulting mathematical model correlates the degradation rate directly to the material lifetime.

Experiments have been conducted using a range of measurement methods. These include Raman spectrometry for chemical structure changes, rheometry for storage modulus, and mechanical testing of tensile and shear strength evolution during degradation. All experiments confirm the validity of the suggested model. The degree of correlation between the model and the experimental process is very good.

The analysis also demonstrates that the chemical and physical degradation rate of a polymeric matrix is an ascending monotonic function of the environment. Consequently, the evaluation of environmental degradation in a laboratory can be conducted in a constant environment and laboratory test results can be directly translated to the real service environment. This is an important conclusion because many authors [1-3] have difficulty relating laboratory tests to actual service conditions.

Based on this mathematical model, a simple and practical prediction method has been suggested. The environmental degradation rate of a material in a real service environment can be determined in a laboratory based on tests conducted in a constant environment. This method requires monitoring only of the chemical structure change or any other material property linearly correlated to the chemical structure. For the environmental conditions to be used in a laboratory, the method requires only the availability of statistical information such as the control chart of environmental variables including moisture, temperature, chemical concentration and ultraviolet ray intensity. Experiments conducted in a laboratory show that predicted degradation of the tensile strength of polyester fibreglass composite, based on this prediction method, is in good agreement with experimentally measured degradation.

The theoretical analysis presented in this chapter assumes that the material undergoing the physical and chemical degradation is not subject to any kind of mechanical load. Results obtained in this chapter apply only to the case where mechanical stresses can be neglected. However, the suggested model provides a

useful tool for assessing the chemical and physical degradation factors in cases involving both mechanical stress effects and physical and chemical degradation. This will be dealt with in the next chapter.

6 COMPREHENSIVE MODELLING AND PREDICTION OF FRP ENVIRONMENTAL DEGRADATION

A comprehensive model of the environmental degradation of fibre reinforced plastics is presented. This model includes all the processes involved in the environmental degradation of these materials. The model is expressed as a dynamic constitutive equation resulting from the combination of the historical variation in chemical link density and cohesive forces and the stress history of the material. Prediction of long-term behaviour can be obtained from short-term tests based on the time-temperature correspondence and the Boltzmann superposition principle.

In the literature, it has been observed that the evolution of the material rheological state constitutes one of the major consequences of environmental degradation. Experimental attempts to use this effect to assess the environmental degradation of polymeric materials have also been reported [1, 90-91]. This analysis presents an analytical demonstration of the fact that the ultimate and comprehensive result of environmental degradation caused by any factor is the change in the material rheology. This effect is expressed through the dynamic constitutive equation.

Detailed modelling of the variation in chemical link density and cohesive forces has been presented in the previous chapter. The present chapter is concerned mainly with presenting a dynamic constitutive equation resulting from the combination of the chemical and physical degradation history with the stress degradation history.

6.1 The Constitutive Equation of Environmental Degradation in FRP

Due to resin viscoelasticity, stress effects are time dependant as the stiffness coefficient changes with time. The Boltzmann superposition principle [86, 92]

takes account of the material stress or strain history and expresses the material stiffness evolution as a dynamic constitutive equation. Let t' represent the instant when a strain $\varepsilon(t')$ is applied to the material. The stiffness coefficient at time t can be written as $C(t-t')$ representing its residual value after relaxation over a period equal to $t-t'$. The Boltzmann superposition principle is then written as:

$$\sigma(t) = \int_{-\infty}^t C(t-t') \frac{d\varepsilon(t')}{dt'} dt' \quad (6.1)$$

Now at the same time, chemical and physical degradation also modifies the material stiffness over time. Therefore, the stiffness coefficient is also affected by the chemical and physical degradation history that can be expressed as a factor $K_{env}(t)$ representing the accumulated effect of degradation up to time t . Thus the actual value of the stiffness coefficient at time t is $K_{env}(t)C(t-t')$. The Boltzmann superposition principle can therefore be modified as:

$$\sigma(t) = \int_{-\infty}^t K_{env}(t) C(t-t') \frac{d\varepsilon(t')}{dt'} dt' \quad (6.2)$$

The above equation expresses the evolution of the material stiffness resulting from stress effects combined with chemical and physical degradation. It provides the constitutive equation of the material under environmental degradation and shows that the ultimate and comprehensive result of environmental degradation caused by any factor, is the change in the material stiffness. This equation can, therefore, be used to measure the comprehensive environmental degradation effect caused by all environmental factors.

When the degradation function is known, the chemical and physical degradation history can be determined through the retention of specific material properties over time. So, if $E_d(t_0)$ is the index that represents the initial value of the material property and $\Delta E_d(t)$ represents the reduction in the material property at instant t , $K_{env}(t)$ is defined as:

$$K_{env}(t) = 1 - \frac{\Delta E_d(t)}{E_d(t_0)} \quad (6.3)$$

This means that $K_{env}(t)$ can be determined from equation (5.37) that represents the physical and chemical degradation function. Subsequently, if $K_{env}(t)$ can be calculated, then at any time, the stiffness of a viscoelastic material undergoing environmental degradation can also be calculated by multiplying by $K_{env}(t)$, its stiffness when not subjected to environmental degradation. This provides an analytical method to predict the environmental degradation of the stiffness coefficient.

However, it has been shown that stresses affect chemical reactions by modifying the activation energy of the reaction as well as that of diffusion [1, 65-67]. The exact value of $K_{env}(t)$ would thus be calculated by introducing a factor accounting for stress into the equation used to determine the kinetic constants as is done in the equation of Zurkov [1, 65]. The latter equation has been successfully used in quite a number of works where there has been a need to evaluate the effects of stresses on chemical reactions [1, 65]. Such calculations are not pursued in this analysis. An alternative method based on experimental measurements is suggested in the next paragraph.

It is apparent from equations (6.1) and (6.2) that stress relaxation is amplified due to environmental degradation and this amplification is a determined function of the degradation time and results from thermally activated processes, namely modification of the chemical link density and modification of the cohesive forces. These observations are sufficient to provide a method to measure and to predict exactly the environmental degradation. They lead to logical consequences that:

- The environmental degradation can be measured through stress relaxation or creep.
- The amplification of stress relaxation by the environmental degradation is thermally activated and obeys, therefore, the time temperature superposition principle.

6.2 Determination of the Laboratory Test Conditions

The above theoretical result show that, the prediction of long-term environmental degradation of FRP matrix can be done by measuring long-term stress relaxation of the material as commonly done through dynamic mechanical analysis (DMA) or rheometry. In this case, the test conditions in the DMA equipment or rheometer must be set in such a way as to represent the degrading environment of interest.

As shown in Chapter four, the upper and lower statistical control limits of the real service conditions provide the constant environmental conditions to be used in laboratory:

It has been shown that the stress relaxation under environmental factors is caused by the physical and chemical degradation as well as the viscoelasticity of the material. Given that the physical and chemical degradation is a monotonic increasing function of environmental factors (subsection 5.9.2), and that the viscoelastic relaxation is also a monotonic increasing function of the temperature, it follows that the stress relaxation during environmental degradation is also a monotonic increasing function of environment factors. Experimental results of Figures 6.5 and 6.9 provide also an illustration of the above. Therefore, the upper and lower control limits of the long-term relaxation can be determined in laboratory from the constant conditions of the control limits of the environment control chart. Alternatively the average long-term relaxation can be determined from the average of the environment control chart.

