ACCELERATED ENVIRONMENTAL DEGRADATION OF GRP COMPOSITE MATERIALS

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ABSTRACT

The use of fibre reinforced polymer composites and development of structural composites has expanded rapidly in the Southern African region over the past ten years. The long-term effect of placing these materials outdoors in the Southern African climate is unknown with exposure data for these materials being primarily European and North American based. This study intends to take a broad-based study to the problem of environmental degradation of advanced composite structures.

This work is intended to study different degradation mechanisms. Work performed includes: a study of literature on degradation and protective measures; identification of dominant degradation mechanisms; manufacture of specimens; accelerated environmental testing; and an assessment of the effect of the exposure on the chemical properties

The goal of this work is to produce information, which can be subsequently used to determine the rate of damage, methods of suitable protection and necessary maintenance intervals for polymer composite components. The approach was: to simulate outdoor exposure within a reduced period of time; to establish correlation of results with actual outdoor exposure; and to determine how the gel coats compare with other protective methods.

As part of the objectives of the study (i.e. to assess the durability of polymer matrix composites materials subjected to environmental exposure), an experimental study was carried out to establish the durability of specific gel coats against ultraviolet (UV) and moisture degradation. An investigation of the effectiveness of the various protective measures has begun with a review of selected gel coats available as a protective coating. Laminates with these gel coats have been set up for both accelerated and natural exposure tests.

3000, 2500, 2000, 1600, and 800 hours of accelerated UV exposure tests were performed on polyester GRP laminates with gel coats. No measurable strength loss occurred on protected laminates; there was significant increase in yellowness on un-protected laminates; all protected specimens showed a fair retention of gloss; fibre prominence occurred on unprotected laminates; and the glass transition of samples had dropped from the normal polyester glass transition temperature range.

Declaration

I declare that this thesis is my own unaided work except where due acknowledgement is made to others. This thesis is being submitted for the Degree of Master of Science to the University of KwaZulu-Natal, Durban, and has not been submitted previously for any other degree or examination.

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Overview

The approach in this work was to investigate the effect of a certain selected protective measure; the effect of the different environmental stress factors; how strength properties change after real and accelerated exposure testing; and the corresponding effect on different materials, through environmental testing and accelerated testing. The protective measure presently being assessed is the effect of el coats on degradation rates. Firstly, a literature survey is presented. This focuses on the various methods and means of protecting GRP composites from environmental degradation. Secondly, environmental exposure conditions to which samples are subjected for both natural and accelerated exposure testing are explained. Part 3 and part 4 detail the experimental work, including the design and preparation of specimens, and accelerated and real exposure testing. Finally, some discussions and conclusions are presented.

1 CHAPTER 1

Objective

This study sets out to produce accelerated exposure tests results that would, in future, be correlated with natural exposure results in order to determine the rates of damage on laminated composite materials. This should in turn help in identifying appropriate protective methods, and hence even maintenance intervals for components made of the tested materials. The approach is to evaluate the influence of UV additives on the durability some selected gel coats with regards to mechanical and physical properties against some selected stress factors such as UV radiation and moisture.

LITERATURE REVIEW

1.1 Introduction

The literature review has been done to investigate other forms of protection for GFRP composites and compare them with the one used in the experimental work in this study. The literature review also covers brief background information on the materials used, namely: polyesters and epoxies; and information on accelerated and natural exposure and the mechanical degradation. Fillers have also been mentioned because they are part of the matrix material and their role is important. The study has been made from the viewpoint of use of composites in aircrafts.

The unique properties created in the formation of composite materials are useful for a wide range of engineering applications. The most important uses of composite materials in today's society are in commercial aerospace, defense, space technology, recreation and general industrial and engineering structures. The existing accelerated testing methods and approach for metals cannot simply be applied to composites. With service lifetimes measured in years, it is almost impossible to do real-time testing under different conditions for the variety of materials.

The durability and the capability to maintain visual and structural integrity with time in typical engineering environments seems to be one of the most important aspects of advanced composite materials. The durability of FRPs is their strongest advantage, particularly when problems with a rapidly aging and deteriorating civil infrastructure and other applications are being addressed. On the other hand, questions concerning uncertainties with the long-term performance of FRPs in terms of ultraviolet resistance, stress corrosion, chemical resistance, and fire exposure are raised around the world. [1]

The primary reasons for using composites in structures include high specific stiffness and specific strength. The difficulty in determining long-term structural integrity of FRPs arises from the number of different types of fibre, resin, and manufacturing systems and their widely different performance characteristics under exposure to permanent loads and various environmental conditions. Accelerated tests and long-term exposure tests are conducted to provide answers to the question of durability. Typically however, these tests are focused on one specific system and application, making extrapolations to other systems and environments uncertain.

This study evaluates the influence of the UV additives on the gel coat performance and mechanical properties. It also compares the accelerated exposure with natural exposure test results. Studying the mechanism of degradation is important in order to best understand the different methods of evaluating durability of coating materials.

The important requirement for accelerated aging studies is the correlation of mechanical property data from accelerated exposure of materials with data from real-time exposure. The comparison with real-time data could help determine the accelerating factor for any given degradation mechanism. This correlation with results from real-time exposure dictates the need to monitor all environmental stress factors (such as temperature and humidity).

For engineering applications the description of mechanical behaviour of any component under the design conditions is generally all that is required. Accordingly, the information obtained from these tests tries to explain why a material has degraded and how it can be improved, to retain even the structural strength. For failure related to molecular activity, additional information is necessary to comprehend the problem fully. Thermal analysis is one technique that can provide some insight as to why some materials fail differently to others.

The mechanical, thermal and chemical properties of fibre-reinforced organic matrix composites change during environmental exposure [2]. The severity of exposure depends on test temperature, time and intensity of the different factors such as UV radiation. The rate of degradation, for example is often proportional to the duration of UV exposure, the temperature at which UV exposure takes place, or both [5]. The UV light induces degradation in polymers that has negative effects on mechanical and physical properties of polymers.

This information on durability seems to suggest that for specific applications, clear long-term performance specifications must be established. In addition to the short-term and accelerated test procedures, carefully planned and monitored outdoor exposure tests must be conducted, to correlate some of the accelerated test data and to develop durability and service life prediction models.

1.2 Protective Measures for Composites

A literature review has been carried out to investigate various forms of protective methods for composites structures against environmental degradation. The literature review was carried out to give brief but comprehensive information on each of the different protective methods. The approach was to investigate each method based on the cost-effectiveness, convenience, efficiency, effectiveness against environmental degradation factors, its durability, and availability. The study of effective protective methods for composites was prompted by the increasing use of composites in Southern Africa.

1.2.1 Gel Coats

The gel coat is a protective layer on the outer surface of a laminate. Gel coats are generally a polyester, mineral-filled coating that can, with the addition of additives, impart decorative, high gloss finishes that require little or no finishing operations.

Gel coats may be applied by hand or by using spray equipment. The thickness of the gel coat applied is most commonly 500μm. This may vary however between 400 to 600μm depending on the application. Gel coats are usually supplied in a range of colours to avoid errors when pigmenting during manufacture. The coating contains UV stabilisers to minimise UV damage to the underlying resin and is commonly based on isophthalic resin to impart improved resistance due to moisture damage. (An isophthalic type resin is a resin manufatured from a meta (i.e. occupying two positions (1, 3) in the benzene ring that are separated by one carbon atom isomer of phthalic acid). Application of the correct gel coat for a particular application would ensure a long-lasting, durable surface.

Major markets for gel coats are marine, automotive and building construction. As the growth of the composites industry continues, gel coats must evolve to meet the increasing demands placed on composites components in new environments as the long term performance of components is determined by the level of protection. The gel coat plays a very important part in composites and needs to perform two primary functions, namely: the protection against weather and decoration [3]. The UV stabilizers that were investigated were added in the gel coat layer.

FRP composites are often protected with a gel coat, which is a resin-rich layer applied to the surface of the composite. Basic gel coats themselves are polymers and therefore are susceptible to UV damage. The gel coat delays the effects of UV exposure, but would not necessarily prevent the damage from occurring or progressing. Repair generally would involve the application of a fresh gel coat or resin layer.

Some of the important uses of gel coats uses are: to improve weathering, filter out ultraviolet radiation, add flame retardants, provide a thermal barrier, improve chemical resistance, by means of additives, and to provide a moisture barrier. Gel coats are used to improve the product appearance such as the surface of a boat hull. A unique benefit of gel coats is that they are supplied in many colours by the incorporation of pigments per the specification of the engineer. [5]

The use of resin-rich surfaces to protect structural laminates is an established practice to: improve the durability of components, protect the laminate from the environment, provide a smooth aesthetic finish, and eliminate the need for painting.

Gel coats are considered to be resins but have a very special purpose. A gel coat is a specially formulated polyester resin incorporating thixotropic (i.e. becoming less viscous when subjected to an applied stress, such as being shaken or stirred) agents to increase the gel coat's viscosity and non-sag properties, fillers for flow properties, pigments to give the desired colour, and additives for specific application properties, such as gel time and cure. Gel coats are primarily used for contact moulding (hand or spray lay-up). The gel coat, usually pigmented, provides a moulded-in finished surface that is weather and wear resistant. The gel coat helps in hiding the glass reinforcement pattern that may show through from the inherent resin shrinkage around the glass fibres. Considerations used for the proper selection of a gel coat are compatibility with the underlying FRP materials to ensure good adhesion of the gel coat, as well as the operating environment.

A variety of base resins can be used to manufacture gel coats with the most common based on isophthalic acid type resins (a colorless, crystalline, slightly water-soluble solid, $C_8H_6O_2$, the meta isomer of phthalic acid: used chiefly in the manufacture of resins and plasticizers). An isomer is a compound that exists in forms having different arrangements of atoms but the same molecular weight. The choice of isophthalic acid based resins rather than orthophthalic acid based resins results from the superior water resistance the former, their superior blister resistance and their superior toughness. This is because the higher molecular weight isophthalic resins have higher tensile and flexural strengths than lower molecular weight phthalic resins. This may be because isophthalic usually form more linear, higher molecular weight polymers than orthophthalics [3].

There are specific gel coat products for either spray or brush applications. If a gel coat is too thin, under 0,4mm it could cause under-cure of the gel coat and too thick a film could crack. While gel coats do not add any structural strength to the FRP part, gel coats should be resilient. Gel coats should be able to bend without cracking [3]. They should be resistant to thermal cracking (cracking that may occur with dramatic changes in temperature).

A brush gel coat is applied with a brush. These gel coats are formulated to have the correct resistance to drag on the brush, release air and level correctly. As with spray grades, proper thickness should be applied to achieve best results.

1.2.2 Gel Coats Additives

Additives are intentionally introduced to enhance or modify many gel coats properties, and thus render a laminate more durable. Typical additives include filler materials, plasticizers, stabilizers, colorants, and flame retardants. The geographic location of exposure and the chemical environment of exposure are among the crucial factors in determining the amount of stabilizer needed for a particular application.

Theoretically [6], the UV radiation degradation of polymer materials used in outdoor applications can be prevented by the use of light stabilizing additives (also called UV inhibitors or light absorbers) into the composite. These are part of a larger additives group, known as excited state quenchers, that either inhibit or delay degradation reactions rather than to stabilize properties [4].

In this study, literature review focuses on the degradation process which mostly affects the surface, at least in the initial stages, and results in chalking, discoloration and sometimes even loss of physical and electrical properties. The product bulk properties of impact strength, tensile strength and elongation may all deteriorate because of degradation process. [4]

A literature survey was carried out regarding the different types of additives which could be assist in protecting a laminate from the degradation process or prevent the initiation of degradation.

1.2.2.1 Fire resistance

A fire resistant additive may not be particularly relevant here, but it is could be important for new developments and safety standards. Combustion resistance is improved by proper choice of resin, use of fillers or flame retardant additives. The flammability of polymeric materials is a major concern. Most polymers, except those containing chlorines and fluorine, are flammable in their pure form. Flammability resistance may be enhanced with the use of additives called flame retardants.

Unsaturated polyester and epoxy resins require flame retardants to meet fire protection standards. There is an increasing demand for non-halogen flame retarded composites for construction and transportation applications. The use of newly developed, effective agent blends of non-halogen phosphorus flame retardants increase the flame resistance of composite materials. These new developments allow a much lower loading of flame retardants to meet the high safety requirements and also provide the possibility to produce light weight construction elements with better mechanical properties and introduce composites into new application areas. [7]

A large growth is expected in glass-fibre reinforced polyester composites for above-ground trains. In the event of a fire on board a moving train, immediate evacuation of passengers is not feasible. Therefore, it is essential that the materials used in the construction and furnishing of coaches are such that they are not easily ignited and have a low total emission of heat, smoke and toxic fumes when exposed to an ignition source.

Polyester and epoxy gel-coats containing the appropriate additives show intumescent properties [8]. That means they form a foamed char layer on the surface of the composites which protects the composites from the heat. The intumescent mechanism is of special interest for gel-coats, where the retarding of the gel-coat can also protect the main structure. The flame retardant is applied only on the surface of the composites, where the material is attacked by the flames. This type of construction provides the possibility to produce weight-reduced composites with better mechanical properties, compared to highly filled systems. The smoke density is also very low. The nature of organic composites which contain oxygen within their chemical structures and are inherently combustible, raises the question of how to improve both the resistance of composites to fire, and their reaction to fire (smoke, heat release etc).

1.2.2.2 Air release

Most laminating resins, gel coats and other polyester resins could entrap air during processing and application. This can cause air voids and improper fibre wet-out. Air release additives are used to reduce such air entrapment and to enhance fibre wet-out. As composites structures are becoming more optimized, the requirements on mechanical properties are increasing in terms of performance and consistency in order to reduce weight and material cost. One aspect, which may have a strong influence on mechanical properties, dielectric properties, surface finish is void content. In other words, it is beneficial to keep the void content to a minimum. [108]

1.2.2.3 Emission control

In open mould applications, styrene emission suppressants are used to lower emissions for air quality compliance [5]. Manufacturers of reinforced plastic composites must reduce Hazardous Air Pollutants (HAP) emissions under a new Maximum Achievable Control Technology (MACT). Industries around the world have to meet the requirements of new legislation set by both national and international groups and enforcement is becoming tough, where lack of compliance could lead to stiff penalties [106].

1.2.2.4 Antioxidants

Composites are sometimes modified with antioxidants, which retard or inhibit polymer oxidation and the resulting degradation of the polymer [5]. The combined action of oxygen and heat cause thermo-oxidation. This phenomenon leads to change in molecular weight that lead to modification of mechanical and physical properties such as yellowing, loss of gloss, chalking, and superficial micro-cracks. This thermo-oxidation process can be inhibited by using anti-oxidants. [9]

1.2.2.5 Foaming agents

These are chemicals that are added to polymers during processing to form minute cells throughout the resin. Materials with foaming agents exhibit lower density, decrease material costs, improve electrical and thermal insulation, increase strength-to-weight ratio and reduce shrinkage and part warping.

1.2.2.6 Heat stabilizers

Heat stabilizers are used in thermoplastic systems to inhibit polymer degradation that results from exposure to heat. It is believed that heat is one of the main factors which induce degradation of polymers [9]. Thermo-oxidation can occur in different moments of the life cycle of polymers.

1.2.2.7 Ultraviolet stabilizers

Under normal environmental conditions, some polymeric materials are subjected to too rapid deterioration, generally in terms of mechanical integrity. Most often, this deterioration is a result of exposure to light, in particular UV radiation, and also oxidation. Ultra-violet radiation interacts with, and causes a severance of covalent bonds along the molecular chain which may also result in some cross-linking. Oxidation deterioration is a consequence of the chemical interaction between oxygen atoms and polymer molecules. Additives that counteract these deterioration processes are called stabilizers.

The UV radiation degradation of polymeric materials used in outdoor applications can be inhibited or delayed by introducing light stabilizing additives (also called UV inhibitors or light absorbers) into the polymer mix. Additives which protect composites by absorbing the UV radiation are called ultraviolet absorbers. These are low cost, effective stabilizers that function through the absorption of UV light [9]. However, the addition of UV absorbers alone may not always give adequate protection; generally they are used in combination with Hindered Amine Light Stabilizers compounds (HALS) [10]. Exposure to sunlight and some artificial lights can have adverse effects on the useful life of plastic products. UV radiation can break down the chemical bonds in a polymer. This process is called photo-degradation and ultimately causes cracking, chalking, colour changes and the loss of mechanical properties.

1.2.2.8 Nickel Quenchers

These quenchers are Energy Transfer Agents that function by “quenching” the excited state of carbonyl groups formed during photo-oxidation and also through the decomposition of hydroperoxides. These types of stabilizers are not in wide use since they contain heavy metal, impart colour to the final product, and are not as effective as the HALS discussed in the next paragraph.

1.2.2.9 Hindered Amine Light Stabilizers (HALS)

Hindered Amine Light Stabilizers are available in a wide range of molecular weights and structures suitable for almost any application. They can also perform as long-term thermal stabilizers (HATS). They function by "trapping" free radicals formed during the photo-oxidation process. HALS are extremely efficient stabilizers against light-induced degradation of most polymers. They do not absorb UV radiation but act to inhibit degradation of the polymer. Significant levels of stabilization are achieved at relatively low concentrations. HALS high efficiency and longevity are due to a cyclic process wherein the HALS are regenerated rather than consumed during the stabilization process.

Since all three stabilizer types function through different mechanisms, they are often used in combinations which can be synergistic. For example, HALS are commonly used with Benzotriazoles (a family of UV stabilizers which are derivatives of 2(-2hydroxyphenyl) benzotriazole and function primarily as UV absorbers.) to minimize colour changes in pigmented systems [5]. All of the above stabilizers will function most effectively in the presence of an appropriate base stabilization package containing both primary and secondary antioxidants along with a residual catalyst neutralizer.

1.2.3 Fillers

Inorganic fillers are a form of protection for laminated composites, and in addition they improve performance of laminates.

Fillers are generally added to polymers to improve tensile and compressive strengths abrasion resistance, toughness, dimensional and thermal stability, among other properties. Materials used as fillers include wood flour (finely powdered sawdust), silica flour and sand, glass, clay, talc, limestone, and even synthetic polymers. The particle sizes of these range from 10nm to microscopic dimensions. Because these inexpensive materials replace some volume of the more expensive polymer, the cost of the final product is reduced. [11]

Fillers influence the fire resistance of laminates. Fillers lower compound cost by diluting more expensive resin and may reduce the amount of reinforcement required. Fillers can influence the mechanical strengths of composites. Fillers serve to transfer stresses between the primary structural components of the laminate (i.e., resin and reinforcement), thereby improving mechanical and physical performance. Uniformity of the laminate can be enhanced by the effective use of fillers. Fillers help maintain fibre-loading uniformity by carrying reinforcing fibres along with the flow as resin is moved on the mould during compression moulding.

The use of inorganic fillers in composites is increasing. Fillers not only reduce the cost of composites, but also frequently impart performance improvements that might not otherwise be achieved by the reinforcement and resin ingredients alone. Fillers can improve mechanical properties including fire and smoke performance by reducing organic content in composite laminates. Filled resins also shrink less than unfilled resins, thereby improving the dimensional control of moulded parts. Important properties, including water resistance, weathering, surface smoothness, stiffness, dimensional stability and temperature resistance, can all be improved through the proper use of fillers.

In comparison to resins and reinforcements, fillers are the least expensive of the major ingredients. These materials are nevertheless very important in establishing the performance of the composite laminate for several reasons:

Crack resistance and crack prevention properties are improved with filled resin systems [5]. This is particularly true in sharp corners and resin-rich areas where smaller particles in the filler help to reinforce the resin in these regions.

Low-density fillers are used extensively in marine putty and the transportation industry. They offer the lowest cost of filled systems, without the increases of weight that affect the performance of the final product.

Effective use of fillers in composites can improve performance and reduce cost. In today's market, many of the filler systems available are providing several different properties for the composite in one filler system: flame/smoke, shrink control, weight management and physical properties.

1.2.4 Chemical Resistant Barrier Layers / Skins

The main function of the barrier layer is to reduce or delay the ingress of the environment into the structural laminate. Since water permeation is controlled by solubility and diffusion processes, it is likely that the solubility of water in a resin matrix is the primary factor controlling laminate degradation [1]. It therefore follows that the thickness of the barrier layer and the resistance of its materials delay environmental penetration, thereby protecting the structural laminate from possible degradation and failure.

The correct choice of barrier layer can provide a long-term protection to both the internal and the external environments. In order to achieve the highest level of resistance it is important that the barrier is fully cured. The level of degradation of GRP in contact with the environment results in varying levels of swelling, absorption, whitening, surface crazing and cracking, depending upon the severity of the environment.

However, highly cross-linked isophthalic acid based polyester resin has been shown to be very resistant, and even suitable for aggressive environments such as the manufacture of underground petroleum storage tanks [12].

The chemical barrier layer is not necessarily structural and can be manufactured from a different resin to that used for constructing the structural laminate. The barrier layer can be constructed using surface tissue, which can be based on glass or polymer fibres depending upon the environment. With the correct choice of resin and barrier layer construction, even underground fuel storage tanks could survive for long periods of time.

The boat industry learned long ago that by using a skin layer of vinyl ester osmotic blistering, or small pimples that appear in the gel coat after a few years, are eliminated. The best skins use 100% vinyl ester resin, but in recent years there have been several vinyl ester blends that have appeared on the market. These are blends of expensive vinyl esters with less expensive resins. [13]

1.2.5 Hangars

Providing adequate protection from the environment is very important and there are many ways to accomplish this objective. Hangars were reviewed as another alternative for protection. The biggest environmental threat is the sun [14]. The sun's heat, and ultraviolet rays attack can deteriorate a boat's or airplane's paint, upholstery, windshield, dashboard and all other exposed plastic surfaces. In addition to the damaging effects of the sun, moisture from rain, mist, fog, snow, and hail can cause metal parts to rust.

The advantage of using a hangar is that it will protect the paint, and interior; and protect against corrosion. As the value of, for example airplanes, increases so does the need to store them in hangars. As the demand for hangars increases the costs increase. [14]

Disadvantages include the fact that airports are running out of land to be developed. Future airport expansion is difficult due to environmental issues such as ecological concerns and public opposition. [14]

1.2.6 Tension Roofs or Soft Canopies

In the study soft canopies have been considered and identified as one of the convenient and efficient structures that could provide environmental protection for large composite components.

Fabric roofs or canopies are thin flexible membranes held in shape by the application of tension, and acting both as structure and as weather shield. Most canopies are currently made either from (PVC) coated polyester or (PTFE) coated glass.

Tension roofs or canopies are those in which every part of the structure is loaded only in tension, with no requirement to resist compression or bending forces. Pure tension is by far the most efficient way of using a slender structural member [15]. It would take a very high load indeed to break a component if the force is applied in tension only. In this case, the member works uniquely up to the full tensile strength of the material. Tension structures are therefore very appropriate when the minimum amount of material is to be used and in which every part is working to maximum efficiency.

Stressed fabric canopies may be chosen in preference to alternative forms of structure (most of which may be cheaper) for their speed of construction, their light and airy appearance, their translucency (the space beneath the fabric canopy can be bathed in a pleasant diffused light, and their cost effectiveness where foldability, demountability and / or portability is an important requirement. Canopies have been used in hot climates, as large open space shading for aircraft (e.g. Hajj Terminal in Saudi Arabia, The Landslide Terminal at Denver in USA) [15].

The PVC coated polyester fabrics tend to pick up dirt and are best avoided in urban or other dirty atmospheres. They must be cleaned regularly to avoid loss of translucency and unattractive appearances. PTFE coated glass fabrics tend to remain clean as dust particles do not stick and are washed away by rain. PTFE coated glass fabric also shows no tendency to discolour with age.

These canopy membranes act to moderate and regulate the external climate. Membranes can save energy due to a significant reduction in the requirement for artificial lighting. The overall light received from natural day light is usually of better quality due to its richer spectrum.

1.2.7 Paints

Paints give long-lasting results and are virtually maintenance-free, but are expensive. However, for badly chalked surfaces, where fibre glass matting shows through the surface, or gel coat with deep cracks, gouges or severe crazing repaired with epoxy, painting is the only option. If the gel coat surface is in good condition, an acrylic finish restores shine and colour [16].

The two major groups of paints are oil or alkyd and water or acrylic. The major characteristic of oil based paints is that they must be thinned and cleaned up with mineral spirits. Water-based paints can be thinned with water. This makes them more user-friendly, allows for easier cleanup (warm soapy water) and also makes them kinder to the environment. Most paint research today is performed on water-based paints, and the improvements in workability and durability have made them the preferred choice for the majority of jobs. Nevertheless, there may be occasions when an alkyd is preferred (e.g. highly humid environments) [17].

1.2.7.1 Acrylic gloss paints

Acrylic gloss paints are formulated with resins with a different chemical composition to those used in solvent based (alkyd) gloss paints [17]. The acrylic chemistry is very similar to that used in acrylic plastic sheet and moulding powder, well-known in applications such as outdoor illuminated signs, street-light covers, and rear light covers on cars. Acrylic paints are also widely used for protecting cars and aircraft. Acrylic resins for decorative gloss paints are designed to maximize resistance to weathering without being too hard or inflexible for use as house paints.