However, care must be taken to compensate the fatigue effect caused by temperature and humidity cycles as shown in Chapter four.

From results of section 6.1, it follows also that, accelerated test conditions can be determined based on the time temperature shift principle.

6.3 Experimental Method

Two series of stress relaxation tests were conducted in a laboratory. In the first experiment, the material was subjected to mechanical stress only. The second experiment combines the application of stresses, the degradation of chemical links by the sodium hydroxide, and the deterioration of cohesive forces by moisture and temperature. The materials used and the test conditions are presented in Tables 6.1 and 6.2.

Table 6.1: Materials

LAMINATE			RESIN FORMULATION	
Composition		Resin/fibre/resin	Resin	Orthophthalic polyester NCS 901 PA
Glass fibre		WR 27.4 g / m ²	Resin (phr)	100
V _f (%)	AVG	2.7	Catalyst-ButanoxM50 (phr)	2
	StD	0.2	Curing cycle	24h/ 25°C, 3h/ 80°C
Thickness (mm)		1.0 ± 0.1		
Void (visual)		No voids		

Table 6.2: Test conditions

Temperatures	50° C, 60° C, 70° C, 80° C
Initial tensile stress	11.4 ± 0.2 MPa
Humidity	100 % (sample entirely wet)
Chemical reagent	5 % sodium hydroxide

6.3.1 Relaxation test procedure

A device was designed to be used on an ordinary tensile machine as shown in Figure 6.1. Samples were wet in a solution of sodium hydroxide and subjected to a tensile stress as follows:

1. The test device was mounted in the weathering chamber of a tensile machine and preheated to the test temperature.

2. The sodium hydroxide solution was also preheated to the test temperature separately.
3. A dog bone laminate sample was mounted in the test device. The preconditioned sodium hydroxide solution was then poured into the device so that it entirely wet the laminate sample. The weathering chamber was then closed and the sample was left to condition for 30 minutes.
4. The data logger was started and the sample was tensioned to an initial stress of 11.4 ± 0.2 MPa. This value was selected to ensure that the resulting strains are in the linear viscoelastic region.
5. The sample was left to relax until the relaxation curve became fairly flat.

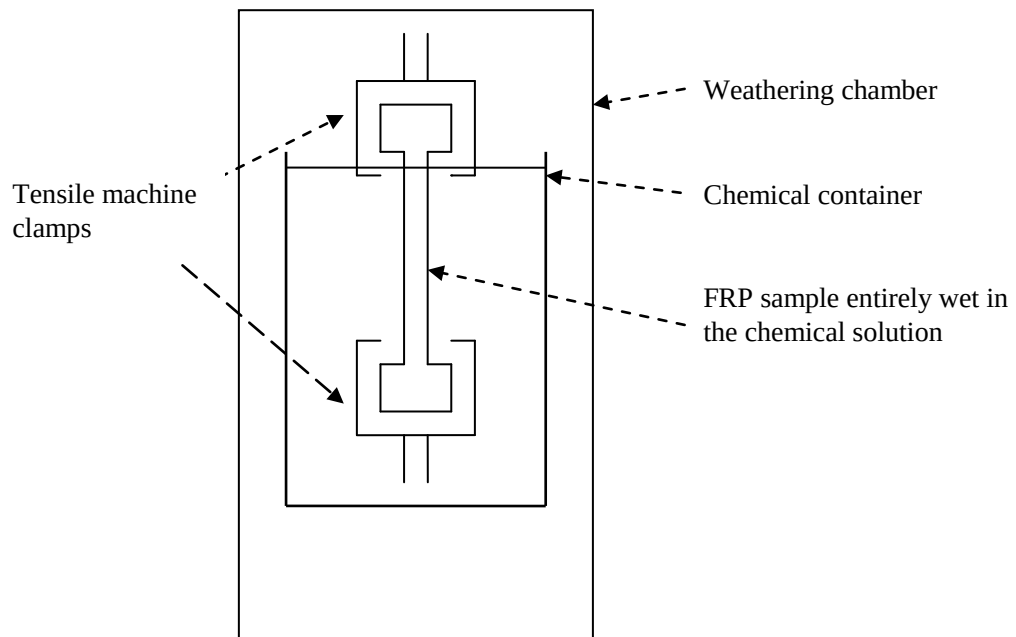


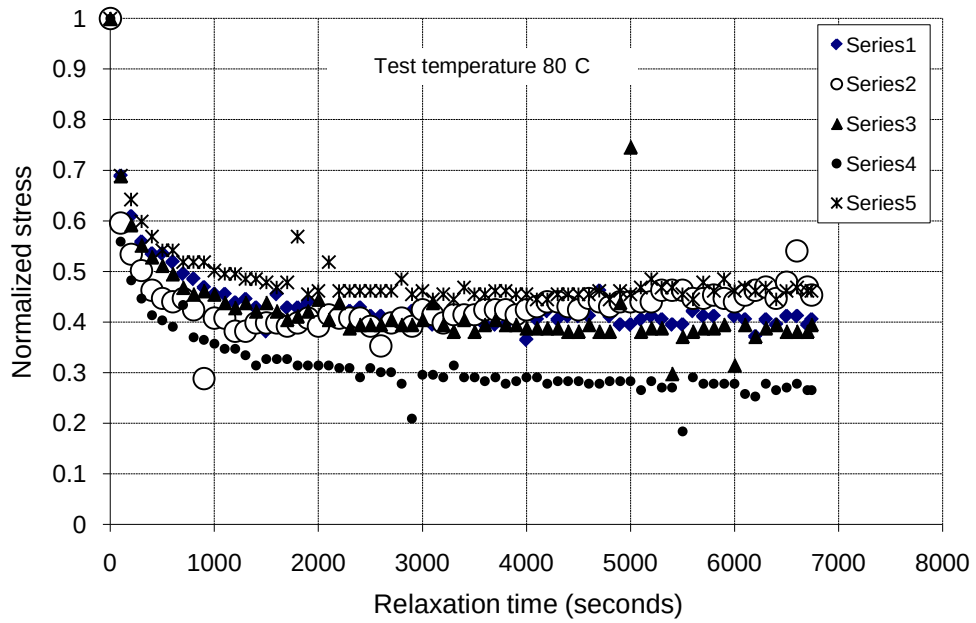
Figure 6.1 Testing apparatus for stress relaxation

6.3.2 Results and discussion

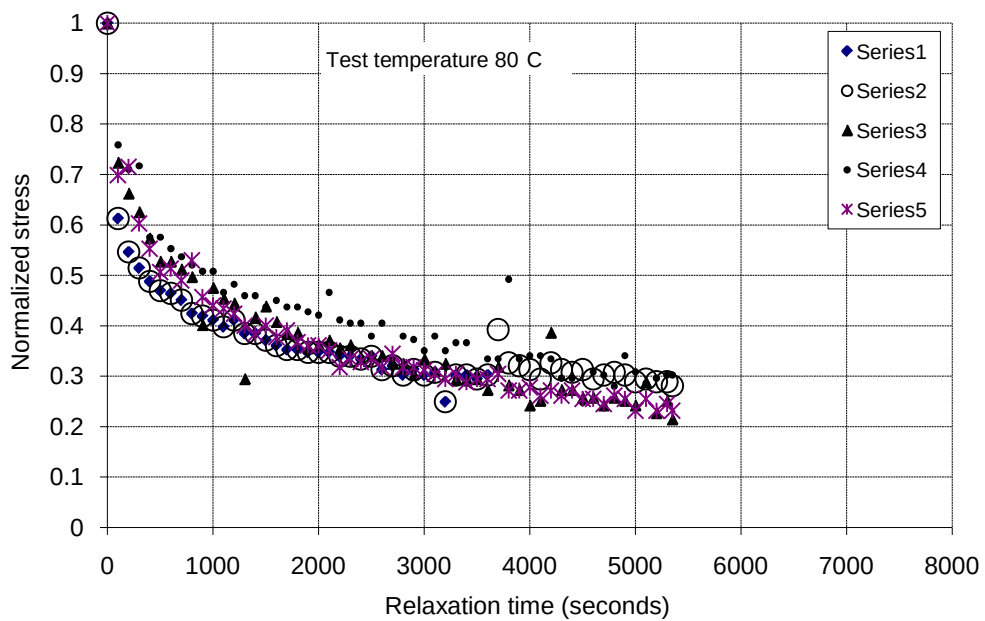
Amplification factor $K_{env}(t)$

Figure 6.2a presents the results of stress relaxation tests under mechanical stresses only while Figure 6.2b presents the results for the combined mechanical stress and

environmental degradation.



a)



b)

Figure 6.2 Relaxation curves. a) under mechanical stress only, b) under mechanical stress and chemical and physical degradation

A comparison of average curves from each of the two relaxations is presented in Figure 6.3. It is apparent that the humid environment slows down the rate of relaxation during the first 1000 seconds. This behaviour is typical of more than ten tests conducted in identical conditions. At longer time scales, however, the comparison shows that the relaxation is amplified by the environmental degradation.

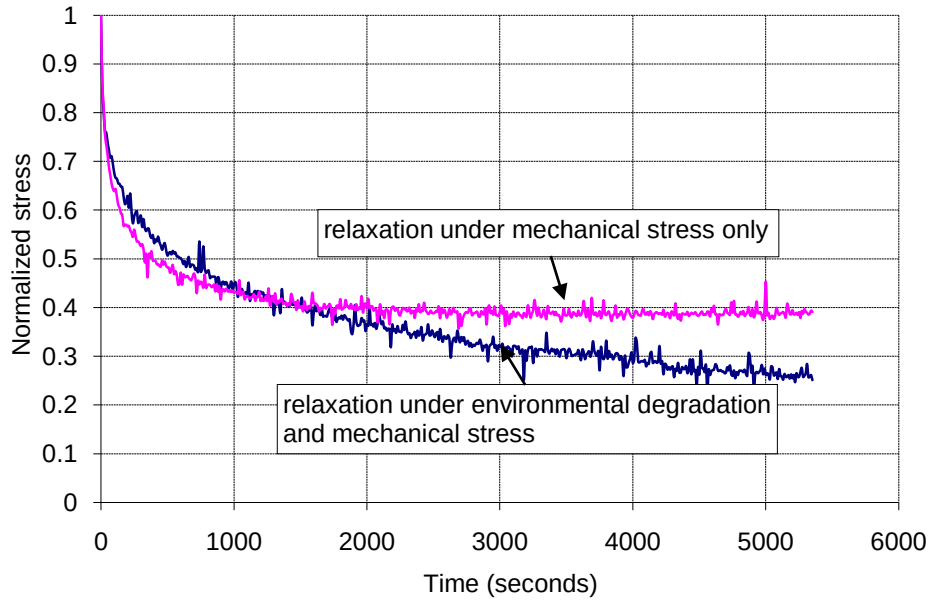


Figure 6.3 Amplification of the relaxation due to environmental degradation

Figure 6.4 presents the inverse of the environmental degradation factor $K_{env}(t)$ which was calculated from the experimental data of Figure 6.3 by using the following expression:

$$\frac{\sigma_{env}(t)}{\sigma(t)} = K_{env}(t) \quad (6.4)$$

The factor $K_{env}(t)$ provides a measure of the increasing effect of environmental degradation including stress effects on the chemical and physical degradation. It is shown that $K_{env}(t)$ is a function of the environmental degradation time. It can be experimentally determined from short-term test and subsequently used to calculate long-term stiffness coefficient.

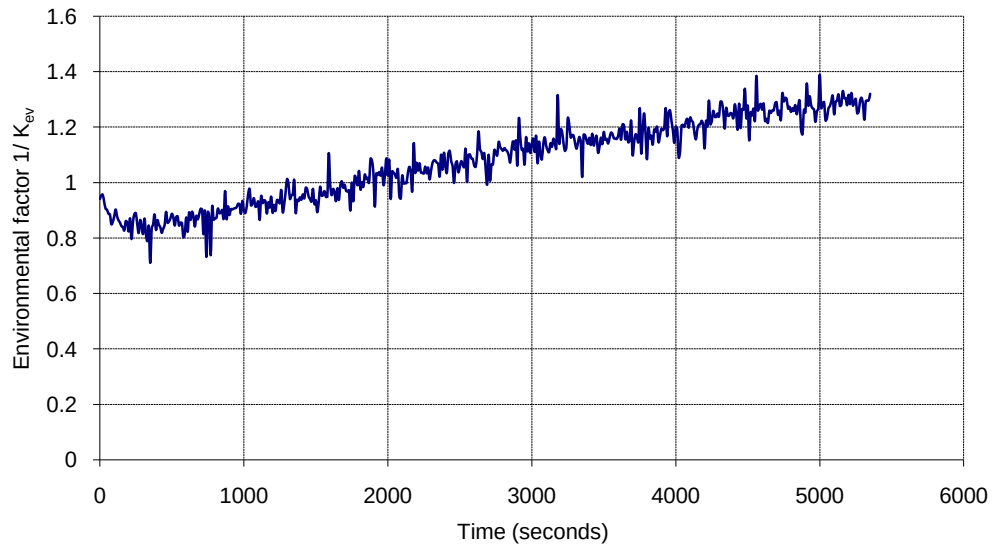


Figure 6.4 Accumulated environmental degradation measured as $1 / K_{env}$

Time Temperature correspondence

The stress relaxation under environmental degradation was also measured at various temperatures. Figure 6.5 shows the relaxation amplitude expressed as a percentage reduction of the initial stress value for 50° C, 60° C, 70° C and 80° C.