It can be predicted from the chemical composition and non-oxidizing nature of acrylic gloss paints that they will be highly resistant to the effects of weather. This theory is borne out in practice, and has been demonstrated in many long-term exposure tests, where the superior gloss retention and resistance to cracking, flaking, chalking, colour loss, dirt pick-up and mildew has been repeatedly proven [18].

According to the commercial exposure facilities conducting research, such as; Allunga Test Services at Townsville, in north Queensland, Australia [18], acrylic paints show resistance to cracking and flaking and demonstrate the superior long term flexibility and extensibility of acrylic gloss paints. Due to the acrylic polymer composition, acrylic gloss paints retain their original colour and are resistant to chalking. Many test results which demonstrate the better resistance of acrylics to the effects of ultra-violet light.

1.2.7.2 Alkyd gloss paints

Alkyd gloss paints on the other hand, have a tendency to be affected by rain and atmospheric pollution, which often appears in the early life of the paint film and cannot be easily removed. These paints are also more likely to support mould growth on the surface, as the oil acts as a nutrient. By comparison, acrylic gloss paints stay cleaner and brighter throughout their life. It can be predicted from the chemical composition and non-oxidizing nature of acrylic gloss paints that they will be highly resistant to the effects of weather.

A decision to use any of the various protective measures would depend on different factors. Some of the protective method can be used only if that composite component is a large one or vice-versa. The one method that has been studied experimentally (i.e. the gel coat and the respective additives), has been found to be a reasonably effective method, especially with the correct relevant gel coat additive.

1.3 Exposure

Many composites are used outdoors. They are exposed to ultraviolet radiation (UV), moisture from rain, snow, humidity, fungal attacks etc. As this study was being done, it was not clear as to what extent the laminates being tested would withstand these influences without degradation of mechanical properties. Glass fibre reinforced polymer composites are increasingly being used for infrastructure and marine applications. Such composites offer significant advantages in comparison with traditional materials of construction. Polymer composite structures, like bridge decks, and hybrid composite-concrete systems, such as composite overlays on concrete and composite reinforcing members in concrete, are among the applications being considered for retrofit and rehabilitation of our infrastructure. However, successful long-term applications depend on their long-term environmental durability.

1.3.1 Natural Exposure

Natural exposure testing has many advantages: it is realistic, inexpensive and easy to perform. However, one may not have several years to wait on result. Natural exposure is needed to produce real-time and accurate results on the degradation of composites. Natural exposure tests should utilize direct measurement data for critical considerations.

Structure must be able to withstand exposure conditions such as vibrations, ultraviolet (UV) light, rain, hail, salt, and temperature extremes. These conditions, when they are long term, translate to stringent performance criteria for material designer [20]. Testing is required to determine the effects on composite properties, of long term exposure to chemicals and environment. The type and degree of outdoor exposure vary greatly from place to place throughout the world, Florida and Arizona being international benchmarks for natural weathering. Florida has high intensity sunlight, annual UV and year-round high temperatures, annual rainfall and humidity. Arizona is hot, and dry and with a high UV radiation environment, and large temperature fluctuations [20].

Exposure to effects such as rain may be similar to condensation [22]. Whereas condensation often occurs at regular daily intervals, rain plays a more infrequent, seasonal role. The frequency and duration of rain is also closely linked with irradiance and temperature excursions. The effects of relative humidity, like liquid water, depend on material characteristics. Relative humidity often receives undue attention simply because exposure facilities report this data. In fact, the amount of water molecules available for materials degradation at the highest possible terrestrial relative humidity (vapour pressures) may represent orders of magnitudes less than amount of water molecules available in a liquid state depending on how the calculation is performed. In sub-tropical environments, high relative humidity often causes biological degradation (algae, mildew, etc.).

1.3.2 Accelerated Exposure

Verified accelerated aging methods are necessary to provide guidance for materials selection and to accurately assess aging changes in the original properties of new materials.

Although UV makes up only about 5% of sunlight, it is responsible for most of the photochemical damage to durable materials outdoors. To simulate the damage caused by sunlight it is not necessary to reproduce the entire spectrum of sunlight. It is only necessary to simulate this short wave UV. The UVA-340 lamp gives an excellent simulation of sunlight in the region from 365 nm down to the solar cut-off of 295nm (Sunlight does not contain UV below 295 [21]). This lamp produces only those UV wavelengths found in sunlight. [23]

The accelerated test was developed to simulate actual outdoor exposure results as closely as possible in a reduced amount of time and still be capable of producing data that could yield a reasonable estimate of material durability. The UVA tubes used for the tests have a frequency curve close to that of natural daylight. With these tests, the long-term weathering performance may be predicted in a shorter time period by exposing specimens to extreme conditions to accelerate the aging process.

Polyester resin degradation is affected by solar radiation, photo-catalytic admixtures, water and moisture, chemicals, oxygen, ozone, temperature, abrasion, internal and external stress, and pigment fading [24]. The following factors; all present in outdoor weathering,; moisture, elevated or lowered temperatures, oxidation and UV radiation are the most important to coating degradation.

Moisture: Hydrolysis occurs when a plastic is exposed to water or humidity. This chemical reaction may be a major factor in the degradation of condensation polymers such as polyesters, where the ester group is hydrolyzed [25].

Oxidation: Due to the presence of oxygen in the atmosphere, the most common type of radiation degradation, photo-oxidation, occurs on all organic polymers. Again, the process will be accelerated by UV radiation and higher temperatures. The chemical reaction can be described by the oxygen attack on the bond in a polymer chain, which may either form carbonyl groups or crosslink [26].

The photochemical effect of sunlight on a plastic material depends on the superficial absorption properties and the chemical bond energies of the material. Light wavelengths that have the most effect on plastics range from 290 to 400 nm. The wavelength of UV radiation whose photon energy corresponds to a particular bond energy in the polymer chain can break the chemical bonds (through a chain splitting), changing the properties, and therefore the performance of the polymer [27].

Ideally, composite materials and their structures intended for long term use should be tested in real time and with realistic in-service environments. Often this is not viable because the time factor would significantly delay product development. However, this long term data is invaluable. In some cases specimens are not affected even up to a period of 5 years.

When a coating is exposed to light which does not duplicate the solar spectrum, especially in the short wavelength UV region of the spectrum, less than 295 nm, "unnatural" photochemistry occurs and incorrect results are produced [28].

1.4 Degradation Mechanisms

A variety of degradation mechanisms and their potential effect on mechanical properties have been researched.

1.4.1 Chemical mechanisms

Chemical degradation occurs through three methods;

1. Chain scission
2. Cross-linking
3. Substitution reactions

Chain scission refers to the breaking down of polymer molecules. Cross-linking and substitution reactions do also occur though substitution reactions are not commonly found. Substitution reactions cause the least property change when compared to the other methods of chemical degradation. Chain scission and cross-linking do occur under normal weathering conditions. Molecular degradation at manufacture, due to shearing generally occur at defects in a molecule.

1.4.2 Photo-oxidation [4]

Photo-oxiditation is the most significant of the three chemical degradation methods. Photo-oxidation can occur in two ways;

1. Dissociation caused by a collision photon (of sufficient energy) with a polymer molecule.
2. Presence of impurities in the polymer, eg. trace metals

1.4.3 Thermal degradation

Thermal degradation does not only imply degradation of the material due to in-service temperature, but can be the result of degradation of the high temperature processing of the material which can lead to photo-oxidation deterioration in service. The first step in thermal degradation is dehydro-chlorination. This entails the stripping off of the hydrogen and chlorine atoms on adjacent chain carbon atoms. The hydrogen and chlorine combine to form HCl, thereby leaving behind a double bond in the polymer backbone. The reaction produces yellowing of the polymer. The HCl produced acts as an accelerator for the reaction unless it is removed. Degradation is accelerated by oxygen but can still occur without oxygen at temperatures above 120°C [33]. Oxygen present during processing reacts with radicals to produce hydroperoxide. Degradation is due to amount of HCl present, degree of unsaturation and on peroxide content [34].

1.4.4 Hydrolysis

Chain scission can be caused by hydrolytic attack in some polymers that would cause the deterioration of mechanical properties. Some polymers become plasticsed upon water absorption resulting in a decrease in the Young's modulus. White and Turnbull have found that with sufficient water absorption, disc shaped defects that act as stress concentrations can develop in polycarbonates.

Regarding pollution, if the pollutant is photolytic (can decompose by the action of radiant energy) degradation of the polymer will result.

1.5 Polyesters and Epoxies

Polyester and epoxy matrix composites are presently exposed in South Africa The field of composites is very wide with a similarly wide range of materials. The study has been narrowed to polyester and epoxy materials and the corresponding experimental testing and analysis. The literature review on the polyesters and epoxies gives information about these materials.

1.5.1 Polyesters

Thermosetting polyesters are the cheapest resins for making glass or carbon fibre reinforced composites, but they have lower strength than epoxies. They can be formulated to cure at or above room temperature. Modifications can improve the chemical resistance, UV resistance and heat resistance without too much change in the ease of processing.

Over 90% of all marine composites are made with polyester and vinyl ester composites. Glass / polyesters are in superstructure, masts (a vertical rounded pole for supporting sails), radomes (domelike shells transparent to radio-frequency radiation, used to house a radar antenna) of large steel ships and in the non-pressure hull casing, sonar domes and masts of submarines [35], The application of glass / polyester composites on offshore drilling platforms include grates, low-pressure pipes and tanks [36]. The disadvantages of these composites however include low stiffness and the fact that the composite absorb water which degrades resin matrix, glass to resin interface and attack the glass fibre. This damage leads to reduction in mechanical properties [37].

1.5.1.1 Structure

Figure 1-1 shows the idealised chemical structure of typical polyester. Note the positions of the ester groups (CO - O - C) and the reactive sites (C* = C*) within the molecular chain.

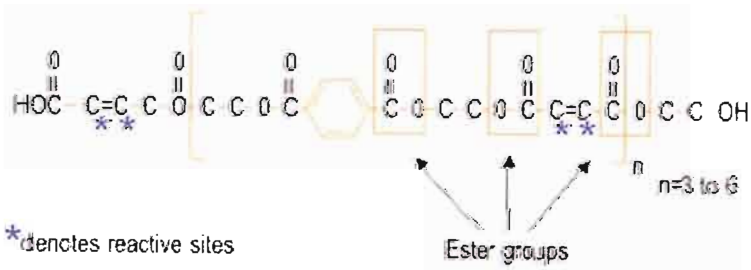


Figure 1-1: Idealised Chemical Srtucture of any typical isophthalic Polyester [37]

1.5.2 Epoxies

Epoxies are thermosetting polymers with excellent mechanical, electrical and adhesive properties and good resistance to heat and chemical attack. They are used for adhesives, surface coatings and, when filled with other materials such as glass or carbon fibres, as matrix resins in composite materials. Typically epoxies are used as adhesives for high-strength bonding of dissimilar materials; they are used as coatings to encapsulate electrical coils and electronic components; and, when filled, for tooling fixtures for low-volume moulding of thermoplastics.

1.5.2.1 The Environment

Both resin and hardener are irritants; their vapours are potentially toxic. Ventilation and skin protection are important, but both achievable. Thermosets cannot be recycled, though it may be possible to use them as fillers. Cutting and machining of glass and carbon fibre composites require special forced-air ventilation to remove the fine glass or carbon dust that is damaging if inhaled [39].

1.5.2.2 Formation of epoxies

Most epoxies are formed by combination of bisphenol-A and epichlorohydrin in the presence of a catalyst. Catalysts include amines and acid anhydrides. The curing temperature, ranging from room to high-temperatures, is determined by the type of catalyst, which also affects the properties of the final product [39].

1.6 Accelerated and natural exposure

Accelerated aging tests are needed to gain information on the durability of a material within a reasonable time frame. The introduction of any new material into use requires knowledge of long-term strength retention under working conditions. This may be obtained from exposure of test samples to real working conditions over the expected working lifetimes, or estimated from the behaviour of samples exposed to more aggressive accelerated ageing conditions over shorter time periods. It is widely recognized that sunlight and moisture are the most important causes of weather damage to polymers [40].

1.6.1 Factors causing conversion difficulty

- The geographical latitude of exposure location (closer to equator implies more UV).
- Altitude (higher above sea level means more UV).
- Random year to year variations in the weather can cause variation in degradation.
- Seasonal variations (winter exposure may be very different from summer exposure).
- Samples orientation (the angle tilt of exposure panel and the direction in which the samples face).
- Sample insulation (outdoor samples with insulated backing often degrade faster than un-insulated samples).
- Local geographical features.

Some reasons for poor correlation between accelerated and natural testing. The reasons that follow are based on the literature survey [41]:

- Continuous exposure to light: Some materials need a ‘rest period’ for certain chemical reactions to take place. Since the natural outdoor exposures will always have a ‘dark cycle’, this would have to be simulated in artificial exposure instruments.
- High light intensities (especially with artificial light sources): Some photo-chemical changes during exposure may be altered at high irradiance levels that do not occur at normal levels.
- Abnormally high specimen temperatures: Unrealistic temperatures during exposure often cause different types of degradation, which do not correlate with outdoor exposures.

- Unrealistic temperature differences between light and dark materials: Radiation sources with only UV radiation will cause unrealistic results or a lack of temperature differences between materials of different colour or structure.
- No temperature cycling: Natural temperature cycling often causes physical changes to materials as a result of the expansion and contraction of material.
- Unnatural levels of moisture: The absorption/drying cycle of water causes physical stresses which can actually cause more (and unrealistic) degradation than a saturated environment.
- Absence of pollutants and other biological agents: Laboratory weathering instruments are rarely, if ever, used to replicate the effects of pollutants or other biological factors, but they are an inherent part of the natural weathering process, and we must bear in mind that there may be cause for less than expected correlation.

Irrespective of these difficulties however, it is still necessary that the mechanisms underlying aging even in high performance material systems be studied. Without an understanding of these underlying processes, there is little hope that accelerated aging studies will be of much use in the materials science community.

The comparison between 'accelerated' tested samples and natural exposed samples was based on visual inspection techniques involve checking for the following signs of photo-degradation: loss of surface gloss, chalking, flaking of surface resin, pitting, micro-cracking, blistering, loss of resin from the surface. These symptoms are listed in order of severity, with loss of gloss, chalking, and flaking being more of a cosmetic than standard problem. Damage is considered to be severe at the point that fibres become visible.

1.6.2 Accelerated Environmental Exposure Conditions

The environmental chamber uses four of the UVA-340 type lamps. The lamp is the best available simulation of sunlight in the critical short wavelength region between 365 nm and the solar cut-off of 295 nm. Its peak emission is at 340 nm.

The environmental chamber has the capacity to reproduce damage caused by sunlight, rain and dew by exposing materials to automated cycles of UV radiation and water vapour condensation at controlled, elevated temperatures. Water is sprayed into the environmental chamber in the form of droplets. The vapour condenses on the specimen surface thereby simulating rain and dew. The temperature inside the chamber can be elevated to provide accelerated degradation.

1.6.2.1 Exposure to UV Radiation Only

Specimens are presently exposed only to UV radiation at a temperature of 30°C (the environmental chamber has been designed for a temperature range from room temperature to 70°C); with an irradiance level set to match the typical maximum irradiance of summer sunlight. The elevated temperature selected to accelerate the degradation process is small compared to the glass transition temperature of epoxy. These epoxy samples have been exposed in the environmental chamber for about 500 hours.

1.6.2.2 Irradiance control in the Environmental Chamber

An advantage that laboratory weathering has over outdoor testing is reproducibility of results. To achieve this, lab testers must control light, moisture, and temperature. Control of irradiance, i.e. the rate at which light falls on a unit area of surface is particularly important because small differences in lamp energy output or wavelength spectrum can cause significant changes to the degradation rates. Higher intensities usually mean faster or more severe tests. Changes in wavelength may affect both the speed and the type of material degradation.

1.6.3 Accelerated dual exposure cycles of laminates

UV-condensation cycles were introduced after the 2500 hours of UV radiation exposure. The cycles are carried out for periods of 8 hours for UV radiation and 8 hours condensation, alternating, and have now run for about 100 hours. The introduction of UV and condensation cycles is aimed at improving correlation with the real outdoor exposure and for investigating moisture effect on the laminates and hence the identification of dominant degradation causes on the laminates. UV and condensation have been shown to offer the best available correlation with outdoor exposure testing [42].

Moisture has an effect on mechanical properties of laminates. According to Lodeiro [43], it has the effect of an overall increase in the Poisson's ratio (the lateral contraction per unit breadth divided by the longitudinal extension per unit length) of the composite and lowering of the glass transition temperature, Tg (the temperature below which molecules have very little mobility) of the matrix due to the plasticization which increases the flexibility of the composite.

A study by Burrell, Herzog and McCabe [44] showed that a gel coat layer is a semi-permeable membrane which allows diffusion of fluids through the membrane to the laminate. In polymers free space exists between molecular chains. This free space allows the polymer to absorb fluids to which they are exposed, especially those with similar solubility parameters. Such absorption physically weakens the polymer and may also chemically attack the polymer. The kinetics of these processes is governed by diffusion and chemical kinetics [45]. After water infuses a polyester laminate, it can attack the polymer matrix by hydrolysis. This is believed to result in residual gel coat surface stresses, compressive or tensile. The stresses could be induced by osmotic pressures, air bubbles in the polyester, bonding imperfections in the interface, and/or other factors. The absorbed water may also seek out and dissolve water soluble inclusions, thereby creating pockets of concentrated solutions which lead to loss of mechanical strength of the composite, either by chemical and physical means.

In theory [46], a minute droplet of solution is separated from the surrounding water by the semi-permeable polymer membrane which consists of a gel coat and a thin layer of laminating resin. Since the outside water and the solution are of different concentrations, water will permeate through the gel coat attempting to dilute the droplet of solution trapped in the laminate. This process is known as osmosis. During this process, more water enters the droplet causing it to expand and create a pressure on the surrounding laminate material. It takes place whenever two solutions of different concentrations are separated by a semi-permeable membrane. This increased pressure is referred to as osmotic pressure. Theoretically, the osmotic flow of water into the droplet should continue until the solution has the same concentration as the water outside the laminate. As water is drawn into the droplet, an outward force is exerted on the laminate and gel coat surrounding the growing solution. When the pressure exceeds the deformation point of the laminate it begins to crack.

This decreases the pressure and allows more space for water to be drawn into the solution. As the pressure grows, a blister can form on the surface.

The importance studying the effect of moisture is that most effects of moisture and solution related deterioration/degradation are on the strength of a composite, with changes in modulus, in most cases, being very small. However, it is noted that once the fibre itself is sufficiently degraded changes in modulus (of the composite) can be fairly large

Studying the effects of the exposure of polymers to UV radiation will also help to ascertain the extent and significance of this form of degradation to the fibre-reinforced material. According to Ken Ashbee [47] exposure to radiation involves cross-linking and is believed to be confined to the surface down to about 10 microns depth, and that beyond the 10 microns mark the intensity of the UV is half its incident value. The cross-linking is also believed to lead to shrinkage and embrittlement and spoils the appearance of the surface. Work will be done to verify this theory.

2 CHAPTER 2

ENVIRONMENTAL EXPOSURE OF COMPOSITES

2.1 Introduction

This section focuses on the types of environments and conditions to which the laminates had been exposed. Numerous new materials are designed and manufactured every day. All of these are valueless if they cannot survive their respective working environments. Most materials are exposed to outdoor environments or ones that contain some form of moisture, high temperature and radiation. These environments can cause changes in properties, appearance and performance including fading or yellowing, colour change and strength loss, embrittlement, oxidation; cracking, chalking, warping, blistering and oxidation [48]. Accelerated testing provides a means to test and redesign materials fairly rapidly thus achieving considerable savings in cost and time. It is essential therefore that prototypes or new materials be tested in simulated environments such as an environmental chamber before they are produced commercially.

2.2 Environmental Test Chamber

Q-Sun Xenon Test Chambers and QUV Accelerated Weathering Testers are the world's most widely used laboratory exposure devices [47]. The QUV uses florescent ultraviolet lamps and condensation to simulate the damaging effects of sunlight, rain, and dew.

QUV UV-lamps were used in the construction of the environmental chamber used in this study. The testing was carried out by exposing the materials to simulated environmental conditions inside the testing chamber. The chamber is capable of simulating different conditions in natural environments. These include temperature extremes, ultra-violet radiation, humidity and water and salt solution spray. These environments are accelerated in order to observe their effects on materials in a relatively short period of time. The environments can also be cycled in a particular order to enhance adverse effects on the materials in accordance with acceptable standards.

2.2.1 Specifications / Design Features

The chamber was designed by final year students at the University of KwaZulu-Natal in 2000 and manufactured at the university workshop. To prevent rust and corrosion, the chamber is coated with epoxy paint on the outside and passivated with a chemical called SP4, (i.e. to treat or coat the metal in order to reduce the chemical reactivity of its surface).

The sun emits a wide variety of electromagnetic radiation, including infrared, visible, ultraviolet A (UVA; 320 to 400 nm), ultraviolet B (UVB; 290 to 320 nm), and ultraviolet C (UVC; 10 to 290 nm). The harmful wavelengths of the sun's spectrum that cause photo-chemical degradation lie in the UV-B and UVA range. The shorter wavelengths are filtered and absorbed by the atmosphere, and do not reach the earth's surface [49].

UVA-340 lamps are used in the chamber. UVA lamps were developed to enhance the correlation between the chamber and outdoor testing. UVA lamps give slower results than UVB lamps, but are more realistic. UVA lamps have been used to test plastics, textiles and coatings. Two types of UVA lamps are commonly used; namely, the UVA-340 and the UVA-351. According to the spectrum diagram the UVA-340 almost replicates natural sunlight.

2.2.1.1 Fluorescent lamps

According to Sersen [50], the most common application of the low-pressure discharge is fluorescent lamps. These operate by means of a discharge between two electrodes through a mixture of mercury vapour and a rare gas, usually argon. Light is produced by conversion of 253.7 nm mercury emission to longer wavelength radiations by means of a phosphor coating on the inside of the glass envelope of the lamp. Lamps are available with many different phosphors and envelopes to produce a wide range of spectral emissions covering the visible (light), UVA and UVB regions. While the continuum emissions of fluorescent lamps are characteristic of the phosphors the narrow peak spectral emissions are dominated by the characteristic line emission spectrum of the low-pressure mercury vapour discharge.

2.2.1.2 Heating of the Chamber

The chamber has an air-heating element and a resistance thermometer probe. The unit's function is to heat to the required temperature and once there maintain it at the required level. A 3kW air-heating element is used for this purpose. The temperature control unit maintains the temperature at the desired level. The controller receives feedback from the temperature sensor and controls the switching of the heating element. If a deviation in temperature occurs, the controller rapidly brings it back to the desired level.

2.2.1.3 Salt Spray / Fog

The salt solution and water are generated and sprayed into the chamber using a liquid siphon set-up. This comprises a solution reservoir, compressed air and an air atomising nozzle. The mass flow control is achieved by the regulation of the compressed air via a pressure regulator. Most existing chambers use this method for simulating salt / water spray. The liquid siphon system conditions the Chamber as described in ASTM B117 standard. The standard sets out requirements for the chamber design and its operating standards. The compressed air supplied must be free of oil and dirt and maintained between 69 and 172kPa. Two fog collectors are placed within the exposure zone so that drops of solution from the test specimens or any other source can be collected.

2.2.1.4 The Chamber Shell

The 3Cr12 stainless steel chamber is effectively a shell [Figure 2-1]. Since its walls are self-supporting, there no frame present. The 3Cr12 has 12% chromium content has an inert tough surface layer of iron-chromium oxide. This passive layer is invisible to the eye, allowing for the natural brightness of metal to be seen. If scratched, the film has the ability to reform instantaneously, thus maintaining protection.

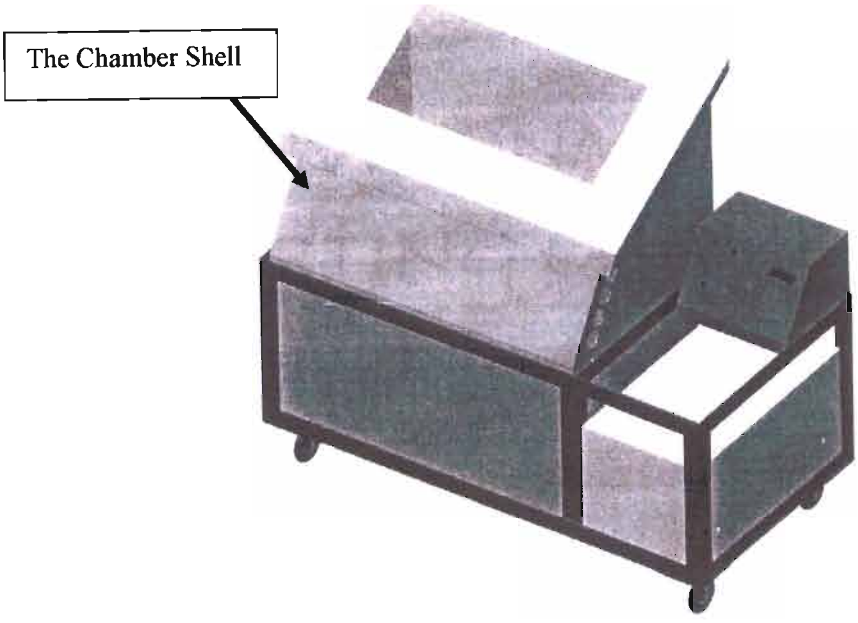


Figure 2-1: 3Cr12 Stainless Steel Chamber

2.3 Accelerated Exposure

Accelerated degradation experiments [51] at high temperature represent the best way of proceeding when long-term data is needed and the test duration is the main factor. However data extrapolation at lower and longer temperatures is possible only under particular restrictions, assuming a simplified degradation process [52].

The exposure of gel coated laminates result in a degradation process due to several factors such as humidity, temperature and exposure to sunlight. One of the primary factors in gel coats durability is the effect of sunlight on the surface of the laminate. At the beginning of an accelerated exposure, attention should be focused on the determination of dominant degradation mechanism(s). The key to this is to determine the material performance after systematic exposure to one or more parameters. The specimens were placed on a panel [Figure 2-2], then subjected to the appropriate exposure conditions.

The procedure followed was to:

- Identify the material to be tested.

- Identify mechanism to evaluate (i.e. strength change, colour change etc.).
- Choose the exposure factor (i.e. UV, moisture etc).
- Conduct exposure experiments within limits of the chosen factor with reference to established methods.
- Perform post-aging tests and compare results to those unexposed specimens.

Figure 2-2: The panel of accelerated exposure laminates

When carrying out accelerated testing it is important to know whether that particular degradation mechanism will be critical for the given application or end-use of the composite. The procedure can therefore be repeated for all degradation mechanisms of interest for that material and should not omit any known degradation mechanisms.

The selected gel coats were exposed to a variety of severe operational environments. These environments stress the gel coat system with the combined effects of temperature and humidity cycling, ultraviolet (UV) exposure, and water. The interaction of the coating system with the specific operational environment must be examined in order to measure, understand, and successfully predict the performance of the coating system. The effects of UV exposure alone, and in conjunction with humidity exposure over time, have been recognized as having the greatest impact on the physical and chemical integrity of polymer resin-based paint and coating systems in comparison to all other common environmental stressors [53]

2.3.1 Ultra-violet (UV) Radiation / Heat

These two factors have been among the most crucial in performing accelerated testing. One of the reasons was that these factors could initiate damage by creating cracks on the matrix, thereby allowing moisture to generate further damage. In reality these factors normally cause degradation in combination. In this study the UV exposure in the environmental chamber was accompanied by heat (60°C)

UV-radiation possess as sufficient energy to penetrate a polymer specimen and interact with the constituent atoms and their electrons. One such reaction is called ionization, in which the radiation removes an orbital electron from a specific atom, converting that atom into a positively charged ion. As a result, one of the covalent bonds associated with the specific atom is broken and there is a re-arrangement of atoms or group of atoms at that point. This bond breaking leads to either scission or cross-linking at the ionisation site, depending on the chemical structure of the polymer and on the dose of radiation. Stabilisers may be added to protect polymers from UV damage. Not all radiation exposure is deleterious. Cross linking may be induced by irradiation to improve mechanical behaviour and degradation characteristics.

Figure 2-3 illustrates the position of short wavelength UV radiation which occurs in the environment and is damaging to the chemical structure of the polymer. The accelerated chamber incorporates a UV light source to simulate the effect of UV found in the natural environment.

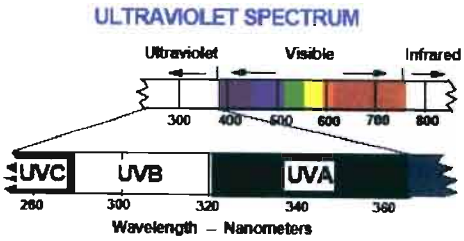


Figure 2-3: A portion of solar radiation [53]

Studying the effects of the exposure of polymers to UV radiation will help to ascertain the extent and significance of this form of degradation to the fibre reinforced material.

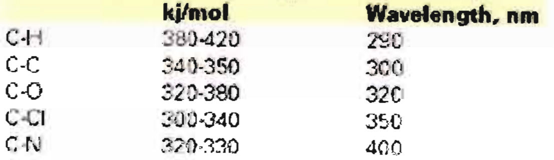
Organic polymers, including polyester resins and most organic-inorganic polymers, do not suffer electrochemical corrosion as metals do. All plastics undergo a certain amount of degradation, either by thermal, photo, chemical or mechanical attack, or by simple outdoor weathering (temperature variations, moisture, sunlight, oxidation, biological attack, and other environmental elements) [55].

Polyester degradation is affected by solar radiation, photo-catalytic admixtures, water and moisture, chemicals, oxygen, ozone, temperature, abrasion, internal and external stress, and pigment fading.[25] Out of all these, all present in outdoor weathering, the most important factors for coating degradation are moisture, elevated or lowered temperatures, oxidation and UV radiation.

When a polymer is subjected to a thermal energy greater than the bond energy that holds the atoms together, it is readily split [56]. Table 1 shows the respective energies of the various bonds. Due to the presence of oxygen in the atmosphere, the most common type of radiation degradation, photo-oxidation, occurs on all organic polymers. Again, the process will be accelerated by UV radiation and higher temperatures.

Capanescu and Cincu [4] state that the photochemical effect of sunlight on a plastic material depends on the superficial absorption properties and the chemical bond energies of the material. Light wavelengths that have the most effect on plastics range from 290 to 400 nm [4]. The wavelength of UV radiation whose photon energy corresponds to a particular bond energy in the polymer chain [Table 2-1] can break the chemical bonds (through a chain scission), changing the properties, and therefore the performance of the polymer [57]. The most damaging wavelength for polyesters is believed to be 325 nm. [55], [4].

Table 2-1: Bond Energies [4]



Bond Type	**Bond Energy, kj/mol**	**UV Absorption Wavelength, nm**
C-H	380-420	290
C-C	340-350	300
C-O	320-380	320
C-Cl	300-340	350
C-N	320-330	400

2.3.2 UV / Moisture / Heat

Materials that are resistant to sunlight or to moisture alone will often fail when subjected to sunlight and moisture in combination [23]. Ultra-violet light, along with oxygen and water, are the three primary agents that induce slow degradation of polymers [23]. Hydrolysis occurs when a plastic is exposed to water or humidity. This chemical reaction may be a major factor in the degradation of condensation polymers such as polyesters, where the ester group is hydrolyzed [25].

Laminates were exposed to condensation cycles to check the extent of the drop in strength. According to literature surveys [24], polymers absorb water. The accommodation of the water produces dimensional changes and hence internal stress. The absorbed water may also seek out and dissolve water soluble inclusions, thereby creating pockets of concentrated solutions which, either by chemical or physical means lead to loss of mechanical strength of the composite.

According to ASTM G-53 [58], the exposure cycles and temperature conditions are not restricted. The severity of the UV exposure is influenced by test temperatures and time cycles. Photo-chemical reaction begins as the UV lamps are turned on. The rate of UV degradation is proportional to time of UV exposure or temperature of UV exposure, or both. UV exposures at temperatures higher than those expected in the service environment can cause abnormal degradation. Water reactions during condensation exposure are affected by the permeability of the specimen and require time to initiate. The rate of water degradation is increased by an increase in temperature. Long hot condensation exposures can cause abnormal degradation. In this experimental study cycles used were 8 hours of UV (no condensation) at 60°C, followed by 8 hours of condensation (no UV light) at 60°C.

In comparison, the cycle used to predict natural Florida exposure is 16 hours of UV (no condensation) at 66°C, followed by 8 hours of condensation (no UV light) at 60°C. The UV lamps used in this study are UVA-340. From the study it is estimated that 3,200 hours of accelerated exposure using the set conditions of UV and condensation described above will yield results to comparable 2.5 years of natural exposure in Florida [59].

In regard to aging by hydrolytic degradation, the degree of plasticity in a polymer will increase due to long-term exposure to moisture. Moisture exposure has two important components: 1) diffusion of water into the sample and 2) plasticization of the matrix. Depending upon the diffusion coefficient of water in the polymer system, significant differences in water concentration can exist from one region of the sample to the next, imposing additional stresses on the system [60].

Theoretically [41] glass and aramid fibres and carbon fibres themselves do not absorb moisture and their physical properties remain unaffected.

2.4 Natural Exposure

This section contains brief information about the southern African climate and a data logger in use. This section has been included because the accelerated testing is intended to produce information that would eventually be correlated with real-time exposure data. A HOBO is small device capable of capturing accurate information at any place for whatever time is specified. Availability of such comprehensive and accurate information makes a meaningful contribution towards correlating accelerated data with real-time conditions. The capabilities of the data logger are mentioned below.

Some of the gel-coated specimens have been exposed to the natural environment at various locations around the country. These locations are an approximate reflection of the general climatic condition in the southern African region. The HOBO data logger is mounted next to the samples panel located in Durban. The HOBO can be launched for a specific period and to record specific data at specified time intervals. The BoxCar Pro 4.3 software is then used to download all data [110].

2.4.1 Climate

Presently climatic data is recorded and supplied by the South African Weather Bureau at most of the test locations in South Africa. The test locations are however not always near the Weather Bureau test stations.

In viewing a climatological map of the world, it is obvious that a wide range of climates exists. These different climates are a result of latitude, weather patterns, topographical and geographical features. Each class of materials is sensitive to a specific group of environmental parameters.

For the southern African climate, the winter months are generally from May to September and are characterized by cold nights and mild days, with rain in the Cape region. Summer is from October to April and is hot with the occasional rain shower.

Florida and Arizona have become accepted internationally as benchmark locations for testing. Each has a climate that allows for rapid testing, under different conditions. Florida is characterised by high intensity sunlight, high rainfall, high temperatures, and high humidity. Arizona is characterized by extremely high sunlight energy levels and very high temperatures [61].

2.4.1.1 Climatic regions in southern Africa

The southern Africa region has a wide variety of climates; from tropical wet and dry to arid or semi-arid, and even desert. The region can be divided into three geographical areas. The central plateau called the highveld, the narrow coastal plains called the lowveld, and the desert area of the Kalahari Basin [Figure 2-4]. The two major ocean currents found offshore affect the temperature of the seasons. The cold current causes moderate temperatures on the west coast, and on the central plateau the altitude tends to keep the average temperatures below 30°C [63].

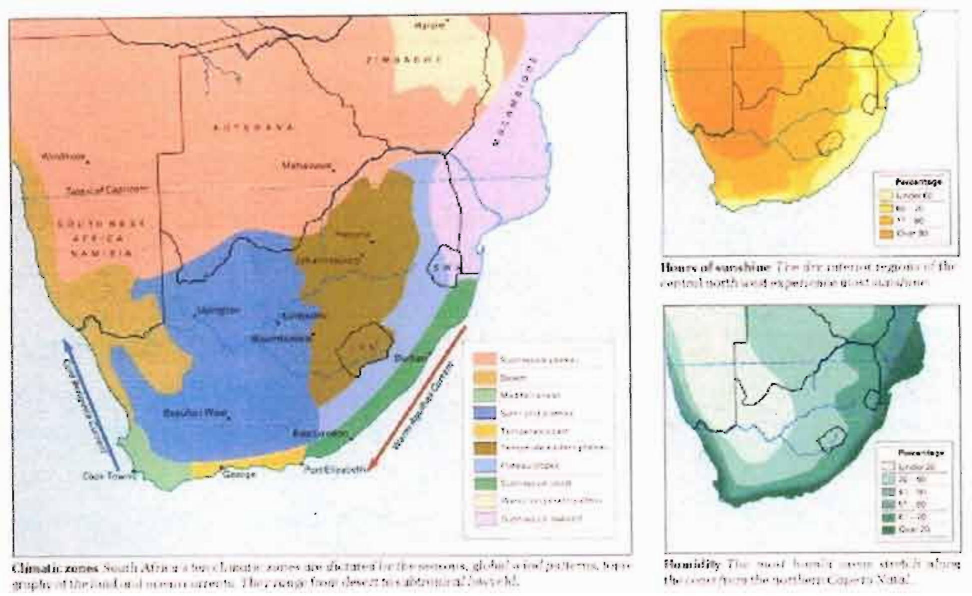


Figure 2-4: Climatic Zones in southern Africa [63]

According to the Atlas of Southern Africa [64], as shown in figure 2-4, the south-western Cape has a Mediterranean climate with hot, dry summers and cool, rainy winters. Further east, the climate is temperate, with warm summers and cool winters, and rain through out the year. From the border of the south to northern kwaZulu-Natal, the sub-tropical coast has humid, wet summers. The winters are warm, but drier than the summers. The west coast, from Namibia to Angola, is hot and dry desert, with a little rain in summer and fog along the coast. Most of the interior of South Africa is semi-arid plateau (a large flat area of land that is high above sea level), with cool, dry winters and hot summers with some rain. East of this to the central Northern Province the temperate eastern plateau has cool, wet summers and cool, dry winters. The north is hotter and dryer. The plateau slopes extends inland. This area has warm, wet summers and cool, dry winters. The sub-tropical lowveld has hot, wet summers and warm, dry winters. The sub-tropical plateau is hot and dry with some summer rainfall, which diminishes towards the west coast. Winters are rainless. More rain falls in the north, where it is hotter

2.4.1.2 Water Patterns and Temperature

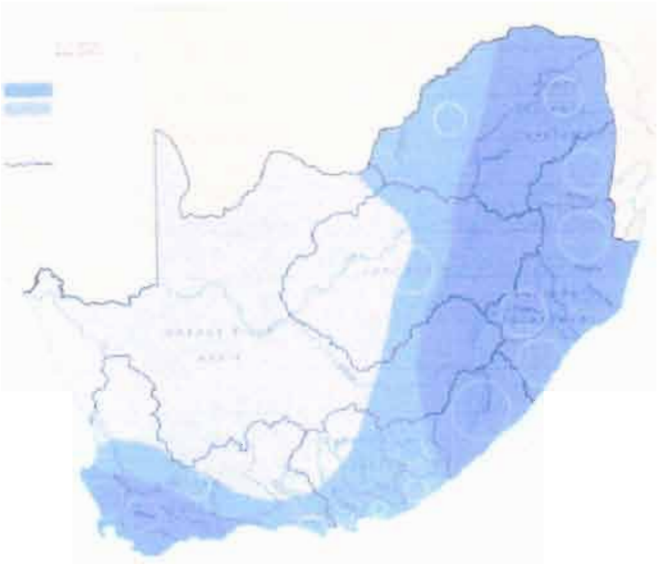
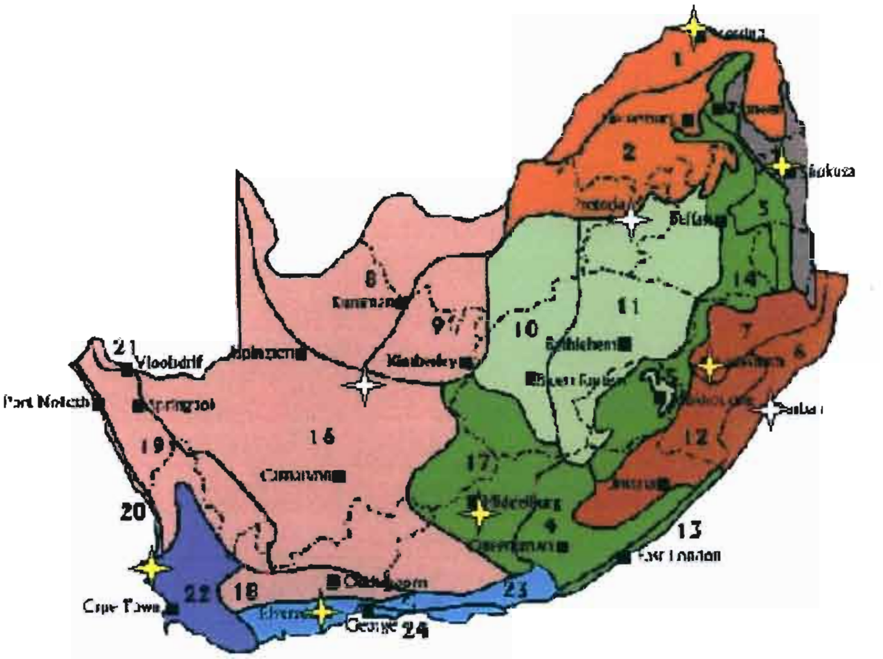


Figure 2-5: Water profile in southern Africa [64]

South Africa has three distinct rainfall regions [Figure 2-5]: the summer, the winter and the all-season regions. About 30 percent of South Africa receives less than 250 mm of rain a year; about 34 percent receives between 250 and 500 mm; 25 percent between 500 and 750 mm and the remainder more than 750 mm. The temperatures are strongly affected by altitude, latitude and ocean currents. The range of temperature is least at the coast and greatest in the interior.

2.4.2 The Test Sites

Eight different climatic regions (with diverse climatic conditions) have been identified, as illustrated in figure 2-6 below. At each of the test sites the panels are set as shown in figure 2-7. The results of this exposure tests will in future be used in conjuction with the accelerated testing in this study to establish a correlation of these exposures.



✧ ✦ The stars represent the different test sites around the country

Figure 2-6: Climatically differing regions in South Africa

There are eight sites that have been identified to represent environments typical of the southern African climate. The description of the environment e.g., high temperature is relative to the average range experienced in South Africa. The white stars represent sites where exposure testing has been started.

1. Irene (Gauteng)

Situated on the highveld. Experiences moderate rain and is cool, with frost. Test site located at Kentron.

2. Alkantpan (Northern Cape)

Dry climate with less than 100mm rain, typical of the Karoo. Extreme temperatures are experienced, high in summer and low in winter. Test site situated at the Alkantpan test range.

3. Durban (KwaZulu Natal)

Wet and humid climate at the coast. Test site located at the University of Natal.

4. Skukuza (Mpumulanga)

The surrounding area forms the lowveld region of Mpumulanga. Climate is hot and wet, typical of a tropical savannah region. Skukuza and surrounding areas are characterised by moderate rain, high temperatures, high humidity, and below-average sunshine.

5. Messina (Northern Province)

Subtropical desert or semi-desert climate typical of the northern province. Messina and surrounding areas are characterised by tropical moderate rain. The region is hot and semi-arid. Light wind during the rainy season lasts approximately. 150 days.

6. Riversdale (Western Cape)

Temperate and subtropical evergreen forests are located in the Western Cape. Region experiences all-year rain with moderate temperature typical of subtropical forests found in the area.

7. Langebaan (South Western Cape)

The Cape Town region has a weather system of its own. There is no representative location as the weather varies significantly with position. Moderate temperatures with winter rainfall can be expected. Test site will be located at the Langebaan airfield.

8. Cradock (Eastern Cape)

Temperate grasslands predominately found at the foot of the mountain range. Temperatures increase gradually as one travels along the foot of the mountain range in a northern direction. Climate is wet and cool.

Figure 2-7: Exposure panel at the University of KwaZulu-Natal

2.4.3 HOBO H8 [65]

The HOBO H8 is a climatic data logger designed to store and analyse weather data in the environment in which it is placed. The system has multiple channels and can therefore accommodate sensors which are sold as standard units. Software for the system is provided to enable the data to be analysed using a computer.

Data loggers are used around the world in many different types of applications, in indoor, outdoor and underwater environments. These are electronic instrument that records measurements (temperature, relative humidity, light intensity, voltage, pressure and events) over time. Typically, data loggers are small, battery-powered devices that are equipped with a microprocessor, data storage and sensor. Most data loggers utilize turn-key software on a personal computer to initiate the logger and view the collected data.

Data loggers are easy to use, reliable and accurate. Their small size makes data loggers ideal for mounting in out-of-the-way locations. Figure 2-8 below illustrates how the HOBO was placed inside a clear and closed plastic cover to shield it from the rain, whilst the walls were perforated to allow air flow. The HOBO was mounted next to the panel in Durban.

Figure 2-8: The HOBO encased in a plastic case (Durban)

Some data acquisition systems require the installation of a DA card in a PC and the connection and wiring of sensors. These systems work well in permanently configured, on-line applications but can be costly and difficult to implement. Data loggers significantly reduce the cost in as they are easier to implement, and can be placed in areas that permanent digital systems can not reach.

Data loggers incorporate the most recent digital technology which makes them smaller, less expensive, more accurate and more reliable. Further, data loggers don not require costly and inconvenient chart supplies because you can view the data on a PC or laptop. The features and specifications [66] are shown in Appendix G.

2.5 Environmental Interaction Effects

The long-term exposure of polymeric composite materials to extreme-use environments, such as pressure, temperature, moisture, and load cycles, results in changes in the original properties of the material. These changes in material properties translate to structural changes that can have a potentially catastrophic effect on load-bearing composite structures. Therefore the study and understanding of the long-term effect of exposure on the time-dependent visco-elastic (having viscous as well as elastic properties) properties of polymeric composite structures is crucial to their proper design, construction, and safe operation [67].

The degradation of composites could result from the following factors: loss of strength of the reinforcing fibres by stress corrosion, loss of adhesion and interfacial bond strength from degradation of fibre-matrix interface, chemical degradation of matrix material, dependence of the matrix modulus and strength on time and temperature, and accelerated degradation caused by combined action of temperature and chemical environment.

The environmental factors influence the fibres, matrix material, and interface simultaneously. Thus the degradation of composites occurs not only with the degradation of the individual constituents but also with loss of interaction between them [68].

Changes in the matrix properties due to environmental exposure are important considerations for polymer composites. Exposure to ambient temperature and moisture influences the distributions of temperature and moisture concentration inside the material as a function of both position and time. These distributions, in turn, influence the performance of the material [69].

3 CHAPTER 3

SAMPLE PREPARATION

3.1 Overview

The main objective was to produce specimens that would be suitable for compressive test and reflect the correct strength of the tested material; furthermore that the method be convenient by improving timeliness and reducing processing errors. The method of preparation of specimens is important for the analysis. In effect, a poorly prepared specimen is not worth analyzing. Whenever possible, the test specimens should be in line with the used standards.

3.2 Introduction

The confidence placed in the design data obtained from testing composite materials can depend greatly on the quality of the specimen used. Even though, in principle most of the specimens are rectangular, which suggests that specimen preparation is straightforward, there are many aspects that affect the quality of the measured data. The use of protective end tabs, for example to transfer the load to the specimen, requires that the tabs used must be well bonded to the specimen to avoid premature failure. In addition, for compression testing of these relatively thin laminates, as well as the test machine loading axially, the tabbed specimen must be symmetrical. Another difficulty regarding compression testing of composites is the prevention of buckling of specimens and minimising of stress concentrations. The document provides background information on all stages and aspects of machining and specimen preparation. In view of the wide range of materials involved and the range of equipment in use, the document concentrates on correct procedures and is not prescriptive on details such as speeds, etc.

3.3 Information on Laminates

3.3.1 Manufacturing of laminates with gel coats

Laminates were produced using the hand lay-up method. This method involved laying-up dry reinforcement and applying resin. Laying-up of laminates was carried out on glass plates polished thoroughly with the appropriate release agent to ensure that the cured laminates did not stick to the glass and damage it when de-moulded. A thin layer (500 μm) of gel coat (catalyzed with 2% of Lupersol DDM-9 methyl ethyl ketone peroxide (MEKP) initiator) was drawn on the polished glass plate surface using a wet film bar applicator to ensure uniform, reproducible and correct thickness. The gel coat was left to cure for about 2 hours. Once the gel coat was cured on a mould (glass plate), the resin was then applied. It bonded to the gel coat before it cured and the laying up was begun.

Each fabric layer was wet out using a roller brush to evenly distribute the resin and thereby remove the air pockets. Another layer of reinforcement was laid on top, after which more catalyzed resin was poured and brushed over the reinforcement. This sequence was repeated for nine layers to make the desired thickness. The layered structure is then allowed to cure. The NCS SUPREME 101 and ULTRAGEL 64 samples were press moulded at 500lb/in^2 and left to cure overnight. The disadvantage with the process is the difficulty of maintaining uniformity. Voids are common problem which makes it important to post-cure the laminates.

The TINUVIN 320, UV ASORB MET, ULTRAGEL 64 and NCS SUPREME 101 gel coats are being tested and had been selected because they contain the light stabilizers which resist the effect of ultra-violet radiation. The basic gel coat, without these stabilizers, was tested alongside these as a benchmark. This basic gel coat is of high quality coating developed for the fibreglass industry. The TINUVIN 320, UV ASORB MET gel coats and the basic gel coat are each added to UPE 1280 resin. The ULTRAGEL 64 and NCS SUPREME 101 are added to NCS 101 PA resin. Some samples without a gel coat at all, using UPE 1280 resin will be used to provide a comparison with gel coated samples.