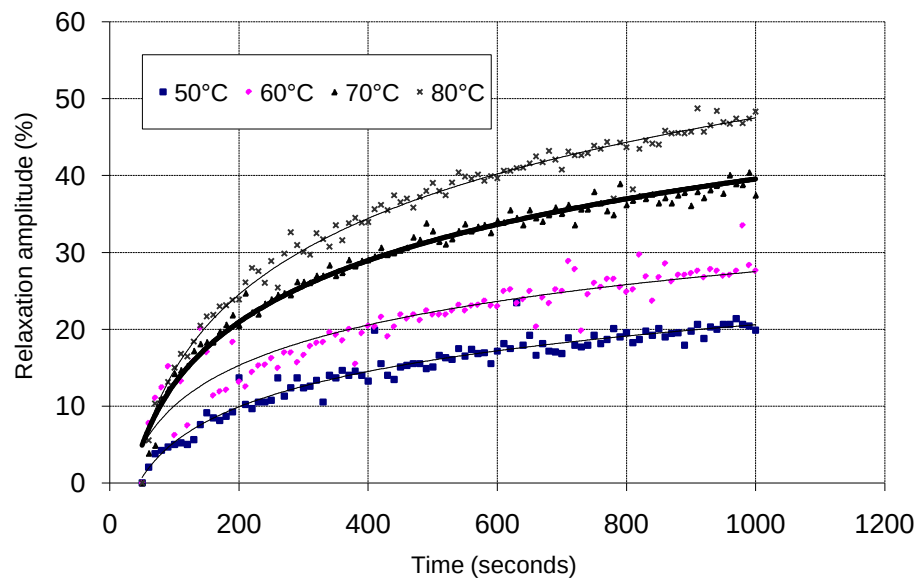


Figure 6.5 Relaxation under chemical and physical degradation at various temperatures

As expected, the elevated temperature environment causes substantial stress relaxation. The role of temperature in stress relaxation (Figure 6.5) is not surprising since the environmental degradation results from the modification of chemical link density and cohesive forces which are thermally activated processes. Therefore, prediction of long-term environmental degradation can be obtained through the time temperature shift principle based on Arrhenius law. The experimental data of Figure 6.5 are now used to make a prediction of long-term relaxation based on the time temperature shift principle. The method uses a shift factor α_{T_i} to determine long-term relaxation time [86, 92]. The time t_{T_i} required to achieve a given stress relaxation at temperature T_i is determined from the time $t_{T_{ref}}$ required to achieve the same stress relaxation measured at a reference temperature T_{ref} . This requires the measurements made at the reference temperature to be shifted by $\ln \alpha_{T_i}$ on the time logarithm scale. The shift factor is expressed as [86]:

$$\alpha_{T_i} = \frac{t_{T_i}}{t_{T_{ref}}} \quad (6.5)$$

Or alternatively as:

$$\ln(t_{T_i}) = \ln \alpha_{T_i} + \ln(t_{T_{ref}}) \quad (6.6)$$

In this experiment, the reference temperature is fixed at 80°C and the shift factor α_{T_i} is calculated from the Arrhenius equation as follows [86]:

$$\ln \alpha_{T_i} = \frac{W}{R} \left(\frac{1}{T_i} - \frac{1}{T_{ref}} \right) \quad (6.7)$$

where W is the activation energy of the process.

Since $\alpha_{T_i} = \frac{t_{T_i}}{t_{T_{ref}}}$, the factor $\frac{W}{R}$ can be determined by plotting $\ln \frac{t_{T_i}}{t_{T_{ref}}}$ against $\frac{1}{T_i}$ for a fixed value of the relaxation amplitude. Equation (6.7) indicates that the plot is a straight line and that $\frac{W}{R}$ corresponds to the slope of this line. This procedure

is applied to the curves fitted to the experimental data of Figure 6.5 for several values of the relaxation amplitude. The straight lines resulting from such plots are usually parallel since the magnitude of the activation energy is normally constant. In the present study, the measured slopes are instead an increasing linear function of the relaxation amplitude (Figures 6.6 and 6.7), which implies that the activation energy also is an increasing linear function of the relaxation amplitude. This results from the interaction between the mechanical stress and the chemical reaction. The above experimental observation is not surprising since it is known that tensile stress reduces the activation energy of chemical reactions [1, 41, 65]. Due to the relaxation, stress decreases over the course of the degradation and so its effect on the activation energy reduces also. As a consequence, the activation energy increases with increasing degradation.

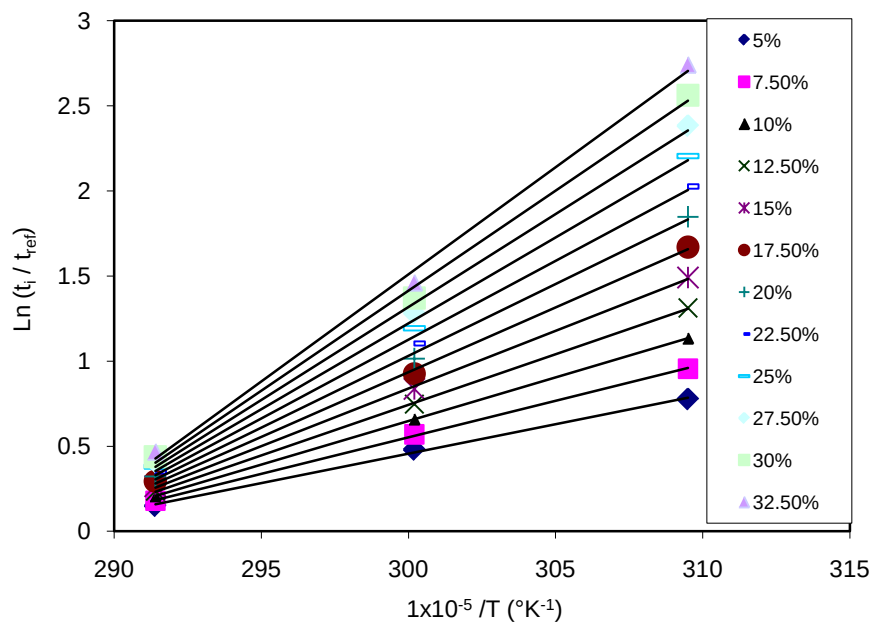


Figure 6.6 Experimental determination of the activation energy for different relaxation amplitudes

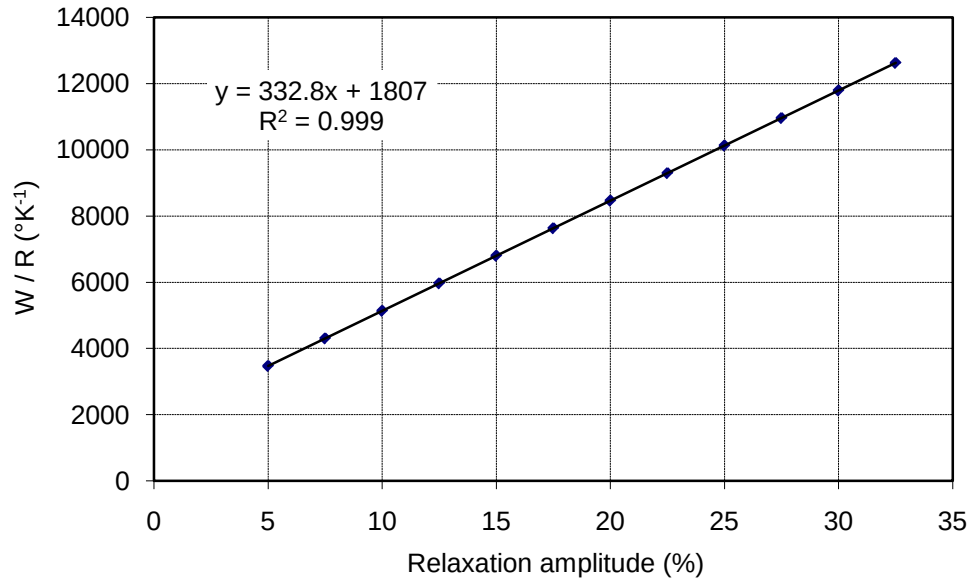


Figure 6.7 Activation energy as a function of the relaxation amplitude

Resulting from the above, an alternative method to determine the shift factor is suggested. Since the activation energy is not constant but is a linear function of the relaxation amplitude, equation (6.6) requires that the shift factor is an exponential function of the relaxation amplitude and can be directly determined from experimental data by plotting $\frac{t_{Ti}}{t_{Tref}}$ against relaxation amplitude (Figure 6.8).