In practice the need for resin-rich surfaces to protect structural laminates was established to improve the durability of components; to protect the laminate from the environment; to provide a smooth aesthetic finish; to eliminate the need for painting. In making a gel coat material, a polyester resin is generally used for the base. To obtain the colour, a pigment powder is blended into the resin. The resin is thickened to prevent run off by the addition of extremely fine silica powder. Certain clays can also be added to help the flow properties. Finally, extenders or fillers can be added to reduce the amount of resin needed in the gel coat and which in some cases add strength. Good mixing is critically important.

Gel coats are available in brush and spray versions and are best put down at a thickness of 0.5mm (approximately 500 g/m^2). If they are too thin, poor cure occurs and fibre pattern will result. If they are too thick, crazing and cracking can occur and the laminate will be more susceptible to cracking damage.

The long-term durability of laminates results from hydrolytic stability, UV light stability, crack resistance, tear resistance, chemical resistance, and flame retardants provided by gel coats additives. Flame retardants show intumescent properties in a burning environment, i.e. they form a foamed charred layer on the surface of the composite which, in turn protects the composite from the heat.

3.3.2 Material Tested [Appendix A]

This section gives about the resins and the respective gel coats. The types of resins used for making laminates are the polyester and epoxy resins. The gel coats are polyester-based. The gel coats have been briefly described in terms of properties and use.

If a gel coat does not have the PA (pre-accelerated) prefix, it means it does not have accelerator in it already and it will not cure (harden) no matter how much catalyst is used. Thixotropic means becoming less viscous when subjected to an applied stress, such as being shaken or stirred, and orthophthalic means the gel coat is based on orthophthalic acid. Unsaturated polyester resins would have the prefix (UP), which means they are very versatile materials. At room temperature, the liquid resins are stable for years but can be triggered to cure easily. If the resin is rigid it means once cured it is incapable of, or resistant to, bending.

3.3.2.1 Product: UPE 1280

Catalyst: MEKP
Supplier: Cray Valley
Description: The resin is a rigid, pre-accelerated, thixotropic, orthophthalic, medium reactivity, unsaturated polyester resin. The resin system is used for high structural performance and maximum durability applications. Products include high-performance boats swimming pools, tanks, car bodies, road tankers, ducting, chemical plant and food containers and is designed for hand and spray lay-up fabrication. [Appendix A]

3.3.2.2 Product: NCS 901 PA

Catalyst: Butanox M50
Supplier: NCS Resins
Description: The resin is a rigid, pre-accelerated, thixotropic, orthophthalic, medium reactivity, unsaturated polyester resin. The resin system has a medium cure rate. Ideal uses include marine application, automotive components and general industrial moldings. Resin is designed for hand and spray lay-up fabrication. [Appendix A]

3.3.2.3 Product: NCS SUPREME 101

Catalyst: Butanox M50
Supplier: NCS Resins
Description: NCS SUPREME 101 P1075 PA is a white, pre-accelerated, thixotropic, unsaturated polyester gel coat. It is formulated using unique new chemistry and raw materials selection to provide superior weathering performance and blister resistance. NCS SUPREME 101 P1075 PA is highly recommended for applications which require long-term outdoor weather resistance and blister resistance. This makes this product ideal for ocean-going yachts and power boats.

3.3.2.4 Product: ULTRAGEL 64

Catalyst: Butanox M50

Supplier: NCS Resins

Description: NCS ULTRAGEL 64 P1075 PA DURABLE WHITE is a white, pre-accelerated, thixotropic, unsaturated polyester gel coat based on Isophthalic Acid and Neopentyl Glycol. It is especially formulated to give excellent durability, colour retention and blister resistance. Ease of application, rapid air release and levelling properties have been combined with improved cure to provide a gel coat with superior performance. NCS ULTRAGEL 64 P1075 PA DURABLE WHITE is recommended for applications which require long-term weathering and blister resistance e.g. yachts, boats and swimming pools. It is a high performance marine brush gel coat.

3.3.2.5 Product: TINUVIN 320

TINUVIN 320 is a highly effective light stabilizer for a variety of plastics and other organic substrates including unsaturated polyesters, PVC and PVC plastisol. Good results are also expected when TINUVIN 320 is used in polycarbonates, poly-urethanes, polyamides, synthetic fibres and in lacquers, particularly those with a polyester, alkyd, epoxy or iso-cyanate resin base. Moreover, TINUVIN 320 is generally suitable for applications where any of the established TINUVIN range are currently used. TINUVIN 320 features strong UV absorption, excellent compatibility in a wide variety of substrates, and low volatility. It protects polymers as well as organic pigments from UV radiation, helping to preserve the original appearance and physical integrity of moulded articles, films, sheets, and fibres during outdoor weathering. TINUVIN 320 discolours slightly more than conventional UV absorbers.

3.3.2.6 Product: UV ASORB MET

Supplier: 3V

UVASORB MET has an excellent solubility in aromatic solvents and in some polar solvents. It is slightly soluble in alcohols whereas it is practically insoluble in water. UVASORB MET protects against solar radiation improving the resistance of clear coating to sunlight modifications.

3.3.2.7 Reinforcement

Reinforcements are supplied in a variety of types and physical form, and this determines the physical performance characteristics of the final laminate. Glass fibre is the most widely used and lowest priced of the major reinforcement types. Twill weave fabrics are very pliable and have excellent drape (the ability of a fabric to conform to a complex surface) while maintaining stability. This was the type used in this study.

- Product: GFHL1102/290/124
- Weight per square meter: 290g/m^2
- Supplier: Advanced Material Technology

3.4 Specimen Preparation for Compression Tests

The main objective is to produce a specimen that will be suitable for compressive test and reflect the correct strength of the tested material, and that the method be convenient by improving timeliness and reducing processing errors. The method of preparation of specimens proves to be important for the analysis. A poorly prepared specimen is not worth analyzing. Whenever possible, the test specimens should be in line with generally used standards.

3.4.1 Summary of the procedure

Samples are first labelled before cutting them to specimen sizes. The specimens are then cut out using diamond blade. The metal tabs are cut to respective sizes using guillotine. Tabs and specimens are then wiped thoroughly in acetone. The epoxy adhesive resin is mixed with the respective hardener according to the stipulated ratio. The adhesive is then drawn into the syringe. Using the syringe, one line of adhesive is applied on either side of the gauge length. Tabs are then bonded to specimens, maintaining a line of adhesive between the two. The bond is clamped in the vice and left to cure over night. The final bonded specimen may need to be ground on the edges to ensure that tabs are still parallel to specimen. The width, gauge length, and the thickness of each final bonded specimen are each measured and recorded. These specimens are then mounted on the compression jaws and compression is performed.

3.4.2 Specimens design

For the INSTRON machine compression testing, straight-sided specimens were used. Stress concentrations from gripping could cause failure, therefore, the specimens required double tabs to be bonded to both sides at the ends. The tabs distribute gripping stresses and prevent specimen failure caused by jaws damaging the specimen's surface. Aluminum, steel, composite are the three identified possible materials.

The dimensions of these specimens [Figure 3-1] are an approximate of the ASTM D3410 standard, where the specimen has a constant cross-section with tabs bonded to the ends. According to the standard the gauge length of all specimens shall be12.70 mm, the width 6.35 mm. These are then cut to size using a diamond cutting blade. The blade leaves a good surface finish on the edge of specimens. The dust produced after cutting with the diamond cutter is, however, of concern due to the nature of the fibre glass. Even with protective gear (safety glasses and dust mask) there is still a need to use a vacuum cleaner to remove the dust.

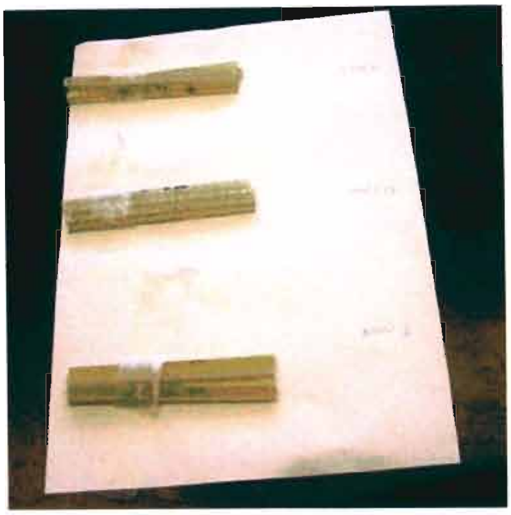


Figure 3-1: Specimen cut to size

The tabs can have the same width as the specimens. In this case tab surfaces may be ground flat after the tab bonding process if there is evidence of nonparallel tab surfaces that will cause the specimens to buckle prematurely. The material used is 2mm thick aluminum. The guillotine equipment is used to cut specimens and tabs to desired length and width. Once the tabs are of the right length, the band saw is used to cut them to the correct width. If using the band saw, it is necessary to file off the edges of the tabs. Using a band saw to cut each tab to size and file each of them off afterwards is a time consuming process.

The second type of specimens was to be tested for compression strength using the Lloyds Machine. These specimens were dog-bone shaped specimens; this design is in line with the SABS 141 Standard. A limited number of specimens were tested using the Lloyds testing machine in order to provide a comparison in terms of the numerical values for compressive modulus and stress obtained from the INSTRON, and a graphical comparison of failure in compression. Two specimens per gel coat were tested. When using the Lloyds testing machine the SABS 141 standard was used.

Dog-bone shaped specimens [Figure 3-2] were prepared for the compression tests for the Lloyds machine in line with the SABS standard.

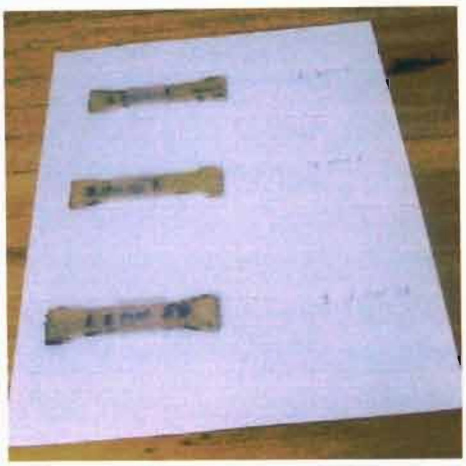


Figure 3-2: Dog-bone shaped specimens

3.4.3 Approximate specimen dimensions

The specimens are cut to flat rectangular sizes of 110 x 6.25 x 2.5 mm. The gauge length is set to 10 mm. Each tab could be 50 x 6.25 x 2 mm. The exact measurements of these dimensions had to be made for each specimen prior to testing. The dog-bone shaped specimens were 84 x 20 mm; the 20 mm width is 8 mm from each end. The gauge section was 14 mm wide, and a fillet radius between the 14 mm section and 8 mm section was 30 mm.

3.4.4 Specimen Naming

An individual specimen naming system should be devised to ensure traceability to the original sample. The naming can be with respect to the resin, type of reinforcement and a gel coat and then numbered accordingly with a marker or an engraving tool on the tabs. The number of specimens is not stipulated in the standard and hence the number of specimen can depend on the size of the sample from which they are cut.

3.4.5 Abrasion of surfaces

Abrasion was done only to the rectangular specimens, since no tabs were to be used for the dog-bone shaped specimens. The smooth surface finish of laminates and the smooth finish of the polished aluminum tabs would result in a weak bond when these are glued together. It was therefore necessary to abrade the surfaces of both the specimens and the tabs for the adhesive to be fully effective. A bastard or second cut grade file or P120 sandpaper could be used to achieve this. To save time the filing on the laminates (leaving out the gauge area) and aluminum strips is done before cutting both these to size. The other quicker method of abrading the aluminum tabs is to sandblast the aluminum sheets before cutting them to size. In this case only the laminate would need to be abraded with a file. Given that each specimen tested in compression needs four end tabs this procedure requires that a large number of tabs be made. For latest tests all specimens were sandblasted to abrade the surface.

3.4.6 Mounting and Cleaning tabs and specimens

It is important to clean the tabs and specimens when preparing to glue them together. If after abrasion there are still particles of aluminum on the tabs or dust on the specimens, the adhesive would not be fully effective and tabs would simply de-bond. The specimens and tabs should be wiped with acetone or paraffin. Either of these is good to use to clean the surfaces because in addition to cleaning off dust particles, it de-greases the surfaces and removes any other dirt that could have been picked up during cutting or handling of the specimens. When wiping specimens with the acetone it is recommendable that a clean cloth or paper be used for thorough cleaning.

3.4.7 Gluing of tabs on specimens

To glue the metal tabs to the glass-fibre reinforced composites H9940 epoxy adhesive [Appendix A] is used [Figure 3-3]. This adhesive cures at a low temperature and hence does not alter the properties of the specimen. The working time on the adhesive is twenty minutes and the specimens can be removed from the clamps after 24 hours. It requires the mixing of the resin and hardener at a ratio: 10:9, until a uniform colour appears. The smell of this adhesive is very strong and thus it is recommended that it should be opened or exposed in an enclosed, ventilated space such as the fume cupboard. The problem to address is the application since it has a short cure period. Pasting the adhesive onto the tab and specimen could be untidy when using a normal wooden spatula. Once mixed, the epoxy is extremely sticky, and needs to be applied quickly for maximum effect. However, if adhesive is drawn into a normal syringe and spread over the tab length the process is neat and saves time. Large syringes would not be desirable since the adhesive cures fast.

Figure 3-3: Gluing of tabs onto Specimens

3.4.8 Hardening in compression

The glued tabs and specimens are clamped in a vice and are left to harden under pressure. The clamping pressure should not necessarily be very high especially because for compression specimens it is recommendable to maintain a certain suitable glue thickness. Unparallel tabs and uneven gauge length would give undesirable compression test results. In the clamping vice, up to five samples can be clamped at once. The samples are ready for testing after overnight curing. It is important to ensure that tabs do not move out of place before clamping which could result in unparallel tabs or distortion of the gauge length. The key obstacle to achieving good compression results is the tendency for specimens to buckle during compressive loading. The compression test is such that the result is sensitive to the various input dimensions such as gauge length, width, thickness, etc. In future, it is important to ensure that, during and after clamping in the vice, dimensions of the final specimens are the desired ones. This can be achieved by fabricating a very simple bonding fixture to accurately position tabs on specimens and maintain accurate spacing and alignment.

3.4.9 Mounting specimens on the clamping vice

The specimens are placed horizontally and are each separated from each other using the perforated paper to avoid specimens bonding with each other. Five specimens can be fitted in the vice at one time. However if they are less that five, a scrap piece of wood could be used to fill the gap. The specimens are then clamped [Figure 3-4] and left overnight to cure.

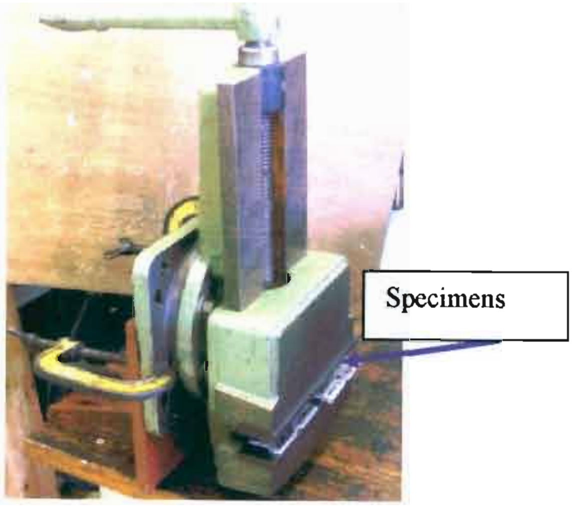


Figure 3-4: Specimens clamped in a vice

3.4.10 Mounting specimens on the press

There were a number of specimens to be prepared due to the fact that for each specimen at least three measurements were required. Each specimen has four tabs to be glued properly [Figure 3-6]. A manual press was then used as shown below, enabling many specimens to be prepared at the sane time. The press was set to about 3 MN [Figure 3-5] and left overnight for curing.

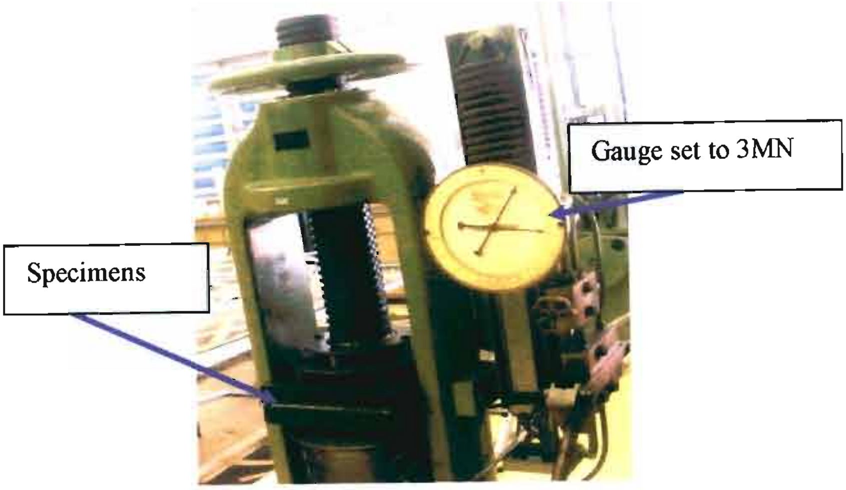


Figure 3-5: Specimens clamped in a press

Figure 3-6: Specimens ready for compression test

3.4.11 Mounting compression jaws

A set of compression jaws designed, modelled and manufactured at the University were used for testing of specimens. The compression holders were fitted to the INSTRON 1500R machine. The base of the jaw holder was bolted to the travelling cross beam on the machine.

To clamp the specimens, the jaws are designed such that thick walled cylinder with threads on the inside move the jaws allowing the jaws to come together thereby clamping the specimen. This would serve the function of moving the jaws to clamp on the specimen when it was mounted. The front of the jaws was exposed to enable the jaws to be worked free should they become "stuck" in the jaw holders. The jaw dimensions were set to accommodate standard specimen thicknesses.

3.4.12 Mounting specimens on jaws

Specimens were placed in such that each jaw would grip the full length of each tab. This could prevent de-bonding of tabs. When mounting the specimens on jaws it was important to ensure that the specimens are in the correct vertical position. This is done by placing any rectangular flat piece of metal or wood against the specimen before closing and tightening the jaws. Specimens may not fail in compression if not placed correctly in the jaws.

The jaws retaining clips are attached to the open side of the jaw holders [Figure 3-7]. Each retaining clip is slotted on the side and attached using screws. These clips ensure that the jaw grip does not rotate side ways in the holder so that the grip surfaces remained parallel during jaw travel. The jaw holder is threaded to fit the adaptor attached to the load cell. The jaw grips have grooves width wise near the bottom to fit together, with a flat tab at the bottom of the inside of the jaw holder. This tab is held in place by a screw, attaching it to the adaptor as shown below:

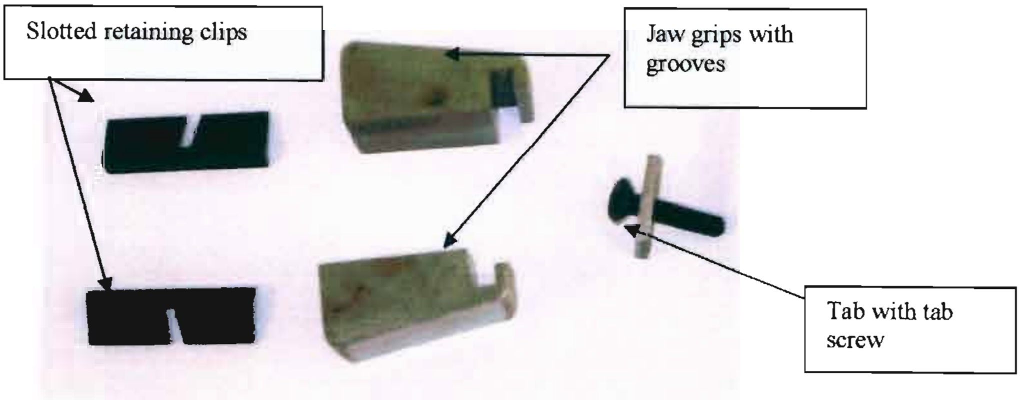


Figure 3-7: Part of the dismantled jaw

The jaw holder has a base with handles which is screwed on to its threaded end as shown below in figure 3-8.

This set of compression jaws and holder were designed, modelled and manufactured at the University for testing of specimens. After manufacture, the design was reviewed, changes implemented and jaws successfully commissioned. At the outset it was decided that the compression holders would be fitted to the INSTRON machine. The mountings on the INSTRON machine were measured so that the jaw holders could be designed to fit easily into position. The first design was primarily a block of steel with a cavity, with inclined planes machined into the centre to accommodate the jaws. The jaws were designed according to the guidelines given in ASTM D3410. The jaw holder was threaded to fit the adapter attached to the load cell. The base of the jaw holder is bolted to the travelling cross beam on the machine.

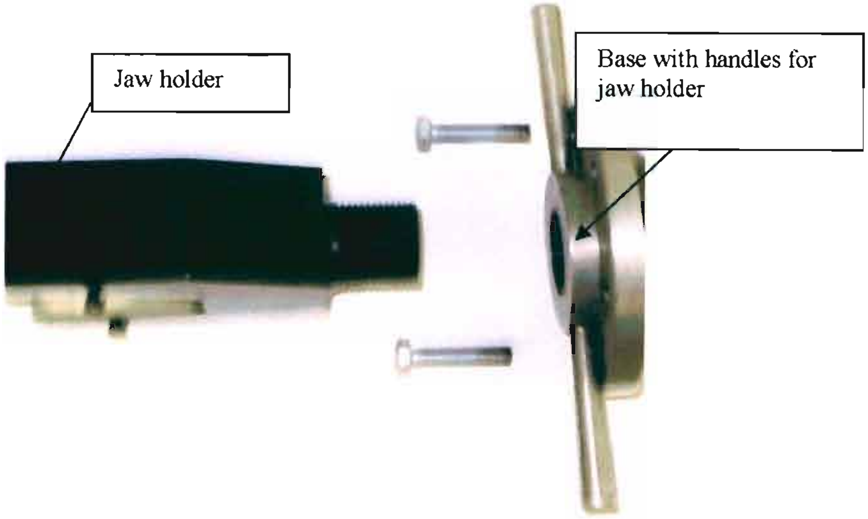


Figure 3-8: Part of the dismantled jaw

The design was subsequently changed to include guide pins that would align the top and bottom jaw holders. This was done to prevent errors in testing due to misalignment. Until this stage, initial clamping of the specimen was due to the weight of the jaw holders providing a preload. The next design change eliminated this clamping problem by incorporating tightening screws that could move the jaws allowing the jaws to come together thereby clamping the specimen. The next design revision entailed having the front of the jaws exposed [Figure 3-9]. This would enable the jaws to be worked free should they become "stuck" in the jaw holders. The jaw dimensions were set to accommodate standard specimen thicknesses. Grooves were designed into the jaws such that the jaw retaining clips would not rotate in the holder and be constrained to move so that the grip surfaces remained parallel during jaw travel.

Figure 3-9: An assembled jaw

The design was later changed to accommodate the manufactured components. This entailed changing the way the jaw holders were mounted onto the INSTRON machine and repositioning of the jaw adjustment shaft. The jaw retaining clips were redesigned so that they could be machined from angle iron. The final design of the jaw holder took into account tools available for machining the holder. A set of fabrication drawings were produced including an additional drawing for an extra set of jaws to test thinner laminates.

Below [Figure 3-10] is the supporting jig. The jig is suitable for supporting a specimen in the testing machine without exerting lateral pressure to an extent that may affect the test result. The ends must be clamped centrally in the jig such that the ends protrude equally. [108]

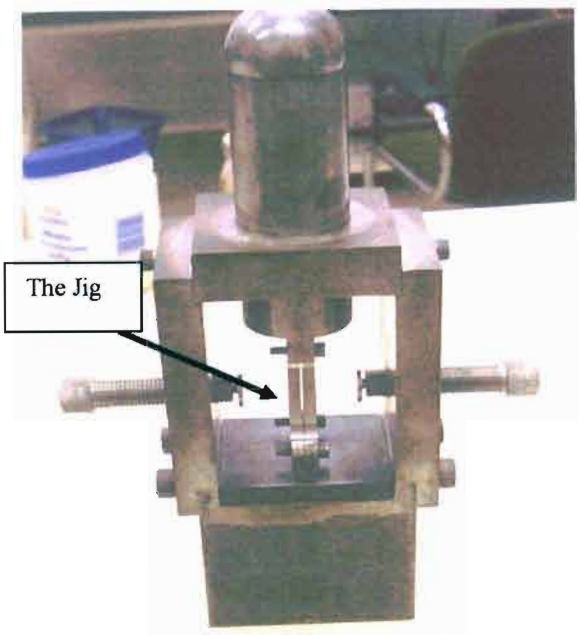


Figure 3-10: The Lloyd machine jig fixture

4 CHAPTER 4

EXPERIMENTAL TESTING

4.1 Overview

Hot and humid environments can degrade some aspects of a material's performance particularly the compressive strength [58]. Water absorption by epoxy resins leads to a reduction in glass transition temperature and to a softening of the resin with loss of stiffness and strength which causes fibre micro-buckling and premature laminate failure [60].

4.2 Introduction

The effects of environmental exposure on the chemical nature of composites were considered. The effects include the changes in the physical and mechanical properties of the composite materials. Such changes are typically related to the degradation or deterioration of the composite material.

4.3 Exposure Testing

The samples were subjected to testing cycles: [Appendix (A)], as summarised below:
Time: 862.12 hours
Temperature: 30 °C
Time: 1606 hours
Temperature: 30 °C
Duration: 2500 hours
Temperature: 30 °C
Duration: 3000 hours

Temperature (UV): 60°C

Temperature (Condensation): 60°C

The specimen panel is positioned in such a way that specimens are 150 mm from the UV source lamp and are parallel to the lamps. Cycles were stopped on Friday evenings and re-started on Monday mornings. This procedure is within the specifications of the ASTM standard.

4.3.1 Equipment

4.3.1.1 Environmental testing chamber

The chamber [Figure 4-1] is located in the Mechanical Engineering building at the University of KwaZulu-Natal and was built by the School of Mechanical Engineering in 2001. Specifications are as follows:

Inside volume: 0.844 cubic meters

Operating temperature: 25°C - 70°C

Four Fluorescent UVA 340 lamps are fitted. This type of lamp is the best available for simulating sunlight in the critical, short wavelength region between 365nm and the solar cut-off of 295nm. Its peak emission is at 340nm. [70]

Figure 4-1: The Environmental Test Chamber

4.4 Properties to be observed

The properties for which the laminates were checked for at each time interval were cracking, chalking, discolouration, mass change and mechanical properties. Cracking refers to matrix cracking. Chalking is the formation of fine powder on the surface of the gel coat film due to weathering. Discolouration is the change in colour. Mechanical properties refer to compressive stress. For each type of gel coat, chalking, cracking and discoloration are checked both visually and by using a microscope. For mass changes, measurements were taken on a digital scale. The strength properties were obtained using an INSTRON universal testing machine. Some samples were immersed in water in order to assess the effects of water ingress on the gel coat and the whole laminate.

Other properties checked for were: the gloss, mass change, colour analysis, glass transition temperature changes, and strength by means of compression testing.

Gloss change was examined using a gloss-meter, and colour analysis was done using the spetrophotoscopy, which is used for evaluation of spectroscopy (the study of the emission and absorption of light and of the electromagnetic spectrum). Gloss is important in verifying the quality of a coating.

The glass transition temperature, Tg, can be used to explain the changes in mechanical properties. A Differential Scanning Calorimetry (DSC) is used to determine the heat flow associated with material transitions as a function of time and temperature or changes in heat capacity using minimal amounts of material.

4.5 Compression Tests

Since the goal of this work is to look into the broad-based problem of environmental degradation, in this study the problem was narrowed to establishing the effectiveness of specific gel coats against ultraviolet (UV) degradation and moisture ingress. These were the two main aspects that were highly relevant.

(1) Studying different degradation processes in the polymers to estimate the gel coat performance in service; and

(2) Detecting and quantifying early stages of degradation on the gel coats.

To address these issues a testing program was devised to test the laminates response to accelerated environmental tests without any physical modifications. After the tests, the material was inspected visually then subjected to strength testing. Differential scanning spectroscopy technique, spectrophotoscopy and reflectance were also used.

Composite materials and structures are designed to withstand different amounts and types of load. To check the mechanical changes of laminates the compression test is preferred. Better understanding of compression failure is important to predict more accurately the strength changes resulting from the use of different resins and fibre. According to the 'ASM Handbook' [69], axial compression testing is a useful procedure for measuring the plastic flow behaviour and ductile fracture limits of a material. The use of specimens having large L/D ratios should however be avoided to prevent buckling and shearing modes of deformation.

According to Tamopol'skii, Zhigun, Polyakov [71], despite large amount of information obtained from flexure tests, bending tests are often considered secondary and not recommended for use in the calculations for composite structures. The reason for this is that the theory on bending uses a number of assumptions. As a result reliable bending tests results which correspond to theoretical assumptions can be obtained only by means of careful selection of loading conditions and specimen dimensions.

Flexural strength does not show as good correlation with resin modulus as does compression strength. Lower compression strength resulting from lower resin modulus leads to lower flexural. The reason is that when a composite is weaker in compression, failure will be initiated on the compressive side in a flexure test, and hence the flexural strength reflects the compressive strength of the laminate. Behaviour under tensile load depends on the stiffness and strength of the fibres, rather than the matrix material, since these are far higher than the matrix material on its own [72].

A flexure load involves the ability of the material to bend. Flexural loads combine tensile, compression and shear loads. When loaded, the upper surface of the laminate is put into compression, the central portion experiences shear, and the lower face undergoes tension [73].

In compression testing, however, the adhesive and stiffness properties of the binder are crucial in order to maintain the fibres as straight columns and prevent buckling. Shear load as well involves trying to slide adjacent layers of fibres over each other. Here, the matrix transfers the stresses across the composite. For the composite to perform effectively, the matrix must exhibit good mechanical properties along with strong adhesion to the reinforcing fibre. There are two main types of shear associated with composites: In-plane shear: the measure of fibre matrix bond within each lamina (or layer); and inter-laminar shear: The measure of bond strength between layers

Compression test determines behaviour of materials under crushing loads. Compressive stress and strain are calculated and automatically plotted as a stress-strain diagrams which is used to determine elastic limit, proportional limit, yield point, yield strength and, compressive strength.

Failure mechanisms of composites can be very complex, with multiple layers stacked in different orientations. Cracks do not necessarily propagate perpendicular to the direction of loading because fibres may bridge such a crack and divert its propagation [68]. A sequence of tests may be required to understand how initial damage creates a reduction in properties to cause a failure.

Failure criteria of the coating system must be based on a parameter that can be visually assessed as well. Visual assessment might include change in gloss or evidence of micro-cracking.

4.5.1 Equipment (The Universal Testing Machines)

4.5.1.1 (INTRON 5500R) [Figure 4-2]

Specifications [74]:
Maximum Load Range: 10 kN
(Tension, Compression)
Rated Load (Speed Capacity): 10 kN up to 500mm/min
5 kN between 500 and 1000mm/min
Testing Speed Range: 0.05 to 1000mm/min
For the test performed, the following specification was used:
Speed: 1.26 mm/min
Mounting: Vertical in compression jaws
Supplier: Front Edge Technologies

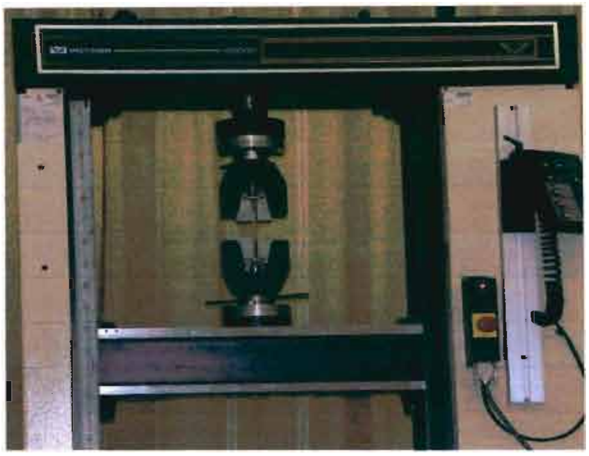


Figure 4-2: The Universal Testing Machine (INTRON)

4.5.1.2 Lloyds Machine LR 30K [Figure 4-3]

Figure 4-3: The Lloyds fixture connected to the machine

4.5.2 Procedure

The nine layer laminates were made by hand lay up at the Cray Valley laboratory during April 2003. The exposure specimens were cut to 150 x 50 x 3mm from the original 500mm x 625mm sheets. These specimens were cut using a band saw. Each gel coat was approximately 0.5mm thick. After exposure these rectangular specimens were further cut down to 110 x 6.5 x 3mm strips. These were then clearly marked, abraded and cleaned in order to attach tabs to each one.

The following gel coats were brushed onto the laminates
a.) TINUVIN 320 (abbreviated as I TIN)
b.) UV ASORB MET (abbreviated as MET)
c.) No UV absorber (abbreviated as NUV) (basic gel coat without UV additive)
d.) ULTRAGEL 64 (abbreviated as ULT)
e.) (NCS SUPREME 101 (abbreviated as SUP)

For the INSTRON compression test performed, the following specification was used:
Speed: 1.26 mm/min
Preload: 5 N
Mounting: Vertical in compression jaws

For the Lloyds compression test performed, the following specifications applied:
Speed: 1.3 mm/min
Preload: 1 N
Mounting: Vertical in compression jaws

4.6 Mass Change

Specimens were removed from the chamber, dried and weighed to three decimal places. Masses were compared to masses recorded before specimen exposure.

4.6.1 Apparatus

Type: Digital Sartorius (ISO 9001) [Figure 4-4]

Specifications:

- Maximum mass: 110 g
- Decimal: 0.1 mg

Figure 4-4: The Digital Scale

4.7 Gloss Change

Measurement of Gloss is an essential part of exposure evaluation programs [72]. Gloss is one of the first properties that is affected during weathering exposure. A smooth surface would reflect everything at the angle of incidence and would thus have a gloss value of 100. Any surface roughness or other imperfection would cause a percentage of the light beam to scatter. This would reduce the amount of light that is recaptured and therefore reduce the gloss value.

4.7.1 Equipment

To measure the gloss a Dr Langa type reflectometer [Figure 4-5] was used. The REFO 3 D is a portable three-angle reflectometer designed for safe and easy application everywhere in production and in the laboratory. The results can be sent via interface RS 232 C to a printer for clear documentation or to a PC using PC-software REFO QC for individual evaluation. REFO 3 D is powered by mains or batteries and stores all measurements made in off-mains condition (up to 350). The stored measurements can be printed or sent to the PC. Involved calibration of measuring instruments takes time and can cause errors which may be costly in subsequent single or series measurements.

Figure 4-5: The Gloss meter

4.7.2 Procedure

Once the specimens had been removed from the Environmental Chamber the Gloss reading were taken. The Dr Lange Gloss meter was set to 60°. As the test is not absolute but comparative, the unexposed specimens on each type of gel coat were used as a control. Five readings were taken on each specimen and, in addition, a comparison was made with the control specimens.

4.8 Colour Analysis

This test measures the percentage of light transmitted or reflected at each wavelength in the visible spectrum (400-700 nm) and yields a spectral power distribution or either reflectance or absorbance data. The sample's colour is also converted to L*a*b* coordinates. If a sample standard is available, the spectrophotometer will also yield ΔE values for assessing visible colour differences. Each spectral power distribution that is produced is specific to the colorant or mixture of colorants used in the object. It may be broad or narrow and have one or more peaks depending on the colorant. The shape describes the colour in a two-dimensional plot [75].

4.8.1 Equipment

The spectrophotometer is at NCS Resins Company. Colour Spectrophotometer (DataColour Spectraflash SF300) D65 / 10 degrees. Spectrophotometer [Figure 4-6] was used for evaluation of Spectrophotoscopy (i.e. the study of the emission and absorption of light and of the electromagnetic spectrum). This instrument performs basic colour analysis, including colour classification, colour matching, & shade sorting.

Figure 4-6: The Spectrophotometer set-up

4.8.2 Procedure

The samples were then placed on a spectrophotometer for colour analysis. The clear laminates were backed with a white background and white laminates were not backed. From this analysis: DE (total colour difference), DL (luminosity difference), DC (saturation difference); DH (shade difference); DA (green-red difference scale CIELab); DB (yellow-blue difference scale CIELab), values were found. A plot of reflectance (percentage) versus wavelength was produced for each specimen. The respective control was plotted on the same axis.

4.9 Thermal Analysis

The glass transition temperature (Tg) is a property of a polymer and is defined as the temperature at which the polymer goes from a rubbery to a glassy state without any change in phase, i.e., local molecular motion is hindered. Below this temperature, polymeric materials undergo considerable changes in their physical properties, becoming stiff instead of flexible. Apart from hardness and brittleness, other properties that are affected by the Tg are thermal expansion coefficients, heat capacity, and dielectric constants.

The glass transition temperature is evaluated using one of the different thermal analysis procedures. Polymers are composed of repeat units. The glass transition temperature T_g is determined by the molecular structure of these repeat units. In the early stages of the degradation the repeat units remain primarily unchanged. There may, however, be secondary factors that influence the glass transition temperature. These include molecular size, extent of cross-linking and concentration of plasticizer.

Chain scission, that is, breaking up of the polymer chain, creates more free chain ends and thus results in a lower T_g. A decrease in plasticizer concentration through diffusion or volatilization results in a increase in T_g. Increasing cross-link density increases T_g. All of the above processes that affect T_g occur in varying degrees depending on distance from the surface. In order to be accurate measurements of T_g have to be therefore have to be taken in a narrow band of material.

Measurement of glass transition temperature can be done by differential scanning calorimetry (DSC), or the related differential thermal analysis (DTA), and dynamic mechanical thermal analysis (DMTA). For the DSC method, the sample temperature is held at the target value during the test by altering the power to compensate for exotherms or endotherms. This is achieved using feedback. The power input is recorded as a function of time and T_g is shown as the change in slope of the thermogram. For DTA, the sample is heated at a chosen rate and the temperature rises at a constant rate. When a physical transition, eg. phase change or chemical reaction occurs, the temperature rise varies. For exothermic reactions, the temperature rises more quickly than the target and for endothermic reactions, the temperature rises below the target rate. Dynamic mechanical thermal analysis [25] involves deforming the sample cyclically and measuring the load and deformation continuously. The storage modulus E', loss modulus E'' and loss tangent $\tan\delta$ are determined. The peak of the tanδ is taken to be at T_g. Samples should be taken from the surface. However practical specimen preparation considerations may hinder obtaining a profile of the depth accurately.

4.9.1 Equipment

The Differential Scanning Calorimeter was set-up as shown below [Figure 4-7].

Figure 4-7: The Differential Scanning Calorimeter set-up

4.9.2 Procedure

A thermal analysis was performed on all specimens using Differential Scanning Calorimetry (DSC). The technique provides quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes of materials during physical transitions environmental degradation. For glass transition measurement specimens had to be presented in the form of powder. Each test needed about one milligram of powder. Each sample powder was collected on a clean sheet of paper and collected into a packet as shown in figure 4-8 below. Metal particles from the file itself, if any, were not going to affect the results. Using a file does not generate a lot of heat to the extent of changing the properties of the material.

Figure 4-8: Packets of ground samples

4.10 Aqueous Exposure

The main objective of this experimental investigation is to study the absorption behaviour of fibre-glass reinforced epoxy matrix composite laminates immersed in distilled water, in ambient temperatures, and its effect on the mechanical properties. This phenomenon represents a flow of aqueous solution through semi-permeable membranes, and particularly through cellular membranes. A flow of solutes through a membrane wall occurs due to difference in concentrations. This was a comparative study carried out to evaluate the properties of dry and water immersed specimens, and to investigate damage caused by the aqueous environment and temperature. Such data can be used to calculate effective diffusion constants for water absorption in these laminates.

4.10.1 Osmosis Effects

The uptake of water causes an osmotic process. This could lead to de-lamination of the gel coat under circular blisters [64]. It is well known unsaturated polyester, epoxy resins and their laminate plies behave like osmotic membranes [76]. In the worst case this can lead to loss of properties. The threshold strain for the matrix crack initiation increases when the laminated are immersed in water in comparison to that of a dry environment [77].

4.10.2 Procedure

Laminates were immersed in clean water in a plastic container at room temperature. The test specimens of size 148 x 48 mm, similar size to other specimens subjected to accelerated exposure testing in the environmental chamber, were cut using diamond cutting machine from the prepared panel. These were labelled and then weighed accurately using an electronic balance. The samples were exposed by immersion in water for 2 months. The water was replaced with clean water at intervals. The appropriately labelled samples, whose dry weights were noted prior to inserting into the water, were withdrawn from the water after 2 months, dried and weighed accurately using the same balance to note the difference consequent to immersion. These samples were then subjected to compression testing. The strength data collected on was compared with the values obtained on dry (i.e., unexposed) samples.

5 Chapter 5

RESULTS

5.1 Overview

For all three types of gel coats a slight decrease of between 0.124% and 1.64% by mass, was recorded. The gel coats with no UV additives changed to a dark yellow colour while the remaining specimens showed no visible colour change after 1606 hours of exposure. No cracking or chalking was observed on any specimens. Based generally on the maximum compressive stress and the modulus obtained from the compression tests, the exposed specimens have higher strength after exposure.

5.1.1 Change in weight

Initial weight loss of a polymer exposed to thermo-oxidative environment may occur due to loss of moisture and residual volatiles and is not related to polymer breakdown. Usually, after several hundred hours of exposure, the sample weight stabilizes and any additional weight loss is indicative of thermo-oxidative degradation. Once polymer degradation occurs, the evolution of gaseous degradation products accompanies weight loss [78].

Change in mass was determined using the digital mass scale. For all three types of gel coats there is a decrease in weight as shown in tables and figure below [Tables: 5-1, 5-2, 5-3, 5-4, Figure 5-1]. The mass change could be due to the drying of samples. This can be attributed to loss of volatile matter and moisture from the specimens. The mass gain or loss was calculated according to the following equation [Equation 1]:

$$\Delta M = \frac{M_{Exposed} - M_{Un\exp osed}}{M_{Un\exp osed}}$$ **Equation (1)**

Table 5-1: Change in mass (800 hours)

Specimen	Mass Unexposed (g)	Mass Exposed (g)	Mass difference (g)	ΔM
Met 6	33.74	33.643	-0.097	-0.0028
N UV 1	32.23	32.189	-0.041	-0.0012
I Tin 7	32.908	32.189	-0.719	-0.022

Table 5-2: Change in mass (1600 hours)

Specimen	Mass Unexposed (g)	Mass Exposed (g)	Mass difference (g)	ΔM
Met 16	35.54	35.3	-0.24	-0.0067
N UV 2	32.81	32.7	-0.11	-0.0033
I Tin 3	34.65	34.5	-0.15	-0.0043

Table 5-3: Change in mass (2500 hours)

Specimen	Mass Unexposed (g)	Mass Exposed (g)	Mass difference (g)	ΔM
Met 4	34.64	27.26	-7.38	-0.270
N UV 1	32.2	27.44	-4.76	-0.173
I Tin 1	33.97	23.95	-10.02	-0.418
K404	35.34	30.05	-5.29	-0.176

Table 5-4: Change in mass (3000 hours)

Specimen	Mass Unexposed (g)	Mass Exposed (g)	Mass difference (g)	ΔM
NUV 3	33.203	33.145	-0.058	-0.00174
NUV 8	32.695	32.157	-0.538	-0.0167
NUV 4	32.179	32.139	-0.04	-0.00124
I TIN 35	34.295	32.359	-1.936	-0.0598
I TIN 4	33.929	33.872	-0.057	-0.00168
I TIN 5	33.588	33.519	-0.069	-0.00205
MET 8	34.186	34.133	-0.053	-0.00155
MET 6	33.74	33.627	-0.113	-0.00336
MET 2	35.457	35.383	-0.074	-0.00209

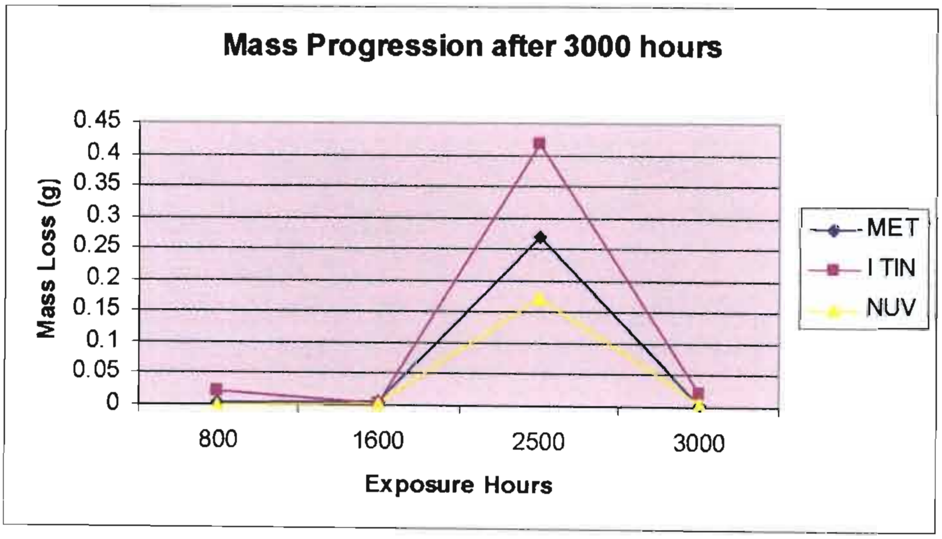


Figure 5-1: Progressive mass change

5.3.2 Colour Analysis

The specimens with no UV additives changed to a darker yellow in colour. Remaining specimens; (with TINUVIN 320 and UV Met) showed no visible colour change after the 800, 1600 and 2500 hrs of exposure. (A slight change was beginning to show after 800 only on the specimens with no UV additive [Figure 5-2]). The uncoated side of samples immersed in water changed colour to white. The colour analysis was performed with a spectrophotometer, after 3000 hours of exposure.

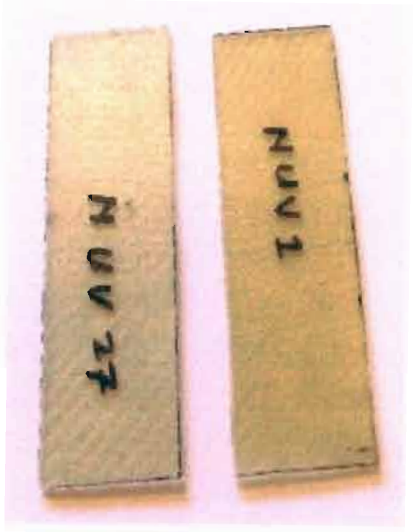


Figure 5-2: NUV 27 was unexposed; NUV 1 was exposed

Spectrophotometer Results

After 3000 hours, the yellowness index on gel coats with no UV stabilisers increased to almost double that of the unexposed specimen. Results on the rest of the specimens reflected only a slight increase of yellowness indices.

Spectrometer

The spectrometer is the most important element of any spectrophotometer, because it separates incoming light into wavelength bands and it measures the amount of light present in each. A spectrometer typically consists of the following: Incoming light, via optics, from sample and/or reference beams; A diffraction grating, separating light by wavelength, and focusing the dispersed light on a fixed array of photo-detectors; sensing the amount of light, and outputting electrical currents; Amplifiers and analogue to digital data processing, converting the currents to digital information for computer input. [74][79] Below are the tables for colour analysis of the various specimens [Table 5-5, 5-6, 5-7].

Table 5-5: NUV (colour analysis)

NUV 16 (standard or unexposed)	DL*	Da*	Db*	DC*	DH*	DE*
NUV 8	-3.38	-0.71	9.88	9.8	-1.48	10.47
NUV 3	-6.74	-0.28	10.35	10.18	-1.89	12.35
NUV 4	-5.13	-0.52	9.3	9.19	-1.52	10.63

Table 5-6: MET (colour analysis)

MET 17 (unexposed)	DL*	Da*	Db*	DC*	DH*	DE*
MET 2	-2.91	0.11	2.04	1.95	-0.6	3.56
MET 8	-1.98	0.12	1.53	1.46	-0.49	2.5
MET 6	-2.07	0.03	1.5	1.45	-0.4	2.56

Table 5-7: I TIN (colour analysis)

I TIN 48 (unexposed)	DL*	Da*	Db*	DC*	DH*	DE*
I TIN 4	1.04	-0.8	4.32	4.39	-0.2	4.51
I TIN 5	0.95	-0.73	2.28	2.39	0.17	2.58
I TIN 8	-0.8	-0.62	2.1	2.18	0.12	2.33

The following tables show the respective yellowness index for each specimen [Tables 5-8, 5-9, 5-10, Figure 5-3].