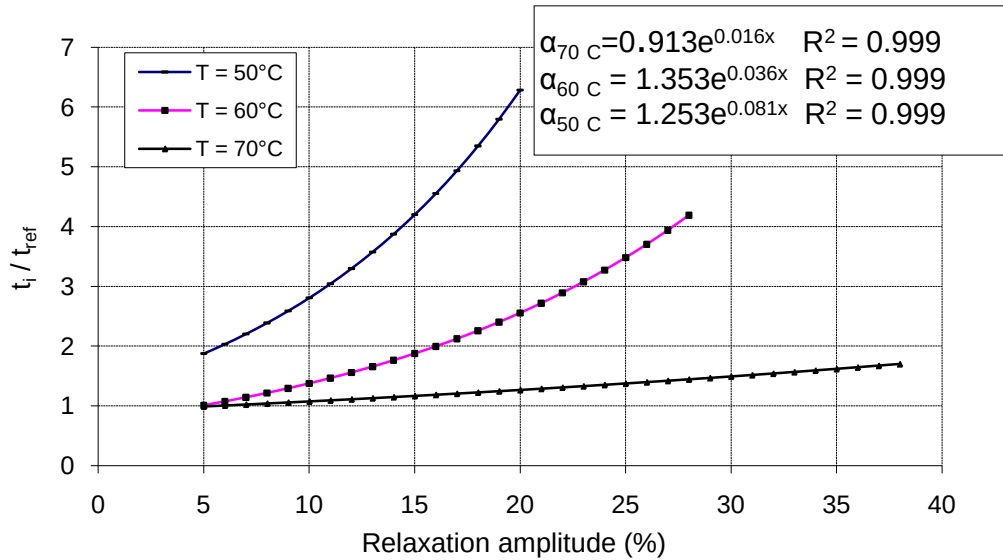


Figure 6.8 Experimental determination of the shift factor as a function of the relaxation amplitude

The above results establish that the process follows the Arrhenius law but, due to the activation energy not being constant, the shift factor depends on the relaxation amplitude and consequently can be theoretically calculated as below.

From the results of Figure 6.8, the shift factor can be expressed as a function of the relaxation amplitude, represented by x :

$$\alpha_{T_i} = k_5 e^{k_6 x} \quad (6.8)$$

The above equation can be rewritten as:

$$\ln \alpha_{T_i} = \ln k_5 + k_6 x \quad (6.9)$$

Furthermore, since the activation energy is a linear function of the relaxation amplitude, equation (6.7) can be written as:

$$\ln \alpha_{T_i} = \frac{W_0 + W_1 x}{R} \left(\frac{1}{T_i} - \frac{1}{T_{ref}} \right) \quad (6.10)$$

or

$$\ln \alpha_{T_i} = \frac{W_0}{R} \left(\frac{1}{T_i} - \frac{1}{T_{ref}} \right) + \frac{W_1 x}{R} \left(\frac{1}{T_i} - \frac{1}{T_{ref}} \right) \quad (6.11)$$

Comparing equations (6.9) and (6.11), it becomes apparent that:

$$\ln k_5 = \frac{W_0}{R} \left(\frac{1}{T_i} - \frac{1}{T_{ref}} \right) \quad (6.12)$$

and

$$k_6 = \frac{W_1}{R} \left(\frac{1}{T_i} - \frac{1}{T_{ref}} \right) \quad (6.13)$$

In the above, W_0 is the value of the activation energy prior to relaxation. It represents the maximum effect of the applied stress on the chemical reaction. W_1 provides a measure of the rate at which the stress effect on the chemical reaction decreases.

The shift factor is thus determined from Figure 6.8. A shift as per equation (6.6) is then applied to the measurements taken at 80°C. Long-term results up to 6000 seconds are predicted for 50°C, 60°C, and 70°C. The relaxation was also measured experimentally up to 6000 seconds at the three temperatures (Figure 6.9). Experimental relaxation times obtained from Figure 6.9, compare excellently to the predicted results, as shown in Figure 6.10.

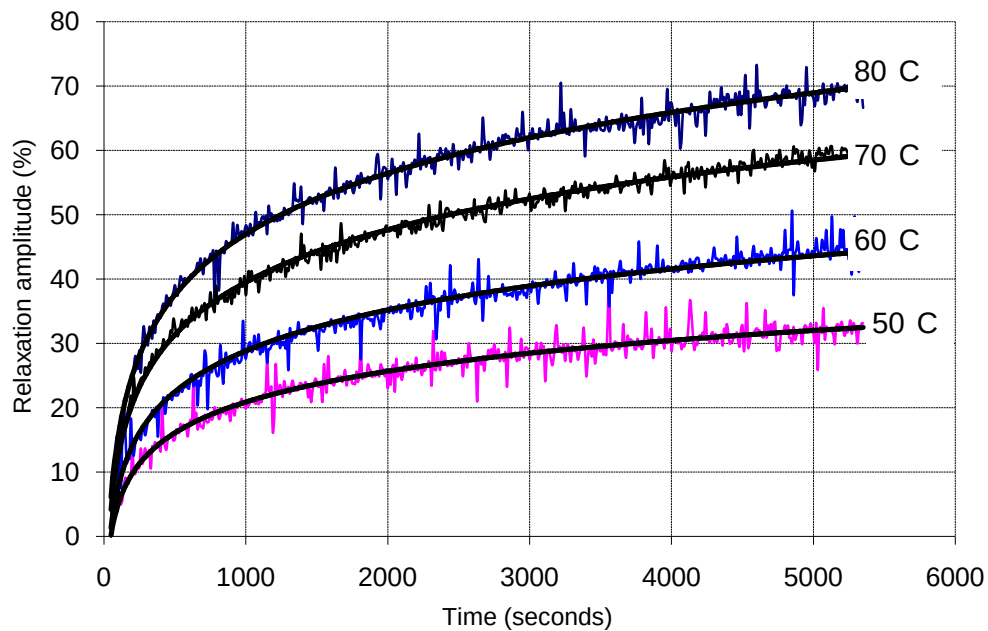


Figure 6.9 Experimental measurement of the relaxation under chemical and physical degradation

It is worth mentioning that, in the above experiment, the limit of relaxation goes up to 60 % (at 70°C) and the temperature up to 80°C. This covers the range of relaxation and temperatures experienced in the real service environment (storage tank and pipe).

It can therefore be concluded that long-term environmental degradation can be predicted using the time-temperature shift principle. The demonstrated method of applying this shift takes account of the variation of the activation energy resulting from the interaction between the stress and the chemical reaction over the course of the degradation.