Table 5-8: NUV

Yellowness Index	Specimens
26.88	NUV 16 (unexposed)
42.16	NUV 8
42.06	NUV 4
44.15	NUV 3

Table 5-9: MET

Yellowness Index	Specimens
28.25	MET 17 (unexposed)
32.28	MET 2
31.2	MET 8
31.19	MET 6

Table 5-10: I TIN

Yellowness Index	Specimens
28.93	I TIN 48 (unexposed)
34.93	I TIN 4
32.04	I TIN 5
32.3	I TIN 8

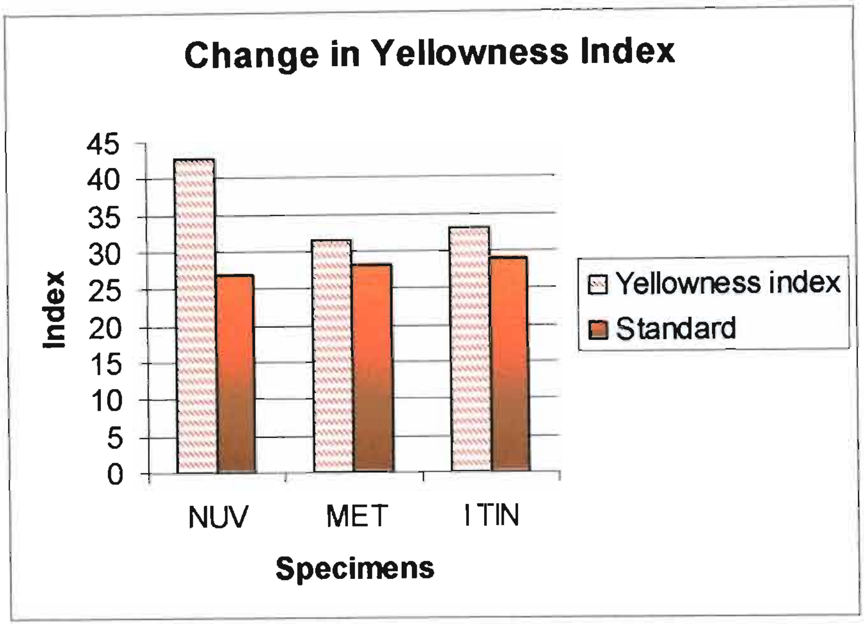


Figure 5-3: Yellowness Index Change

Graphs of wavelength versus the respective index are shown on the spectrophotometer print-out in Appendix C.

5.3.3 Mechanical Degradation

Mechanical degradation mechanisms are irreversible processes that are observable on the macroscopic scale. These degradation mechanisms include matrix cracking, de-lamination, interface degradation, fibre breaks, and inelastic deformation; and thus have a direct effect on engineering properties such as bulk stiffness and strength. In some cases, mechanical degradation mechanisms dominate only after chemical degradation mechanisms have modified the polymer properties in such a way that loads and stresses are not tolerated in the aged materials as they would be in the unexposed material [78]. When observed under the microscope at 100X magnification, none of the specimens showed signs of cracks. Chalking was not visually observed on any specimens.

Selected specimens were removed from the environmental chamber for compression testing. For comparison purposes for each type of gel coat, both the exposed and unexposed specimens were tested in compression. Compression strength of exposed specimens was graphically related to those of unexposed specimens. For each type of gel coat, four samples were tested.

The formulas employed by the INSTRON machine software to calculate, present, and graph stresses and strains are presented below:

Strain = Change in length (ΔL) over original length (L)

Strain, $t = \Delta L / L$

Stress = Force (F) divided by Area withstanding Force (A)

Stress, $s = F / A$

Young's Modulus E = Stress (s) / Strain (t). This is a property of a material

$E = s / t$

Tabs

Tabs were necessary to ensure a uniform stress distribution along the test specimen. These tabs [Figure 5-4, 5-5] were prepared for specimen testing after 1600 hours.

For the compression testing after 2500 and 3000 hours Aluminium end tabs were still used. The tabs are made of 2mm thick aluminium strip. These were cut to size (14 x 50mm) using a guillotine. A 6.5mm slot was centrally machined onto the tabs to a depth of about 1mm. The gauge length (length between tabs from either end) of the compression specimens averaged 10 mm. The slotted side of the tabs were shot-blasted and the specimens were abraded using a file to ensure effective adhesion. Both tabs and specimens were then wiped with acetone and bonded together using H9940 epoxy adhesive.

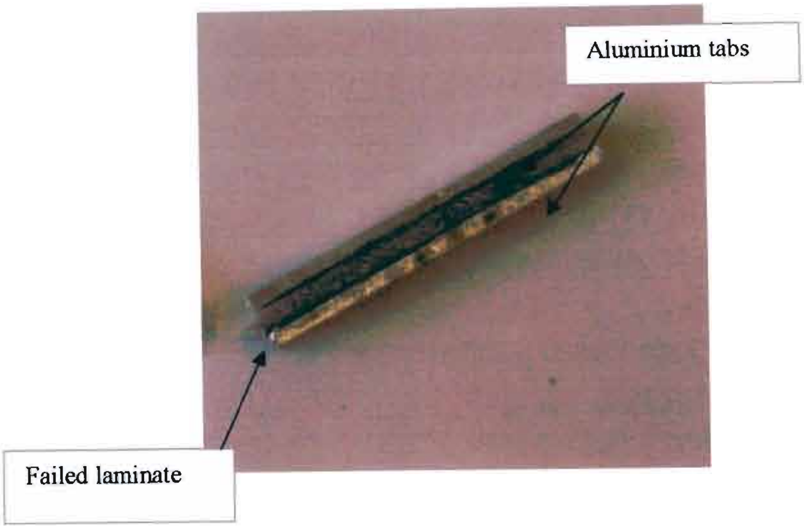


Figure 5-4: Tabs bonded to a specimen (1600 hours)

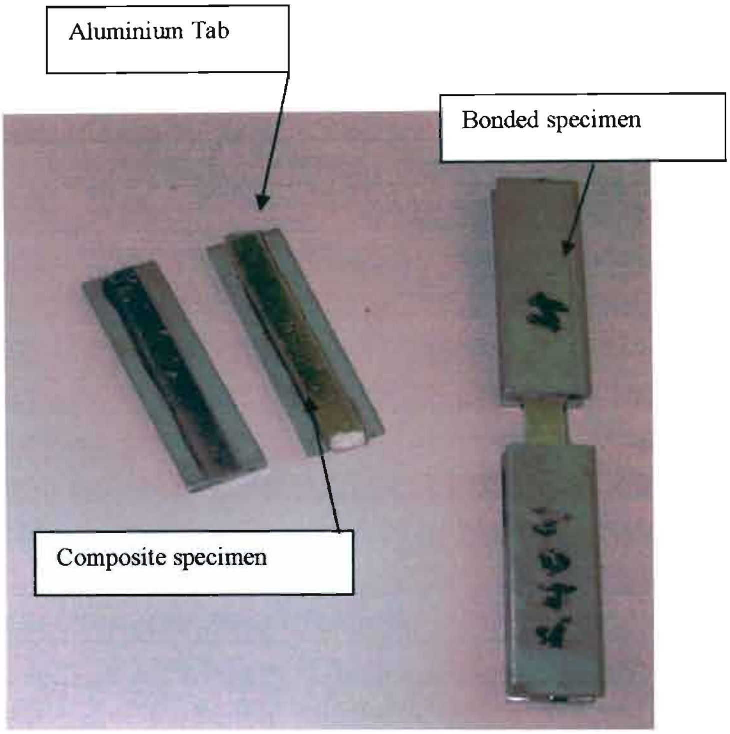


Figure 5-5: Tabs bonded to specimens (after 2500 hours)

The Lloyds Testing Machine was used to clarify the flat portion on the compression testing from the INSTRON stress-strain test results. The thinking was that it would be unlikely to have different machines give the same type of slippage, if slippage was the cause of this problem.

For the SABS 141 procedure [108] supporting jigs were used rather than the tabs. They support the specimens without exerting lateral pressure to an extent that may affect the results. The specimens were mounted symmetrically onto the jig and were allowed to protrude by about 1.5 mm from each end [Figure 5-8]. The clamping of the jig had to be firm but not excessively so (the fastening nuts finger tight).

In this SABS 141 procedure, the width and thickness of specimens were accurately measured before the test. These dog-bone shaped specimens [Figure 5-9] have to fail in the gauge length (thin section) [Figure 5-6] for the results to be valid. If failure occurred at the ends then those results were disregarded [Figure 5-7].

The Lloyds Testing Machine was employed to carry out compression on six specimens to establish reliability of the INSTRON testing machine results. The Lloyds tests were to give clarity with regards to the linearity (the flat part) on the compression testing graphs from the INSTRON stress-strain test results.

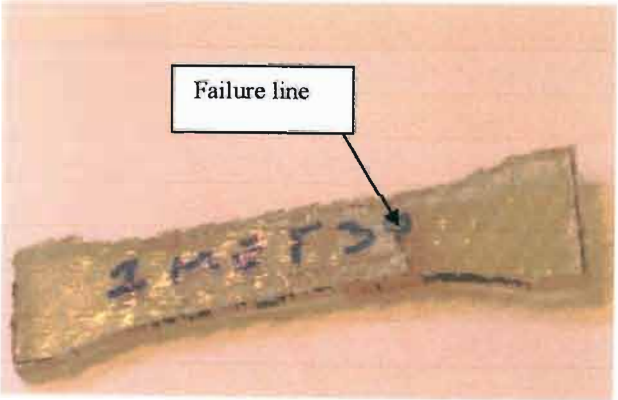


Figure 5-6: Lloyds 'correctly' failed specimen

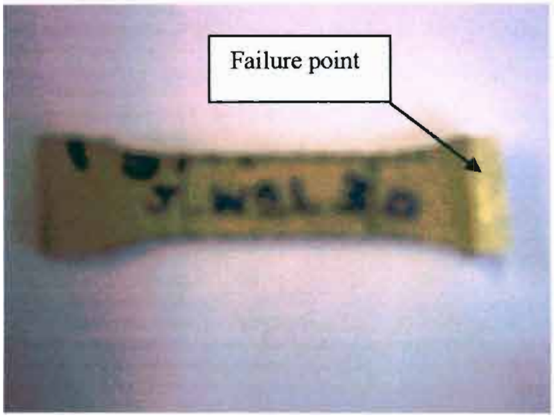


Figure 5-7: Disregarded failure type

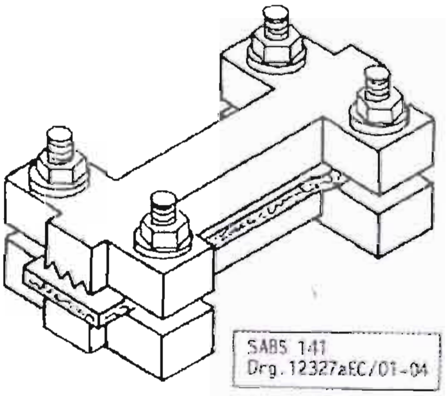


Figure 5-8: Specimen clamped in the jig [108]

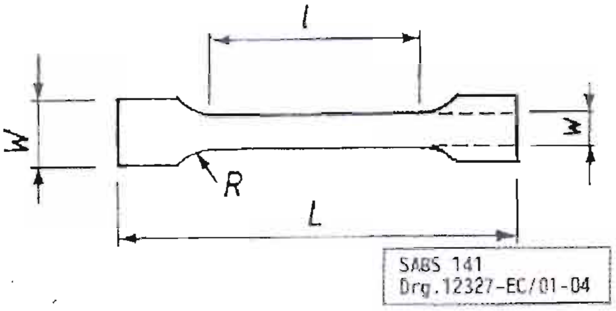
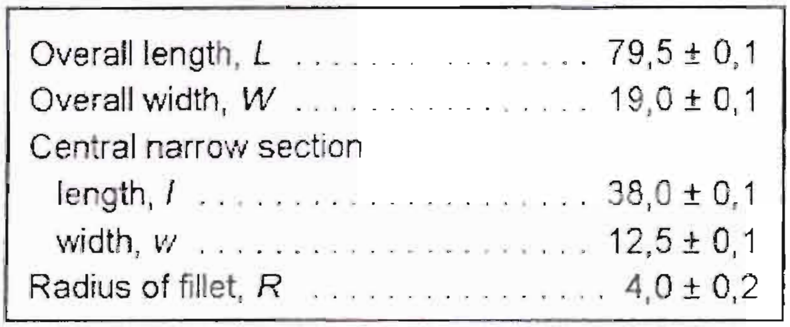


Figure 5-9: Labelled dog-bone shaped specimen [108]



Overall length, *L*	79,5 ± 0,1
Overall width, *W*	19,0 ± 0,1
Central narrow section	
length, *l*	38,0 ± 0,1
width, *w*	12,5 ± 0,1
Radius of fillet, *R*	4,0 ± 0,2

Above are the specimen dimensions according to SABS 141

5.3.3.1 Failure Modes

Figure 5-10 below illustrates the modes of deformation in compression testing. (a) Buckling, when $L/D > 5$. (b) Shearing, when $L/D > 2.5$. (c) Double barreling, when $L/D > 2.0$ and friction is present at the contact surfaces. (d) Barreling, when $L/D < 2.0$ and friction is present at the contact surfaces. (e) Homogenous compression, when $L/D < 2.0$ and no friction is present at the contact surfaces. (f) Compressive instability due to work-softening material [80].

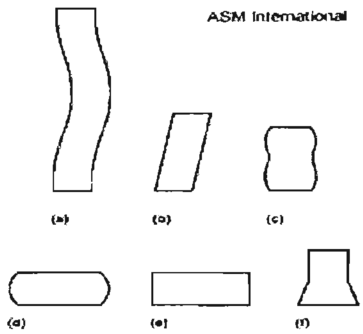


Figure 5-10: Types of Failure Modes [80]

For the manufactured compression specimens, the L/D ratio is 1.5 and typically conditions (d), (e), and / or (f) were thus expected in accordance with the theory above [80].

Failure modes depend largely on lateral support provided to the specimen during loading. If a fibre buckles, the matrix/fibre interface may fracture in shear, and lead to ultimate failure as observed in figure 5-11 below. The other failure mode is pure compression [Figure 5-12]. In this case, the fracture surface is likely to be at an angle of about 45° to the direction of loading [81]. The outer plies of the specimen buckled. The compressive strength results are summarized below [Tables: 5-11, 5-12, 5-13; Figures: 5-13, 5-14, 5-15, 5-16, 5-17].

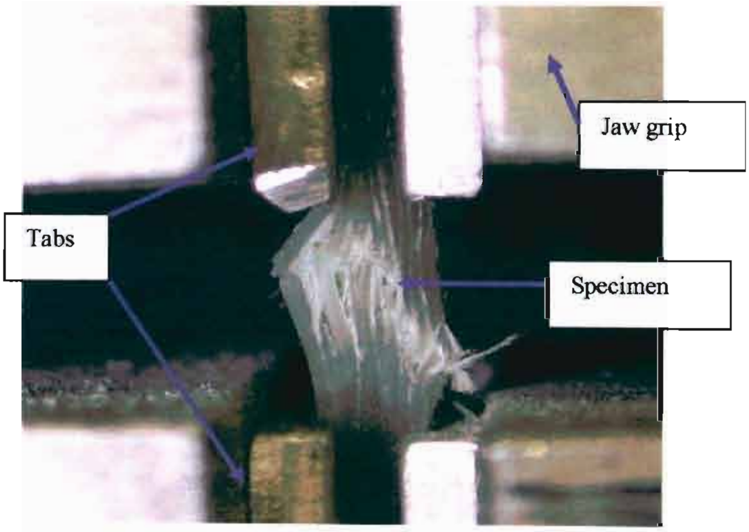


Figure 5-11: Failure in Shear

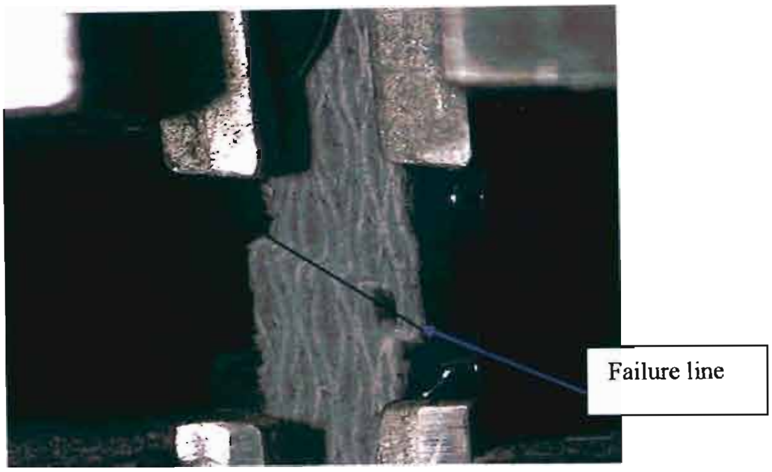


Figure 5-12: Failure in Pure Compression and Buckling

Table 5-11: Maximum Compression Stress and Modulus (1600 hours)

Average values (MPa)	NUV 2 exposed	NUV 17 unexposed	I TIN 3 exposed	I TIN 47 unexposed	MET16 exposed	MET 23 unexposed
Max. Comp. Stress (Mpa)	422.798	421.78	389.818	325.013	380.859	320.217
Modulus, E1 (Mpa)	4338.2	1640.2	1601.9	2805.1	1903.6	1301.1

Table 5-12: Maximum Compression stress for exposed Specimens (2500 hours)

Average values (MPa)	NUV	MET	I TIN
Compressive stress 2500 hrs	458.26	404.93	418.60

Table 5-13: Compression Stress for Unexposed Samples (2500 hours)

Average values (MPa)	NUV	I TIN	MET
Compressive stress 2500 hrs	475.45	446.53	513.89

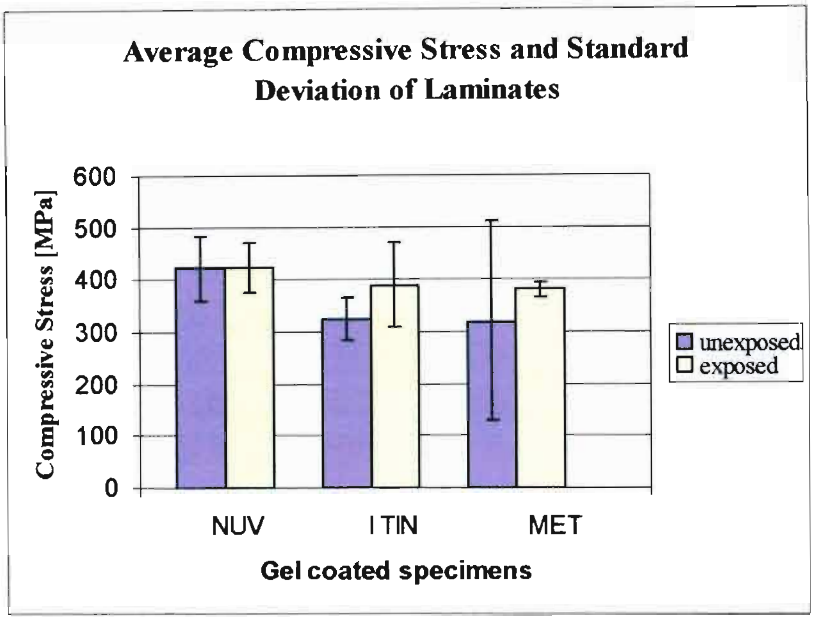


Figure 5-13: Compressive Stress of Specimens (1600 hours)

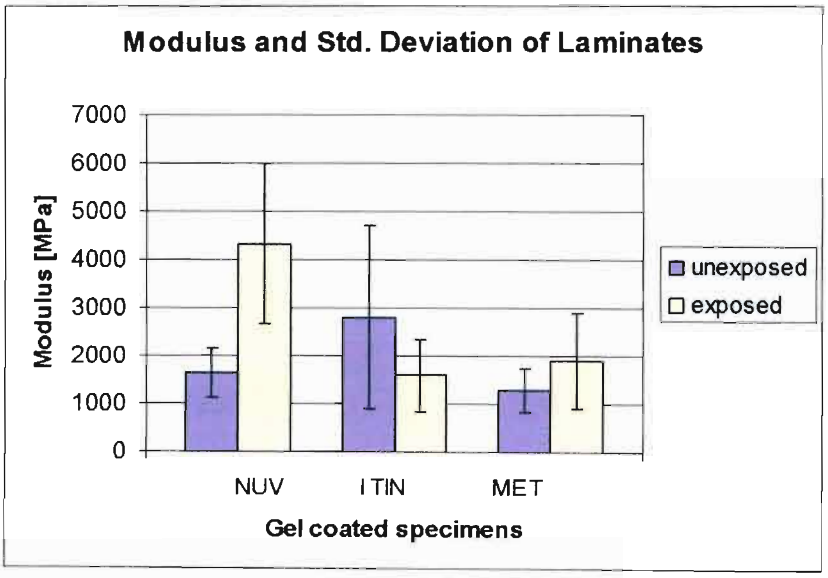


Figure 5-14: Modulus of Specimens (1600 hours)

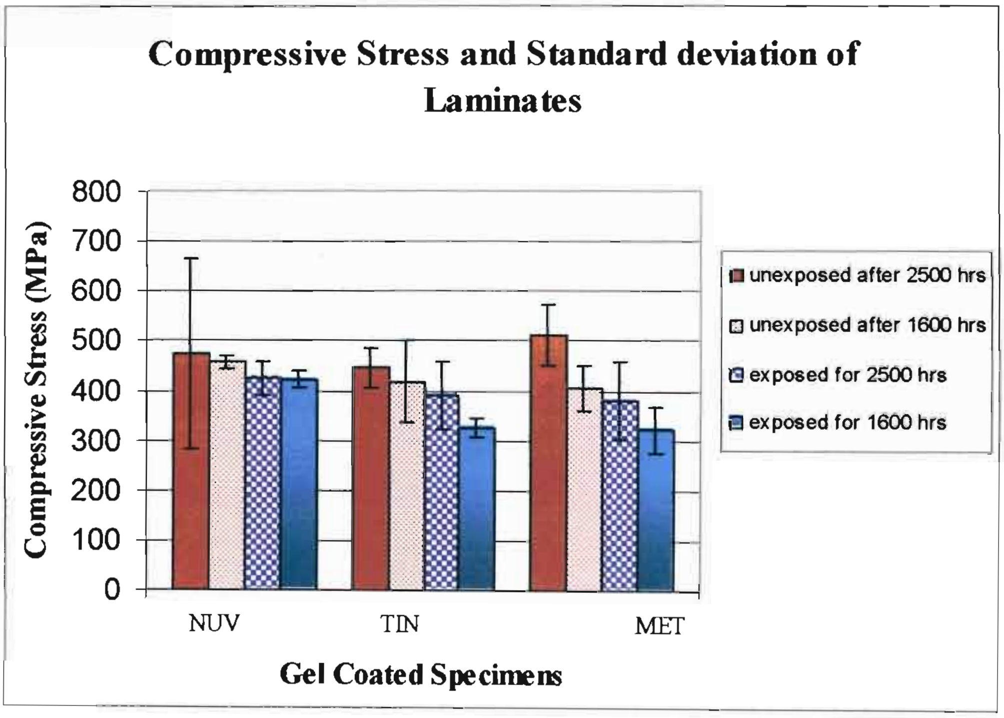


Figure 5-15: Compressive Stress of Specimens (2500 hours)

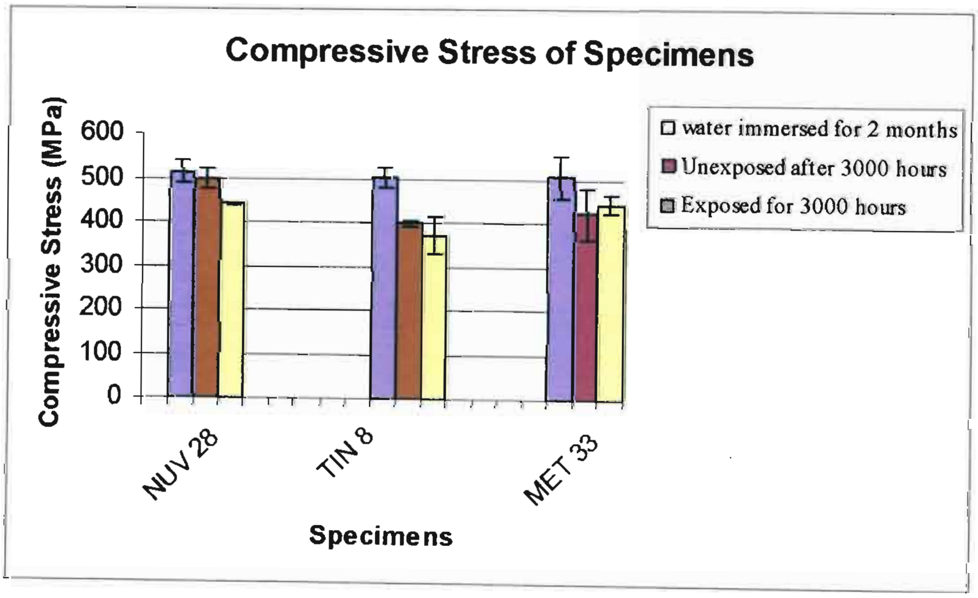


Figure 5-16: Compressive Stress of Specimens (3000 hours)

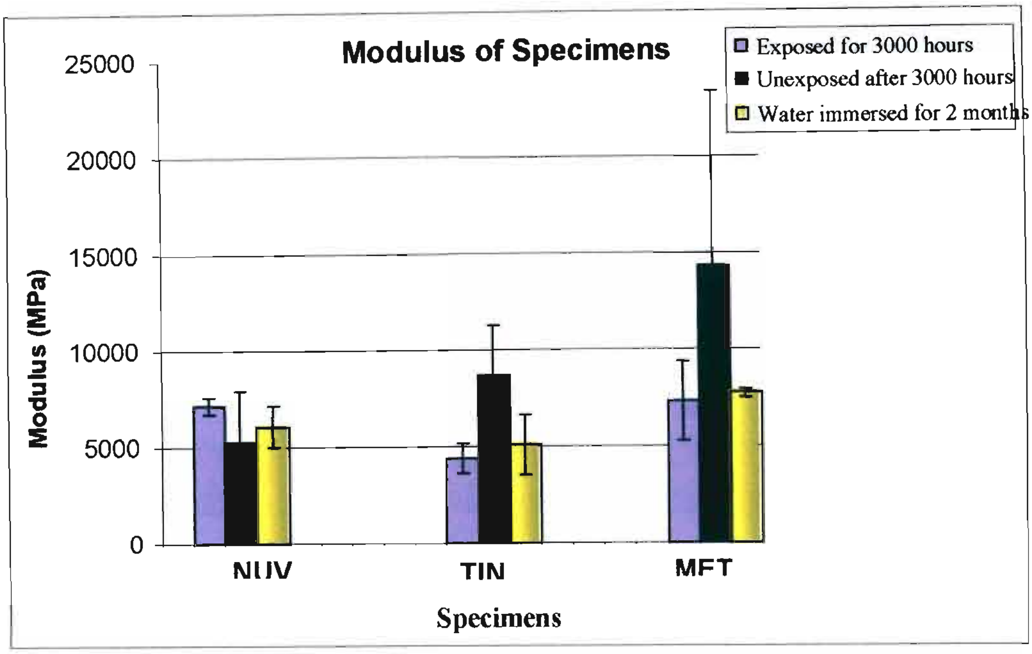


Figure 5-17: Compressive Modulus of Specimens (3000 hours)

The error bars indicate the standard deviation.

Un-gel-coated laminate

A un-gel-coated epoxy sample was also subjected to accelerated testing in the environmental chamber for comparison. The values obtained would give a comparison of strength and modulus between the exposed and the unexposed sample. This was done to show the extent of degradation on this un-gel-coated laminate. The result [Appendix B] is for 1617.55 of UV exposure only followed by 500 hours of UV and Condensation cycles.

Summary of Lloyds Compression Results [Table 5-14].

Table 5-14: Average Lloyds Test Values

Average Values		
	Compressive Stress (Mpa)	Compressive. Modulus (Mpa)
NUV	370	9100
MET	280	7100
I TIN	281	7000

5.3.4 Gloss measurement Results [5-15]

G. Wypych [10] describes the sequence of events during degradation and the results of exposing coating to weather, such as chalking, discoloration or cracking. He considers gloss to be the most sensitive measure of deterioration because the degradation process affects the surface first, followed then by the colour change.

The three main angles are 20°, 60° and 85°, with two more specialist angles of 45° and 75°. Therefore, depending on the material, surface texture and gloss levels required, different angles are specified for different materials. For example, a 20° angle, which gives the best resolution, is applicable to high gloss paint finishes such as cars, plastics, varnishes and polished metals. A 60° angle is probably the most universal, and is usually specified for normal paints and varnishes, plastics, leathers, anodised aluminium surfaces etc. The 85° angle is applicable to low gloss finishes such as matt paints, car interior plastic parts or even textiles (BS 3424: part 28). Of the specialist angles, the 45° angle is sometimes used for measuring the gloss of plastic films and some types of ceramics, while the 75° is specific to the paper industry [82]. In this study the 60° setting was preferred.

The REFO 3 D used in this study to measure gloss, is a portable three-angle reflectometer designed for safe and easy application everywhere in production and in the laboratory. The results can be sent via interface RS 232 C to a printer for clear documentation or to a PC using PC-software REFO QC for individual evaluation. REFO 3 D is powered by mains or batteries and stores all measurements made in off-mains condition (up to 350). The stored measurements can be printed or sent to the PC. Involved calibration of measuring instruments takes time and can cause errors which may cost dearly in subsequent single or series measurements. To solve the measuring problem, a selection can be made among these measurements:

1. The one-angle measurements as single or multi-measurements, including the determination of mean value, standard deviation and coefficient of variability.

2. Multi-angle measurements as single or multi-measurements, including the determination of mean value, standard deviation and coefficient of variability.

3. Gloss difference measurements against a reference standard. REFO 3 D measurements can be immediately documented on a printer. The printout from the LD 200 printer is fast, easy to read and retains the data over long periods [83].

Table 5-15: Gloss readings for specimens subjected to accelerated exposure

(Values are an average of five values)

Specimen	NUV 4	NUV 8	NUV 3	I TIN 5	I TIN 8	ULT 36
Gloss	94.58	95.02	95.26	94.44	92.66	89
Specimen	I TIN 4	MET 6	MET 8	MET 2	SUP 41	–
Gloss	90.62	83.58	85.14	83.44	84.3	

The objective of assessing gloss of surfaces with the reflectometers described in DIN 67530, is to ensure quality assurance and surface quality optimization in the paints and plastics industries [84].

The three main geometries are 20°, 60° and 85°, with two more specialist angles of 45° and 75°. Therefore, depending on the material, surface texture and gloss levels required, different angles are specified for different materials. A 60° angle is probably the most universal, and is usually specified for many applications [85].

5.3.5 Glass Transition Temperature

The glass transition temperature, Tg, can be used to explain the changes in mechanical properties. The glass transition temperature (Tg) is a property of a polymer and is defined as the temperature at which the polymer goes from a rubbery to a glassy state without any change in phase [86].

The glass transition temperature for polyester is between 68 and 81°C, so at room temperature polyester is glassy. Chains or segments of chains cannot move. However when you heat this material above Tg (glass transition) then segments of chains can move. Then depending on the temperature to which the material is heated the amount of shrinkage will be different. [87]

The glass transition temperature (Tg) is a useful parameter that characterizes the temperature dependence of the physical and mechanical properties of coatings [88].

Above a certain temperature, the plot as shown below [Figure 5-18] will shift downward:

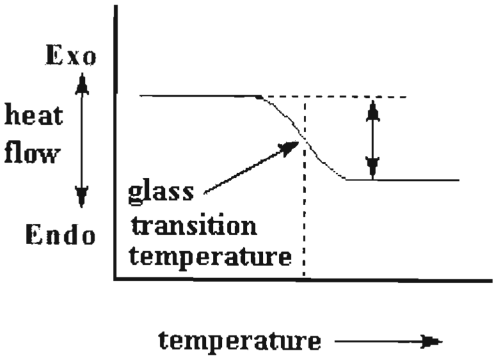


Figure 5-18: The Glass Transition Temperature [89]

ISO 11357 [90] specifies methods for the thermal analysis of polymeric materials, including composite materials using DSC.

The glass transition temperature depends on four factors [91]:

- Free volume - the volume of polymer mass not occupied by the molecules themselves. If the molecules are tightly packed and have little room to move, they need high energy or a higher temperature to move.
- Rotation about bonds - more energy is needed for rotation to occur, again resulting in a higher T_g.
- Stiffness of chain - more or less similar to the factor above, in that if a chain of molecules needs more energy to bend or twist, a higher T_g is required for the motion to occur.
- Chain length - the chain length of molecules affects their motion which affects the T_g Plasticizers soften a polymer by interfering with the chain motions. In adition, the plasticizer forms secondary bonds with the polymer thereby reducing the bonding forces between the polymer chains.

Crosslinking hinders chain mobility and thus increases the apparent T_g. Generally, the strength of polymeric materials above the glass transition temperature is inferior to the strength below T_g. Even in the glassy state however, the strength of an amorphous polymeric material is less than that of oriented crystalline polymers [92].

In a short time frame, an increase of T_g points out cross-linking effects [93]. As the temperature increases and as a long-term time frame is considered, thermo-oxidation effects appear. It is now recognized that chemical ageing can considerably affect mechanical properties. The increase in cross-linking density leads to an increase in brittleness and a decrease of viscous flow due to reduction in free volume and so in molecular mobility. Several creep tests on composite specimens have been conducted and show that cross-linking effects occurring for the first time of ageing may lead to a decrease on strain, compared to non aged specimens [94].

Tg is an important characterization parameter associated with a material and can provide very useful information regarding the end use performance of a product. It represents the lower end use temperature since a material cannot be processed or worked with once its temperature drops below Tg .The Tg of a thermoset material is related to the degree of cure. Tg increases significantly as the curing reaction proceeds to completion due to the establishment of a cross-linked molecular structure [95].

The chemical nature of the polymers is reflected in the interaction parameter and in their glass transition states. The glass transition temperature gives information on mobility of polymer chains. Chemical changes and changes in mechanical properties accompany the gradual degradation of individual polymers [96].

The technique of DSC involves recording the energy necessary to establish a zero temperature difference between a substance and a reference material against either time or temperature as each specimen is subjected to an identical temperature program. The ordinate value at any time or temperature is related to the difference in heat flow between a standard sample and the unknown; this is related to the kinetics of the process [97].

The glass transition temperature is always over a certain range. The range start at a point referred to as the left limit, to the midpoint and the right limit, where the transition ends. The detailed DSC scans for these specimens are shown in Appendix F.

Table 5-16: Glass Transition Temperatures for Exposed Specimens

Specimens	**Tg (°C)**		
	Left limit	**Midpoint**	**Right limit**
MET 6	43.24	74.73	92.90
I TIN 5	29.64	37.90	73.62
NUV 2	28.64	36.77	64.14

5.3.6 Laminates immersed in water

The primary problem with weathering test panels in the laboratory is one of chemistry. The first step toward the development of a general accelerated weathering test suitable for all coating chemistries is to determine which aspects of accelerated exposure are most likely to distort weathering chemistry. In this study laminates were immersed in water for a period of 8 weeks to assess how water ingress affects these laminates. This would help establish whether water alone is the dominant degradation factor.

Some samples were immersed in water and others were exposed to the water in an environmental chamber during condensation cycles. Long-term or short-term exposure to aqueous environments can cause irreversible changes in the chemical and physical properties of fibre-reinforced polymer composites. These changes often compromise the load carrying properties of the material, with the level of degradation increasing as moisture content increases. Reductions in stiffness and strength, and changes in thermo-mechanical behaviour can often be linked directly to the amount of moisture absorbed. The extent and rate of moisture absorbed by the composite material depends on a number of factors, including temperature, relative humidity, and moisture equilibrium levels, area of exposed surface, fibre content and diffusivity [98].

An important property of any resin is its ability to withstand degradation from water ingress. The most significant issue is how the absorbed water affects the resin and resin/fibre bond in a laminate and leading to a gradual and long-term loss in mechanical properties [99].

Moisture has the effect of an overall increase in the Poisson's ratio (the lateral contraction per unit breadth divided by the longitudinal extension per unit length) of the composite and lowering of the Tg (the temperature below which particles have very little mobility) of the matrix due to the plasticization which increases the flexibility of the composite. [44]

Mass Change [Table 5-17]

Table 5-17: Mass Change for Water Immersed Samples

Specimens	Mass before (g)	Mass (g) After	Mass Change (g)	ΔW
MET 19	34.926	34.915	-0.011	-0.031
MET 33	33.595	33.583	-0.012	-0.035
I TIN 63	34.559	34.547	-0.012	-0.034
I TIN 61	32.503	32.488	-0.015	-0.046
NUV 32	33.629	33.623	-0.006	-0.017
NUV 28	34.099	34.079	-0.020	-0.058

After removal from water the samples were left to dry for three weeks. The mass loss on these laminates ranged between: 0.017 and 0.058.

Colour Change after Water Immersion

After immersion in water the uncoated side of the laminates changed colour to white as shown in the figure below [Figure 5-19].

Figure 5-19: The colour change on water immersed laminates

Mechanical Change

After immersion in water at 25°C for 2 months, none of the types of samples compressive strength was significantly affected. Table 5-18 shows stresses and moduli of specimens that were not immersed in water, and Table 5-19 shows stress and moduli of immersed specimens. There was however a slight increase in tensile modulus.

Table 5-18: Table Compression Stress and Modulus for I TIN Samples (3000 hours)

Condition	unexposed	unexposed	unexposed
Specimen	**NUV**	**I TIN**	**MET**
Stress (Mpa)	497.982	397.763	421.295
Modulus (Mpa)	5236.445	8734.124	14329.606

Table 5-19: Compression Stress and Modulus for MET Samples (3000 hours)

Condition	water	water	water
Specimen	**NUV**	**I TIN**	**MET**
Stress (Mpa)	435.5905	372.352	443.528
Modulus (Mpa)	5947.731	5047.109	7723.361

6 Chapter 6

DISCUSSION OF RESULTS

6.1 Overview

No comprehensive correlation between natural exposure and accelerated exposure could be made because the natural exposure testing is still on-going. The accelerated testing conducted does provide results to work out detailed correlation in future. There is a need to expand the types of materials being tested to establish confidence over a wide range of different materials since the results obtained may not be applicable to other materials.

The results obtained would be very important in considering the use of gel coated laminates. Once these results are compared with the outdoor exposure test results an important correlation would be made and provide predictive models for failure.

The mechanical degradation is a critical factor in this study. The failure modes observed during compression testing therefore requires an insight unique to this type of material. Failure modes would normally qualify the state of the material being tested. Since these laminates are built from distinct layers, it is essential to understand how loads are transmitted among these layers. It is also important to be able to distinguish between resin-dominated failures and fibre-dominated failures. Understanding the different failure modes makes it possible to redesign for better re-distribution of stress in the laminates in order to withstand potential failure.

The failure modes especially in composite structures, can be classified as either strength or stiffness dominated [106]. Strength limited failures occur when unit stress exceeds the load carrying capability of the laminate. Stiffness failures result when displacements exceed the strain limits (elongation to failure) of the laminate. [106]

It is said that tensile failures of composite materials is fairly rare, as filament reinforcements are strongest in tension along their primary axis. However, tensile loading in the transverse is different.

Compressive failures in composites are probably the hardest to understand or predict. Failures can occur at a very small-scale, such as the compression or buckling of individual fibres. With sandwich panels, skin faces can wrinkle or the panel itself may become unstable. Indeed, incipient failure may occur at some load well below an ultimate failure. Out-of-plane loading, such as hydrostatic force, creates flexural forces for panels. Classic beam theory would tell us that the loaded face is in compression, the other face is in tension, and the core will experience some shear stress distribution profile. For three-dimensional panels, predicting through-thickness stresses is somewhat more problematic. Bending failure modes to consider include core shear failure; core-to-skin de-bonds, and skin failures (tension, compression, and local).

6.2 Degradation Effects

Based on the maximum compressive stress, the exposed specimens have higher strength after exposure compared to unexposed samples from the same laminate, and as shown in the graphs [Figures: 5-13, 5-14, and 5-15]. This is contrary to what may have been expected after the 3000 hours of exposure. It was thought that after the 2500 hours mark the specimens would begin to deteriorate in mechanical strength. The higher strength of exposed laminates at 3000 hours as compared to similar laminates unexposed 3000 hours may have been due to a post-curing effect. However some of the unexposed laminates significant increase in their compressive modulus.

The grip marks on the aluminium tabs were not consistently appearing along the same central part along the tabs. At times the marks were closer to the sides or the ends of the specimen. The length, width and thickness of the gauge section of each specimen were entered in the INSTRON Machine; any inaccuracies in any of these would give wrong results. The individual different failure modes of the specimens also contribute to the standard deviations.

The differences on the standard deviation of specimens [Y-bars on figures: 5-13, 5-14, and 5-15] from the same sample is mainly attributable to the method of manufacture of specimens which may have resulted in fibres not being aligned within the laminate or the tabs not being accurately parallel.

The exposed specimens had higher strength after 2500 hours of exposure than at 1600 hours of exposure. This could imply that since the laminates were not post-cured before exposure in the environmental chamber, the heat in the environmental chamber may have a post-curing effect.

After 3000 hours, the yellowness index on gel coats with no UV stabilisers increased to almost double that of the unexposed specimens. Results on the rest of the specimens reflected only a slight increase of yellowness. The slight change of the yellowness index on gel coated specimens with a UV stabiliser, compared to a larger scale change on gel coats with no UV additive indicated the effectiveness and importance of these stabilisers.

Many inferences can be made from the DSC curve. To enable a more useful thermal analysis of the DSC curves, it is necessary to know the main aspect of the analysis. According to the graphs, it seems like the 1TIN 5 is more of a pure polymer, showing the transition at 350-400 °C, which could be the melting of the polymer. NUV 8 is the least pure polymer with less of a distinctive transition from 350 to 400 °C. Met 6 shows some sort of transition, showing more polymer presence than NUV 8. Care must be taken when taking the T_g measurement, The observation made on all graphs suggest that there is more distinct transition in ITIN 5 and in MET 6 than in NUV 8 which has an initial transition and no further transition when compared to the previous two scans.

Samples exposed to UV / Condensation cycles in the Environmental Chamber had an oily layer on the surface. This layer obscured the gloss. However, once the layer had been removed, these specimens showed retention of gloss.

6.2 Exposure Results

The gel coats with the UV additives appeared not to have been affected after about 800 hours of exposure. This was presumed based mainly on the fact the specimens after 800 hours visually appeared not to have changed colour, had no cracks when observed under the microscope, and no chalking. The physical condition of these specimens, compared to the unexposed specimens visually appeared unchanged. As a result therefore, no tests on mechanical properties were performed since the specimens with UV additives had not reached a defined level of degradation. Only the specimens of the gel coat that had no UV additive were already beginning to change (in colour). 1600, 2500, and 3000 hours that included hours of accelerated UV / Condensation exposure testing were performed on the polyester GRP laminates with gel coats. Condensation cycles were introduced after 2500 hours. No visible change was found on laminates protected with the UV stabilizers. Mechanical tests were performed to determine change in mechanical properties. The test is in line with the ASTM D3410 compression testing [58].

6.3 Compression Graphs

There were two aspects that needed to be investigated from the compression graphs. Firstly, the compression stresses versus strain graphs depicted a rather large failure strains: up to 30% for testing after 1600 hours, and up to 15% after 2500 and 3000 hours of exposure [Appendix B]. These values appear to be quite high when compared to theoretical failure strain values. The Lloyds machine was used to test similar specimens to verify the values that were obtained from the INSTRON. The graphs from Lloyds Machine provided a comparison to establish confidence in the results.

Secondly, the stress–strain graphs produced from the INSTRON testing have a flat portion after about 100 MPa (compressive stress) [Figure 6-1], whereby there is no change in stress, but only the strain increases as illustrated in the figure below. The Lloyds Machine even in this case, would help to ascertain whether this is not due to machine slippage from the INSTRON.

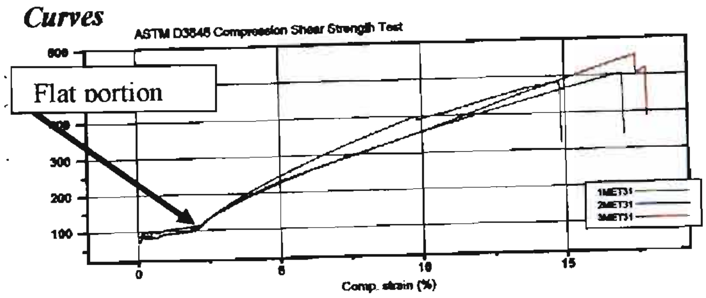


Figure 6-1: Stress vs. Strain (MET 31)

These aspects were a common feature on almost all the graphs. However, whilst these two features were being investigated, a conclusion could still be reached concerning the strength pattern of the tested specimens. The flat portion of the stress – strain graphs was thought to be either due to buckling or slippage during testing. On the Lloyds machine no slippage or buckling was observed. It was believed that the flat portion of the graph was subsequently responsible for the high strains.

6.4 Comparing Accelerated and Natural Exposure

6.4.1 Introduction

The coordinated information between natural exposure and accelerated exposure relies on the use of standardized test methods and data reported. The data should indicate potential long-term performance by acceleration of appropriate mechanisms Environmental stress factors such as temperature, UV, moisture exposure, etc. can have an effect on degradation mechanisms. Normally, one or two environmental stress factors dominate the degradation of a material system. Each degradation mechanism may need to be investigated separately in order to determine the dominant mechanisms.

As with any type of light, sunlight is composed of various wavelengths. The composition of the wavelengths of light is called a spectrum and is unique to each type of light. The entire range of the light spectrum goes from high energy, short wavelength ultraviolet (UV) light, through visible light to lower energy, long wavelength infrared. Absorption of such energetic light by a polymer produces self-propagating, free radical species, which break it down causing gloss loss or chalking.

In order to accurately evaluate end-user weathering requirements and competitive weathering data, the method of testing must be evaluated. The most important factor is the degree of correlation that can be expected between the data and actual service performance. The most accurate determination of the outdoor durability a customer will see on his product is found in testing by Florida exposure.

6.4.2 Procedure

Laminates with gel coats have been removed from panels for observation and testing to compare with the samples under accelerated exposure. Samples without gel coats were examined after 3000 hours (about 25 weeks) of accelerated exposure and about 6 months of natural exposure. These were examined under the optical microscope at 100X magnification. The physical properties which the laminates were checked for include: colour analysis, gloss loss, cracking, chalking. Samples were then cut to size for mechanical testing.

6.4.3 Observation of Visual changes to laminates

Surface fibre appearance change — the increase in fibre prominence on the naturally exposed samples without gel coat is due to resin erosion. The 'accelerated' samples did not show any resin erosion. The difference could be due to the fact that the outdoor samples have been exposed to more water, particularly from rain compared to the condensation in the environmental chamber.

Regarding apparent colour change, the total effect in colour change as a result of resin yellowing and pigment fading was obvious on all exposed laminates.

Gloss loss (the change in glossiness or light reflection of the samples) occurred on all samples to different degrees. Ultraviolet light is believed to have caused oxidation of the epoxy resins used in making the laminates. The damage resulted initially in loss of surface gloss and gradually in a chalky appearance.

Figure 6-2, which follows depicts the contrast in visual changes on the laminates subjected natural, accelerated exposure and unexposed laminates.

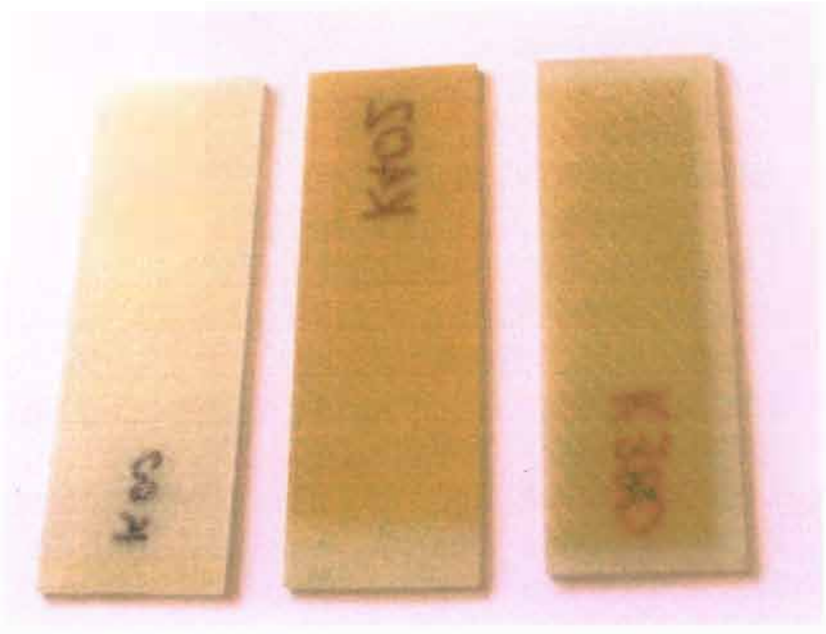


Figure 6-2: **Accelerated, Naturally Exposed and Unexposed Samples**

Since the objective of this work is to try and correlate the accelerated exposure to exposure outdoors, there is a need to show how accelerated results directly relate to natural exposures. Only direct comparison between identical specimens exposed to natural and accelerated methods can achieve confidence in the accelerated methods for specific material types and formulations.

The factor of the spectrum of the light source compared with sunlight appears to be the most critical in producing results, which are comparable with actual outdoor service life. The lamps are UVA-340 lamps with peak emission at 343 nm and a spectral power distribution as shown in figure 6-3 [70]. Materials exposed to UVA-340 lamps are subjected to an irradiance of 0.72 W/m^2/nm and is averagely 0.68 W/m^2/nm at 340 nm [70]. The UV irradiance from 295 to 400 nm is 39 W/m^2 [70].