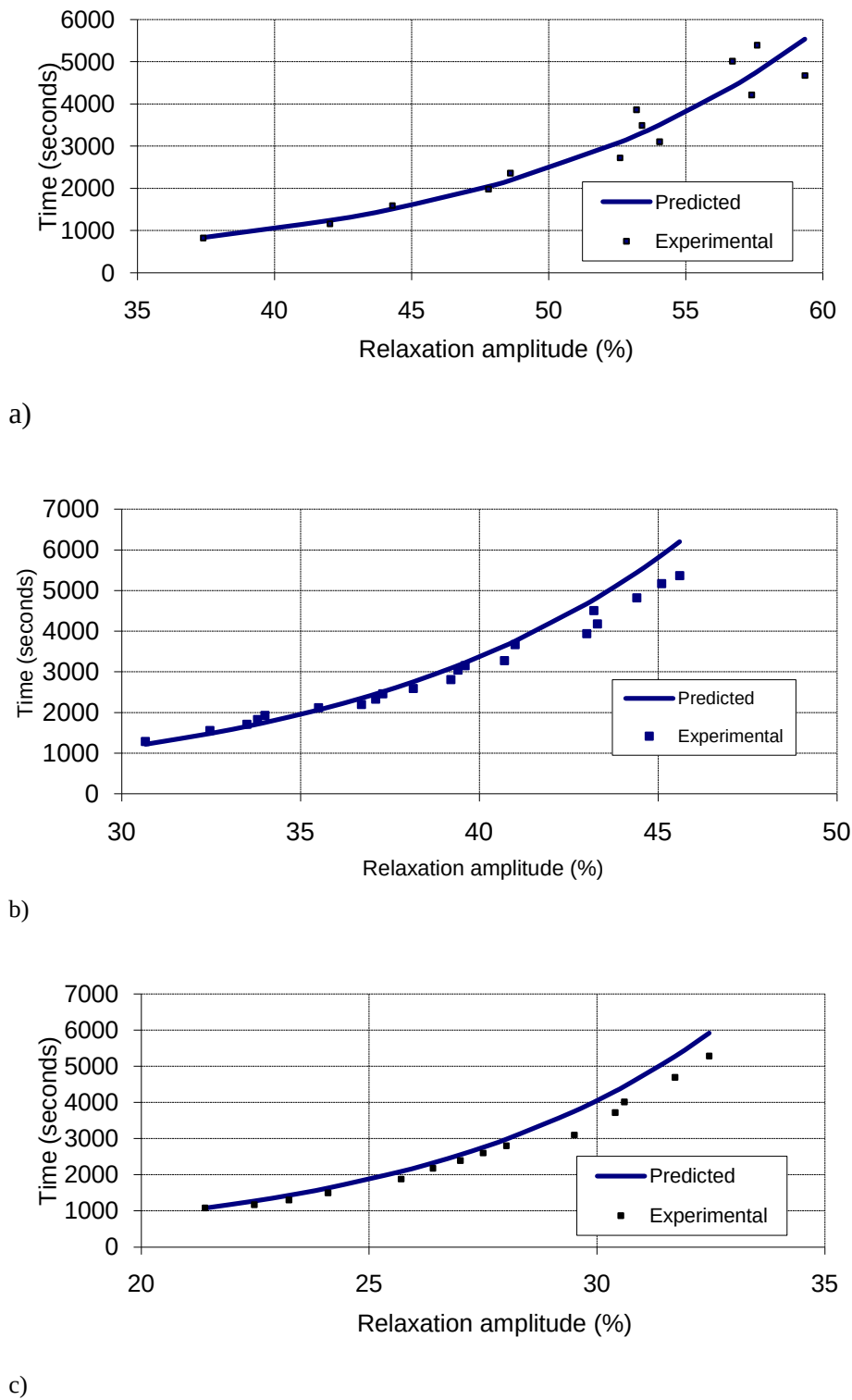


Figure 6.10 Experimental relaxation times compared to the relaxation times predicted from times measured at 80°C. a) T= 70°C, B) T= 60°C, c) T = 50°C

Relaxation measurements taken at one temperature can consequently be used to predict the degradation rate at any other temperature once short-term measurements are taken at both the reference temperature and the temperature of interest.

6.4 Conclusion

The complexity of the environmental degradation of FRP is resolved into only three components including chemical degradation, physical degradation, and modification of the stress state. The common effect of these three sub processes is to change the material rheology over time. This has permitted the development of a qualitative model based on the evolution of the material stiffness over time. This model is expressed as a dynamic constitutive equation arising from the combination of the historical variation in chemical link density and cohesive forces with the stress or strain history of the material. This equation shows that the environmental degradation causes amplification of stress relaxation and the amplification factor is a determined function of the degradation time. Therefore, the amplification factor provides a method to predict comprehensively FRP environmental degradation. It can be determined experimentally from accelerated stress relaxation test. The dynamic constitutive equation indicates also that the process is thermally activated and prediction of long-term degradation can be obtained from time-temperature superposition principle as experimentally demonstrated. Application of this principle, in the case of environmental degradation, takes account of the variation of the activation energy resulting from the interaction between the stress and the chemical reaction over the course of the degradation.

7 FINAL CONCLUSION

Efficient use of FRP materials requires reliable method to quantify, predict, and control the long-term environmental effects on the material, hence the need for modelling the degradation process. Throughout the literature, it was shown that modelling and prediction efforts have been hindered by the complexity of the process. Most of the published works are limited to characterization of effects and mechanism or partial models, most of the time empirical. No viable prediction method was yet available for the environmental degradation of the material mechanical strength. The literature showed that major unresolved issues were firstly, the difficulty to take into accounts all the processes involved and their interactions in a comprehensive model and secondly, the uncertainty related to the translation of laboratory tests conditions to the real service environment conditions [1 - 3].

This analysis has suggested a theoretical approach resolving the complexity of the degradation process into only three components including a chemical degradation, a physical degradation, and an alteration of the stress state. Methods to manage the variability of the real service environment were also introduced. The main outcomes are described in the next three subsections.

7.1 Determination of the Long-term Degradation as an Average Value with Upper and Lower Limits

This analysis has demonstrated that the average of the degradation rate as well as its upper and lower limits can be determined in laboratory in a constant environment. This was shown as below.

Based on material science theories, the analysis has demonstrated that, in a constant environment, the chemical and physical degradation of a polymeric

matrix follows an exponential law. This results from interactions between the transformation of material rheology and the diffusion process. The transformation of the material rheology results from changes in the internal structure of the material caused by temperature, moisture, chemical attack, or irradiation by UV rays.

It was shown that the material rheology is mathematically related to the chemical link density and environmental factors including moisture, temperature, and concentration of the chemical in the material. The material rheology is proportional to the chemical link density, inversely proportional to a power of the diffused moisture, and proportional to a power of the material temperature.

Then, the material rheology was related to the diffusion coefficient via the Stokes-Einstein equation [84, 85]. This has permitted effects of the change in material rheology caused by environmental factors to be introduced in the diffusion coefficient equation besides the temperature effects on the activation energy defined by the Arrhenius law.

Subsequently, the material rheology was related to the chemical degradation through the law of chemical rates and Fick's law.

All the above has led to the integration of the chemical and physical degradation into a mathematical relation too complex to solve, due to the variability of environmental factors.

To be able to manage the variability of the environment in the modelling process, a method to transform a variable environment into a constant environment was suggested. It was shown that environmental condition history could always be modelled as a sequence of constant environmental states.

Therefore, the complex mathematical relation of the chemical and physical degradation was applied in a constant environment. The resulting mathematical

model is a simple exponential equation that relates the degradation rate directly to the material lifetime.

Experiments have been conducted using variable measurement methods. These include Raman spectrometry for chemical structure changes, rheometry for storage modulus, and mechanical testing of tensile and shear strength evolution in the course of degradation. All experiments confirm the suggested model. The degree of correlation between the model and the experimental process is very good as shown by the coefficient of linear correlation being very close to one.

The analysis has also demonstrated that the chemical and physical degradation rate of a polymeric matrix is an ascending monotonic function of the environment. This has provided the basis for the determination of laboratory test condition. Since the degradation rate is a determined function of the service environment, it was concluded that the statistical control limits of the degradation correspond to degradations measured at the statistical control limits of the service environment. Thus, laboratory tests can be conducted in constant environments that express exactly the variability of the real service environment. This constitutes a solution to problems related to the translation of laboratory tests conditions to the real service environment conditions [1 - 3].

The use of a constant environment in laboratory also implies that, the determination of the physical and chemical degradation requires monitoring only of the chemical structure change or any other material property linearly correlated to the chemical structure.

The ultimate outcome from all the above is that the average degradation rate, the upper and lower limits of the degradation rate, hence the average long-term degradation and its limits can be determined in a laboratory in a constant environment, as exponential functions of the degradation time.

7.2 The Constitutive Equation of Environmental Degradation in FRP.

Following, the analysis has also shown that, the common effect of the three sub processes constituting the environmental degradation is to change the material rheology over time. This has permitted to develop a qualitative comprehensive model based on the evolution of the material stiffness over the time. This model is a dynamic constitutive equation arising from the combination of the historical variation in chemical link density and cohesive forces with the stress or strain history of the material. This equation shows that, the environmental degradation causes the amplification of the stress relaxation and that the process obeys the time temperature superposition principle. This has permitted to conclude that:

- The environmental degradation can comprehensively be quantified as stress relaxation amplitude.
- The prediction of long-term effects is possible using the time temperature superposition principle.

Experimental evidence of the above was provided. A polyester composite laminate was used and exposure mode corresponded to that of a storage tank or pipe.

The amplification function $K_{env}(t)$ was experimentally determined by mean of a stress relaxation test and was shown to be a determined function of the environmental degradation time.

Experimental data obtained up to 1000 seconds on the degradation time scale, were used to predict longer time scale degradation up to 6000 seconds. Agreement between predicted and experimental result was excellent showing that the time temperature shift principle can be used to accelerated prediction test of the environmental degradation of FRP. However, due to the interaction between stresses and chemical degradation, a modified method to determine the shift factor was introduced. The method requires the amplification factor to be directly

determined from short-term experimental data by plotting $\frac{t_{Ti}}{t_{Tref}}$ against relaxation amplitude.

Therefore, the average long-term degradation and its upper and lower limits can be comprehensively measured in a constant environment through a stress relaxation test in laboratory. The resulting short-term test method is as described in the next section.

7.3 Short-term Test Method

Resulting from all the above a short term test method is suggested as follows:

7.3.1 Determination of the laboratory test conditions

Laboratory tests are conducted in a constant environment determined by the upper and lower control limits of the environment control chart or its average.

Care must be taken to compensate the fatigue effect caused by temperature and humidity cycles. To this end, the material exposed to a constant environment must additionally and in the same time, be subjected to cyclic stresses equivalent to those caused by the temperature and humidity cycles. The amplitude of the cyclic stress in laboratory is also determined by the upper and lower control limits of the cyclic stress in the real service environment.

7.3.2 Prediction of long-term stiffness coefficient based on $K_{env}(t)$

Tests are to be conducted on specimen representing a barrier coat according the following steps:

- a. Short-term stress relaxation under mechanical stress only
- b. Short-term stress relaxation under physical and chemical degradation.

- c. From experimental results of stress relaxations, the amplification factor $K_{env}(t)$ is determined according to equation (6.4).
- d. Determination of the long-term value of the stiffness coefficient $C(t)$ by applying the time temperature shift principle.
- e. Determination of the long-term stiffness coefficient under environmental degradation by multiplying $C(t)$ by $K_{env}(t)$.

7.3.3 Prediction of relaxation times based on time temperature shift principle

The time temperature shift principle can be applied to determine long-term relaxation time as follow:

- a. Determination of the reference temperature.
- b. Short-term stress relaxation both at the reference temperature and the temperature of interest.
- c. Experimental determination of the shift functions by plotting $\frac{t_{Ti}}{t_{Tref}}$ against relaxation amplitude.
- d. Determination of relaxation time by multiplying the time measured at the reference temperature by the corresponding shift factor as per equation (6.5)

It should be noticed that, in cases involving liquid environment, the reference temperature is limited by the boiling point of the liquid and so acceleration of the predictive test is limited. Thus, for prediction to longer time scales, the amplification factor $K_{env}(t)$ offers better capability. The time temperature shift principle will only be helpful, accelerating the determination of the amplification factor.

7.4 Recommendations for Future Works

The implementation of the methods suggested in this analysis requires the availability of reliable method for environmental stresses determination. As mentioned in section 4.2, these stresses are of many kinds including hygrothermal stresses from humidity and temperature cycles, erosive stresses from friction with circulating liquid in pipes or tanks or friction with wind and dust, stresses from rainfall impact, and vibration stresses in the vicinity of industrial engines. As part of the real service environment, all these stresses need to be known and taken into account when determining the laboratory test conditions. Therefore, the design of methods to determine these stress constitute a compulsory next step in this analysis.

Theoretical principles demonstrated in this analysis lay also useful basis for the design of practical instruments for experimental evaluation of FRP environmental degradation. The need for practical instruments to allow for rheological test in a multifactor environment has been demonstrated. A typical basic idea for the design of instruments to be used for the test of FRP environmental degradation is that represented by the device used in this research (Figure 6.1). This offers further opportunity for research in the field of environmental degradation.

The contribution of the present analysis is mostly to demonstrate theoretical principles that will provide the basis for the development of useful analytical techniques for the measurement of environmental effects on FRP. The development of the mathematical model was mainly based on a theoretical demonstration. However, experimental evidences provided further support to theoretical conclusions. The resulting prediction method is a rigorous and logical consequence of the mathematical model.

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APPENDIX A

It is shown that equation (4.1) is a common expression of well-established laws that govern energy and mass transfer in materials. It corresponds respectively to the Newton's law for calorific flux, Fick's law for moisture or chemical solution flux and the definition of UV ray intensity. Equation (4.1) can be rewritten as

$$\frac{dW_{env}}{dt} = k_0 f_j(t) \quad (A.1)$$

- If W_{env} = heat energy, $f_j(t) = \Delta T$ the temperature difference and $k_0 = \frac{A_{ar} h}{L}$, where A_{ar} is the exchange surface area, L the material thickness, and h the heat conduction or heat convection coefficient (in which case $L=1$), then equation (A.1) corresponds to the Fourier law or the Newton's law for heat transfer.
- If W_{env} = photon energy from UV rays, and $k_0 = 1$, then equation (A.1) corresponds to the definition of the UV rays intensity and $f_j(t) = I_{UV}$.
- Equation (A.1) corresponds also to the first law of Fick for mass diffusion. It is understood that the diffusing mass conveys the mechanical or chemical energy that causes the physical degradation (hygroscopic expansion) or the chemical degradation. The conveyed energy is proportional to the diffusing mass or volume. The first law of Fick is expressed as

$$J = -D \frac{\partial C_x}{\partial x} \quad (A.2)$$

where J , D , and C_x are respectively the diffusivity, the coefficient of diffusion, and the concentration of the diffusing material at a distance x from the exposed surface. If k_{18} being the coefficient of proportionality between the diffusing mass

and the energy, A the diffusion area, then the diffusing energy through an elementary thickness dx is expressed from equation (A.2) as

$$\frac{\partial^2 W_{env}(x, t)}{k_{18} A \partial x \partial t} dx = -D \frac{\partial C_x}{\partial x} \quad (A.3)$$

The diffusing energy through a laminate of thickness L is then obtained by integration of equation (A.3) as

$$W_{env} = -k_{18} A_{ar} D \int_{t_1}^{t_2} \int_0^L \frac{\partial C_x}{\partial x} dt dx \quad (A.4)$$

Taking as reference the unexposed side of the laminate, the integration of equation (A.4) shows that the first law of Fick corresponds exactly to the equation (A.1) where $f_j(t) = C_0$

$$W_{env} = k_{18} A_{ar} D \int_{t_1}^{t_2} C_0 dt \quad (A.5)$$

APPENDIX B

DISCRETE INTEGRATION OF EQUATION (5.14)

Let the figure i1 represents a laminate. According to pipe or tank model the diffusion occurs in the direction perpendicular to the laminate. It is admitted that in the direction perpendicular to the diffusion, the material is homogeneous and therefore the diffusion coefficient is constant throughout a surface perpendicular to the diffusion direction.

A : total laminate area

Δs : unit area

Δx_i : unit thickness

C : chemical concentration

l : total thickness

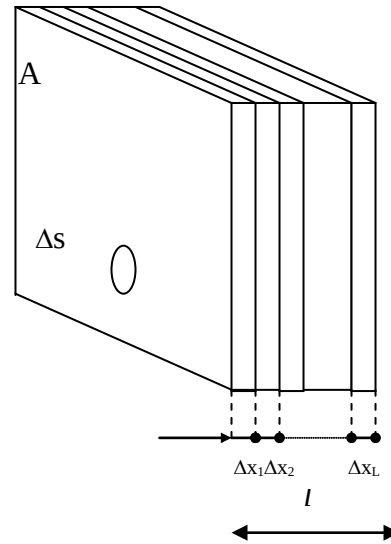


Figure B.1: Laminate portion

The flux of the diffused material through Δs is given as follows:

$$\Delta J_s = -D \frac{\Delta C}{\Delta x_i} \quad [B.1]$$

Assuming that the total area is made of n unit areas, the total flux through the area A will be as follows:

$$\sum_{s=1}^n \Delta J_s = \sum_{s=1}^n \left(-D \frac{\Delta C}{\Delta x_i} \right)_s \quad [B.2]$$

As the diffusion coefficient is constant throughout A the equation [B.2] may be written as follows:

$$\sum_{s=1}^n \Delta J_s = -nD \frac{\Delta C}{\Delta x_i} \quad [B.3]$$

The total flux through the laminate thickness l is given by the sum of the individual flux crossing each single surface layer as expressed below.

$$\sum_{i=0}^l \sum_{s=1}^n \Delta J_{s,i} = -nD \sum_{i=0}^l \frac{\Delta C}{\Delta x_i} \quad [B.4]$$

Now the sum of all the partial concentration gradients through the unit thickness Δx_i is equal to the total concentration gradient throughout the total thickness l

$$\sum_{i=0}^l \frac{\Delta C}{\Delta x_i} = \frac{C_l - C_0}{l} \quad [B.5]$$

The total diffused material content in the laminate, at any instant, is exactly given by the total flux crossing the laminate at this instant. And this flux is given by the equation [B.4]. Then taking into account equation [B.5]

$$C_{ch} = nD \frac{C_0 - C_l}{l} \quad [B.6]$$

In practice as $C_0 \gg C_l$, one can approximate the difference $C_0 - C_l$ to C_0 .

$$C_{ch} = nD \frac{C_0}{l} \quad [B.7]$$

APPENDIX C

SOLUTION OF THE DIFFERENTIAL EQUATION OF THE DEGRADATION RATE

The degradation rate equation was found to be as follow:

(See subsection 5.9.2)

$$\frac{dE_d}{dt} = \alpha_0 TC_0 E_d + \alpha \quad (C.1)$$

To simplify the notation, let be:

$E_d = y$, $\alpha_0 TC_0 = \text{constant} = u$, $\alpha = \text{constant} = v$, and $t = x$.

Then equation (C.1) may be noted as follows:

$$y' = uy + v \quad (C.2)$$

The derivation of equation (C.2) gives

$$y'' = uy' \quad (C.3)$$

Thereby,

$$\frac{y''}{y'} = u \quad (C.4)$$

Equation (C.4) can be integrated as follows:

$$\int_0^t \frac{y''}{y'} dx = \int_0^t u dx \quad (C.5)$$

$$[\ln y']_0^t = [ux]_0^t \quad (C.6)$$

$$\ln \frac{y'(t)}{y'(0)} = ut \quad (\text{C.7})$$

$$y'(t) = y'(0)e^{ut} \quad (\text{C.8})$$

From equation (C.2), we take:

$$y'(0) = uy(0) + v \quad (\text{C.9})$$

Now $y(0) = E_{d(t=0)} = 0$ as at the initial instant there is no degradation. Thus

$$y'(0) = v = \alpha \quad (\text{C.10})$$

Equation (C.8) then becomes:

$$\frac{dE_d}{dt} = \alpha e^{\alpha_0 TC_0 t} \quad (\text{C.11})$$

APPENDIX D

DETERMINATION OF THE MATERIAL LIFETIME BASED ON THE VARIATION IN CHEMICAL LINK DENSITY

The rate of variation in chemical link density was obtained from Raman peaks by numerical regression followed by derivation. Then, the variation rate of index L_d was determined by the opposite of the variation rate of Raman peaks:

$$\frac{dL_d(t)}{dt} = -\frac{dR_p(t)}{dt} \quad (D.1)$$

where $R_p(t)$ represents the Raman peak at time t . This has led to equation (5.44) (page 91).

Integrating equation (D.1):

$$\Delta L_d(t) = -\Delta R_p(t) \quad (D.2)$$

$$L_d(t) - L_d(0) = R_p(0) - R_p(t) \quad (D.3)$$

$L_d(0) = 0$ because there is no degradation at the initial time. The value of $R_p(0)$ is obtained from equation (5.44) and is equal to 1992.7. Then from equation (D.3), the degradation index of chemical link density is expressed as

$$L_d(t) = 1992.7(1 - e^{-0.260t}) \quad (D.4)$$

Values of L_d were calculated from equation (D.4) for various value of time and represented in Table 5.4

Resolving equation (D.4) with respect to time, the material lifetime for a maximum allowable degradation Δd is expressed as

$$t = \frac{-1}{0.260} \ln(1 - \Delta d) \quad (D.5)$$

In equation (D.5), the degradation Δd is expressed as a fraction of the initial value of the material tensile strength.

According to the suggested model, the degradation of L_d corresponds to the degradation of the mechanical strength. Equation (D.5) was then used to predict material lifetime for various degradation in tensile strength shown in Table 5.5.

For illustration, the maximum allowable reduction in tensile strength is given as 80 % of the initial value. Then, the material lifetime is determined as a maximum allowable exposure time as

$$t = \frac{-1}{0.260} \ln(1 - 0.8) = 6.2 \quad (\text{D.6})$$

Now, taking account of the scale used for the measurement of time, this value is reduced to 6 days.