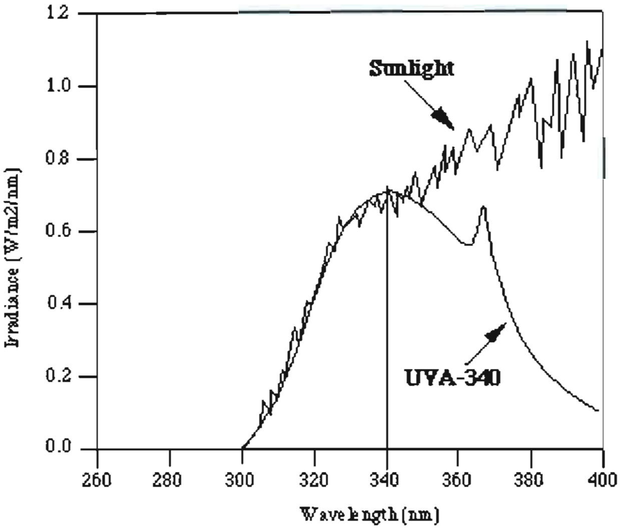


Figure 6-2: UVA-340 and Sunlight [70]

Figures 6-4 and 6-5 show irradiance graphs from other types of bulbs to show how these bulbs correlate with the sun's spectrum and to compare these irradiance patterns to that of the UVA-340 bulb [Figure 6-3], used in this study.

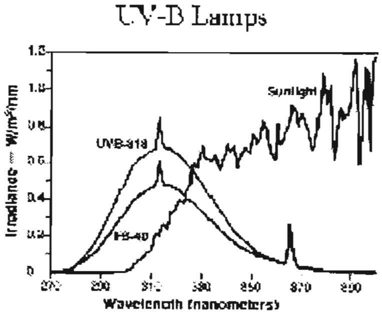


Figure 6-3: UV-B and Sunlight [102]

The limitations concerning the UV B-313 and FS-40 bulbs are the emitted radiations wavelengths which are than the solar cut-off of 295 nm. UV A-340 certainly correlates better with normal sunshine in the UV region, as shown here [102].

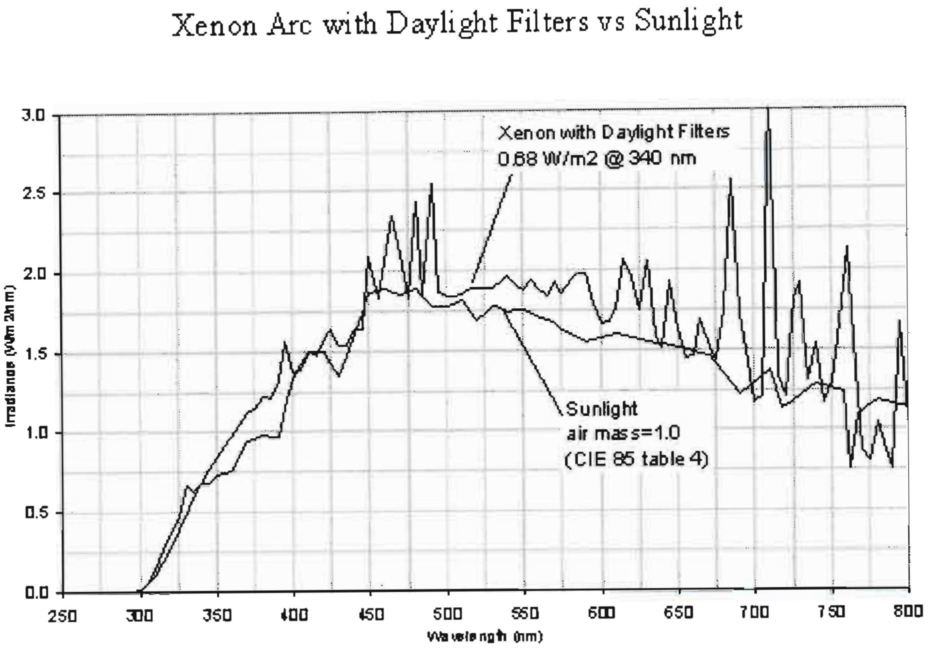


Figure 6-4: Xenon Arc and Sunlight Spectrum [102]

While the Xenon arc lamps match the solar spectrum more closely, it however still has a number of "spikes" in the energy emission at various wavelengths. These may still lead to unwanted, unexpected weathering events [102].

6.4.4 Comparison Using Energy Values

One approach could be the energy approach [103]. This could be done by first determining the amount of energy that is affecting the laminates in the environmental chamber in the laboratory. The energy comes from the four-40 watt Fluorescent UVA 340 lamps. These are affecting a surface area of about 1.40 x 0.40 m. The product of these numbers is taken and it is determined that the energy affecting the laminates is $= \dfrac{4 \times 40}{1.40 \times 0.40} \equiv 285.7 \, {}^{W}\!/_{m^2}$

Next the energy in the natural environment can be determined. The UV lamps in the environmental chamber produced a wavelength of 340 nm. This value of 340 nm could be found on a chart of solar spectral irradiance [Figure 6.2] above and, in turn, correlated to an energy value of 0.72 $W/m^2/nm$ (+/-10%). The UV irradiance from 295 to 400 nm is 39 W/m^2 (+/-10%). This value is equivalent to the amount of energy produced by UV radiation of this wavelength in the natural environment. Therefore after working out the energy affecting the samples in the chamber, a laboratory/outdoor ratio can be developed. This means that the energy given off in the lab is $\frac{285.7}{39} \equiv 7.33$ times stronger than that which is given off in reality. This also means that one unit of time in the lab is equivalent to 7.33 units of time in the natural exposure.

This data can then be used to correlate the accelerated exposure time to outdoor natural exposure time for a series of laminates located at different locations in South Africa. This can be done by using the UV exposure radiation data from South African weather bureau for all the different locations. These values can then compared to the times in the accelerated exposure and converted into a reality time in years. This means that for each length of exposure, 1500, 2500, and 3000 hours, the number of years of exposure in natural exposure for various locations could then be calculated.

The table below uses Pretoria as an example for correlation of energy density values. The energy density given for the Pretoria winter was 9 $MJ/m^2/day$ and 32 $MJ/m^2/day$ last summer [104]. The energy density (D) generated by a pulsed emitter in free space is defined as D = S PW when D is expressed in J/m^2, S is power density expressed in W/m^2, and PW (Pulse Width) is expressed in seconds. Therefore S=D/PW.

To obtain the number of natural exposure years as shown in the example below, the procedure is to first convert the number of accelerated exposure hours to years, then multiply by the lab/outdoor ratio, which is then multiplied by the second ratio worked out using the energy value calculated above (285.7W/m^2) and the real average energy value (in this case for Pretoria (237.27 W/m^2). An illustration for 1600 hours accelerated exposure time is shown below:

$$\text{Natural Exposure years} = \frac{1600/24}{365} * 7.33 * 1.204 = 1.61 \text{ years}$$

Table 6-1: Correlation Accelerated exposure time to Natural Exposure years

Location	Lowest Daily Average	Highest Daily Average	Annual Daily Average	Ratio	Natural Exposure (years)		
	(W/m^2	($W/m^{2)}$	($W/m^{2)}$	Accelerated / Reality	Laboratory = 1600 hours	Laboratory = 2500 hours	Laboratory = 3000 hours
SA (Pretoria)	**104.17**	**370.37**	**237.27**	**1.204**	**1.61**	**2.52**	**3.02**

However due to the factors that contribute to poor correlation, such as the fact that the most damaging rays of the sun are those that impact a surface at a ninety degree angle, the locations that are closer to the equator, which therefore have a higher percentage of perpendicular rays, are calculated to have a longer exposure time in reality than those further from the equator; the fact that the reality exposure times are calculated on the basis of continuous exposure whereas in reality exposure is not continuous since UV rays are not present during the night; and also that the most damaging, perpendicular rays only occur for one to two hours per day, depending on the distance of the location from the equator. For outdoor exposure as well, choosing a specimen exposure angle also has a significant effect on each of the following test parameters: solar energy dosage, specimen temperatures and moisture and time of wetness. The angle of exposure, called tilt angle, has a significant impact on the specimen's response to its environment because it determines the dosage of solar radiation, rate of heat build-up and cool down, and the amount of time that the specimen is wet because of dew formation, rainfall, or drying winds. [105]

These factors lead to discrepancies with regards to the approach outlined above. For such discrepancies the values in years calculated would have to be multiplied by a certain uncertainty factor that could be calculated depending on the nature of the discrepancy, and hence a component could be designed for that particular life span.

7 Chapter 7

CONCLUSIONS

7.1 Overview

The gel coat, according to the experimental results of accelerated exposure, is more effective as a protective measure when especially comprising of the specific additive against the respective environmental stress factor. The experimental approach is a long term project that would provide invaluable results and information specific to the types of materials tested. The literature review into the various protective measures for laminated composites provided an insight into the benefits of providing preventative measure against physical and mechanical deterioration.

7.2 Exposure

There has been a decrease in strength and weight after 2500 hours of exposure on gel coated laminates. After 1600 hours of exposure there was a slight tendency towards strength increase. No change in colour on specimens with UV additives was observed visually. After 2500 hours the results have greatly been influenced by the post-curing effect on both exposed and unexposed laminates. After 2500 hours of exposure, all laminates in the environmental chamber were then subjected to both UV and condensation cycles. This exposure will focus on the effect of the UV - moisture combination on the laminates

The study of natural and accelerated exposure and the subsequent effects on the performance of laminated materials is a challenging and difficult task. However, it is important that a knowledge-base is built up as the demands on such material systems increase. Only through long-term, dedicated perseverance in addressing the difficult and complex issues surrounding this area of research can one expect to extend the use of these materials systems safely and reliably to the most demanding, challenging and rewarding end-use.

7.3 Gloss Retention

To evaluate the gloss retention, longer periods are necessary (more than one year if possible) due to the complex multi-process (photo-oxidation, hydrolysis) nature of degradation chemistry. No theoretically based model has been used to predict deterioration associated with weathering. There are, however, several proposed laboratory accelerated test methods, which were tested in the study. Each one can provide important information, but none actually can accurately match the real-life outdoor weathering data exactly. From this study it is believed that the colour change occurs first, followed by a gloss reduction due to chalking attributed to moisture.

7.4 Moisture Effect

The oily layer formed on the laminates during exposure cycles in the environmental chamber might have protected the laminates further, for example, the loss of gloss. The oily layer could have been caused by heat in the chamber which could have melted a dry thin layer of the release agent used on the mould. There is capacity to model the weight loss due to the heating in the environmental chamber. The temperature could be varied to the different levels while the weight is monitored periodically.

7.5 UV / Condensation Cycles

Based generally on the experimental results and theoretical considerations described earlier, the degradation included both physical and chemical effects. The main physical effect was the evaporation of volatiles due to elevated temperature and the chemical effect could have been the post-curing effect, which is as well reflected in the change in Tg. The 3000 hours of harsh environmental exposure gives some indication that this kind of protective measure could provide reasonably durable protection for the laminates.

7.6 Water immersion effect

There was no observed weight attributed to the moisture as one could have expected. There were no cracks observed on laminates, this could mean that any water gain could have been restricted to the resin matrix. This factor could be further and widely explored as a method to establish specific time-temperature-moisture relations, which could enable the prediction of life under any specific temperature and moisture condition. After immersion in water at 25°C for 2 months, there was a slight decrease in compressive strength as well in compressive modulus for all of the types of specimens.

7.7 Thermal Analysis

There has been a definite change in the chemical structure of exposed laminates. The glass transition of samples had dropped from the normal polyester Tg range. This drop is associated with a change in the chemical structure. This implies that a physical change such as strength should be expected. It is postulated that a much clearer result could have been achieved if the TMA - Thermomechanical analysis was performed as compared to the DSC – Differential Scanning calorimetry. This technique shows both the chemical and mechanical changes.

7.8 Mechanical properties

There has been an increase in strength 3000 hours of exposure on gel coated laminates. Strength had increased from around 400 to 450MPa, and around 500MPa. All gel coated laminates showed fairly good gloss retention. According to colour analysis performed the colour on specimens with gel coats had not changed much in colour. Yellowness index for the gel coats with no UV additive had increased by almost 50% after 3000 hours of exposure. The UV additive has been effective in protecting the laminates from discolouration. Gel coats protected with the UV additive had even more resilience to the accelerated degradation of about 3000 hours.

7.9 Colour Analysis

An increase in the yellowness index was clear on all specimens and significant on specimens coated with NUV gel coat. From the colour analysis: DE, DL, DC; DH; DA; and DB values were found and showed a difference from the standard. Even though only the DE values showed a significant change, all specimens showed a certain amount of change.

7.10 Compression Jaws

The design limitation of one of the set of jaws was that, when the jaws were aligned vertically there was a possibility that the top jaw may not have been screwed in tightly because its tight position was away from its vertical alignment position. As a result, clamping the specimens would have resulted in the jaw being moved slightly and thus twist the specimen. Precise alignment in the test fixture is critical, because even a slight angle can produce an unexpected failure mode and invalidate the test. To overcome this, it could be good to modify the design of the jaws to make sure that both top and bottom jaws align in their tight positions.

7.11 Further Work

Further work recommended includes the continuation of:

(1) The study of literature and technology on degradation and protective measures

(2) Accelerated environmental testing

(3) Exposure testing (real life)

(4) Identification of dominant degradation mechanisms

(5) The use of experimental data to establish a degradation model

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A Appendix A

Gel Coats and Adhesive Data Sheets

A-1: Ciba TINU VIN 320

Benzotriazole UV Absorber Characterization

TINUVIN 320 is an ultra violet light absorber of the hydroxyphenyl benzotriazole class, w which imparts out standing light stability to plastics and other organic substrates. Particularly it is recommended for rigid PVC and polyester.

Chemical Name: 2-benzotria zol-2-yl-4,6-di-tert-butylphenol
CAS Number: 3846-71-7
Structure re; TINUVIN 320
Molecular weight 323 g /mol

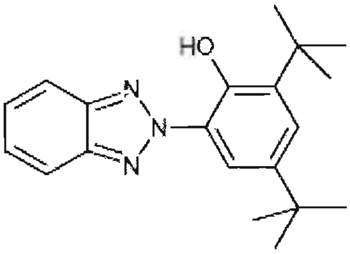


Figure A-1: The TINUVIN 320 Structure

Applications

TINUVIN 320 is a highly effective light stabilizer for a variety of plastics and other organic substrates including unsaturated polyesters, PVC and PVC plastisol. Good results are also expected when TINUVIN 320 is used in polycarbonates, polyurethanes, polyamides, synthetic fibers and in lacquers, particularly those with a polyester, alkyd, epoxy or isocyanate resin base. Moreover, TINUVIN 320 is generally suitable for applications where any of the established TINUVIN range are currently being used.

Features/ Benefits

TINUVIN 320 features strong UV absorption, excellent compatibility in a wide variety of substrates, and low volatility. It protects polymers a swell a s organic pigments from UV radiation, helping to preserve the original appearance and physical integrity of molded articles, film s, sheets, and fibers during outdoor weathering. TINUVIN 320 is slightly more discoloring than conventional benzotriazole UV absorbers.

Product Forms

Code: Appearance: TINUVIN 320 slightly yellow crystalline powder.

Guidelines for use

The use levels of TINUVIN 320 range between 0 .10 and 1.0%, depending on substrate and performance requirements of the final application. The product can be used a lone or in combination with other additives such as light stabilizers (hindered amines), antioxidants (hindered phenols, phosphites, thiosynergists, hydroxylamines, lactones), and other functional stabilizers. Extensive performance data of TINUVIN 320 alone or in combination with other additives are available in many of the substrates listed above.

Date first Edition: Oct-66 Prod u ct Na m e: TINUVIN 320 pa g e 21
Printing Date: Oct-97 ©Ciba Specialty Chemicals, Inc.

Physical Properties

Melting Rang e 152-155°C
Flash point 215°C
Specific Gravity (20 °C) 1.18 g /cm 3
Vapor Pressure (20 °C) 7.2 E-6 Pa

Solubility (20°C) % w /w

Water < 0 .0 1
Acetone 3

Benzene 21
Chloroform 24
Cyclohexane 10
Ethylacetate 7
n-Hexane 5
Methanol 0 .3
M ethylene chloride 26

Volatility (pure substance; TG A, heating rate 20 °C/min in air)

Weight loss (%): Temperature (°C)

1.0:170
2.0:185
5.0:20 8

Absorption Spectrum (10 m g /l, Chloroform)

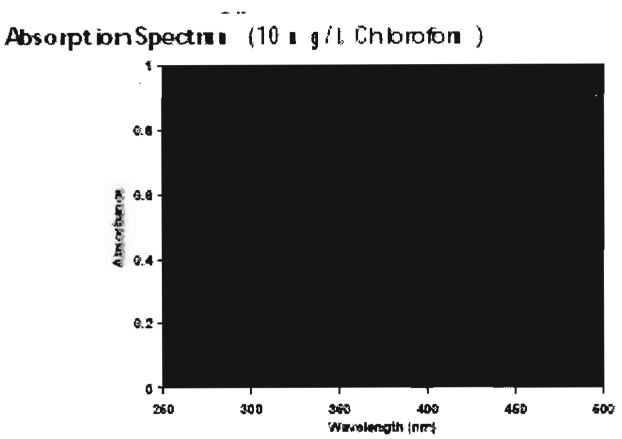


Figure A-2: Absorption Spectrum

TINUVIN 320 exhibits strong absorbance in the 30 0 -400 nm region and minimal absorption in the visible region (> 400 nm) of the spectrum. The absorption maxima are at 304 nm and 346 nm (= 14520 l/mol cm) in chloroform solution.

Handling & Safety

In accordance with good industrial practice, handle with care and avoid unnecessary personal contact. Avoid continuous or repetitive breathing of dust. Use only with adequate ventilation. Prevent contamination of the environment. Avoid dust formation and ignition sources. For more detailed information please refer to the material safety data sheet.

Registration

TINUVIN 320 is listed on the following Inventories:
Australia: AICS Canada: DSL China: First Import Europe: EINECS Japan: M ITI Korea: ECL Philippines: PICCS USA: TSCA

IM PORTANT

The following supercedes Buyer's documents.
SELLER MAKES NO REPRESENTATION OR WARRANTY, EXPRESS OR IMPLIED, INCLUDING OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE.

No statements herein are to be construed as inducements to infringe any relevant patent. Under no circumstances shall Seller be liable for incidental, consequential or indirect damages for alleged negligence breach of warranty, strict liability, tort or contract arising in connection with the product(s). Buyer's sole remedy and Seller's sole liability for any claims shall be Buyer's purchase price. Data and results are based on controlled or lab work and must be confirmed by Buyer by testing for its intended conditions of use. The product(s) has not been tested for, and is therefore not recommended for, uses for which prolonged contact with mucous membranes, abraded skin, or blood is intended; or for uses for which implantation within the human body is intended.

A-2: NCS ULTRAGEL 31 P100 PA

NDS032/035
LOW POROSITY
SPRAY GELCOAT

DESCRIPTION

NCS ULTRAGEL 31 P100 PA is a high opacity white, pre-accelerated, resilient, isophthalic unsaturated polyester gelcoat for spray and flat-bed applications. It is the product of an intensive research and development programme to identify and incorporate the optimum blend of qualities into a single gelcoat.

NCS ULTRAGEL 31 P100 PA incorporates excellent spraying characteristics with exceptional flow, levelling and air release properties, yet has sufficient thixotropy to minimise sag on inclined surfaces.

FEATURES and BENEFITS

Thixotropic
Good film thickness without drainage but with excellent flow and levelling

Pre-accelerated
Rapid cure for improved mould turn around

Isophthalic
Excellent weather resistance and designed for use in marine, building and general applications.

Improved rheology
Ideally suited for flat panel manufacture and can be applied by roller brush, squeegee or Venus application.

Rapid air release
Low porosity with excellent blister resistance.

Specially formulated
Excellent spray characteristics at low pressure enabling increased productivity.

Pigmented
High hiding power using superior pigments.

Contains UV absorber
Ensures long term gloss retention and weather resistance with improved resistance to yellowing.

OTHER VERSIONS

NCS ULTRAGEL 31 NAT PA clear spray version of NCS ULTRAGEL 31 P100 PA
NCS ULTRAGEL 31 PA Is also available in a selected range of colours.
NCS ULTRAGEL 31 NAT PA E Improves stability export version.
NCS ULTRAGEL 31 P100 PA E Improved stability export version.

Table A-1: TYPICAL LIQUID PROPERTIES

PROPERTY	**SPECIFICATION**	**NCS TEST METHOD**
Viscosity @ 25°C, mPa.s	18 000 - 20 000	5.3
Geltime @ 25°C, 2 phg* BUTANOX M50, minutes	6 – 8	8
Volatile content, %	41 maximum	7
Liquid appearance	Opaque White	2
Stability in the dark, months	6 minimum	4.1
***phg = parts per hundred gelcoat**		

FORMULATION

NCS ULTRAGEL 31 P100 PA has been carefully formulated to give the best application characteristics, ensuring freedom from drainage on inclined or vertical surfaces, adequate cover with good wetting properties, rapid gelation and good adhesion to the backing laminate. Major modification of the gel coat would upset the balance of properties that have been achieved by a critical combination of flow additives during manufacture of the gel coat. Users are therefore advised to follow the instructions given in this data sheet.

CURING CHARACTERISTICS

NCS ULTRAGEL 31 P100 PA is supplied pre-accelerated, needing only the addition of catalyst to start the curing reaction.

The recommended catalyst for NCS ULTRAGEL 31 P100 PA is BUTANOX M50 or a 50% solution of medium reactivity MEKP. Low reactivity 30% MEKP catalysts are not recommended.

NCS ULTRAGEL 31 P100 PA must be allowed to attain workshop temperature (23°C) before being formulated for use.

At a mould temperature of 18° - 20°C, the gelcoat will be sufficiently cured for lamination to commence approximately 1 hour after application. Commencement of lamination can be delayed, provided that the surface remains uncontaminated for up to 8 hours at 18° - 20°C. If users wish to delay the commencement of lamination further they are advised to carry out their own tests to ensure adequate adhesion will be obtained.

The following cold curing formulation should be used with NCS ULTRAGEL 31 P100 PA:

COMPONENT PARTS BY MASS

NCS ULTRAGEL 31 P100 PA: 100
BUTANOX M50: 2

The ambient temperature and the amount of catalyst control the gel time of the gel coat formulation. This can be approximately determined from the table below which shows the gel time of 100 parts by mass of ULTRAGEL 31 P100 containing 1, 1,5 and 2 phr BUTANOX M50.

Table A-2: Parts of BUTANOX M50 to 100 parts ULTRAGEL 31 P100 PA

Parts of BUTANOX M50 to 100 parts ULTRAGEL 31 P100 PA	**1**	**1,5**	**2**
Geltime @ 15°C, minutes	34	24,5	19
Geltime @ 20°C, minutes	23,5	15,5	12,5
Geltime @ 25°C, minutes	14	9,75	8
Geltime @ 30°C, minutes	9,5	6,5	5,5

APPLICATION

NCS ULTRAGEL 31 P100 PA is specially formulated for spray application. Due to problems associated with the addition of pigment pastes to spray gel coats, it is advisable to use spray gel coats which have been supplied pre-pigmented. This ensures complete compatibility and freedom from separation to prevent shadowing or a mottled surface.

All catalysts and pigments added to the gel coat must be thoroughly mixed in. Pigment mixing should be carried out by a mechanical stirrer which should be of a type which does not introduce air, preferably air driven.

NCS ULTRAGEL 31 P100 PA is particularly suitable for use with catalyst injection airless or air-assisted airless spray systems. It can be successfully used in conventional air-atomised equipment provided that spraying takes place within the limited pot-life.

A gel coat wet film thickness of 0,5 to 0,625 mm is recommended for most applications. Inexpensive, disposable wet-film thickness gauges are available which will enable the operator to keep a check on gel coat thickness. As a general guide, approximately 550 to 650 g/m^2 of gel coat will give the required thickness for normal use.

SPRAY APPLICATION GUIDE

Mix NCS ULTRAGEL 31 P100 PA slowly before use, by hand or low shear mixer. Do not high shear as the viscosity may drop too much, causing the gel coat to run down vertical surfaces. High shearing will also result in excessive air entrapment.

Check the temperature of the gel coat. Ideally, NCS ULTRAGEL 31 P100 PA should be 23°-25°C and the mould temperature 1 or 2 degrees higher. Temperatures below 20°C will require higher pressures and may result in increased porosity.

Check the spray gun and lines for contamination such as solvent, water or oil. Clean and correct as necessary before spraying.

Check the air pressure before spraying and adjust to achieve proper flow, spray pattern and break-up of the gel coat.

If catalyst injection is used, make sure the catalyst is flowing properly. Do not let raw catalyst fall on the mould or the sprayed gel coat.

Adjust the catalyst level according to the temperature. Do not use less than 1,2 phg catalyst.

Keep the gun perpendicular - about 45 cm from the moulding during each stroke and spray a continuous film without arcing the gun.

To minimise porosity spray 3 to 4 coats of 150 microns each.

Do not apply less than 250 microns, or more than 650 microns. Under 250 microns NCS ULTRAGEL 31 P100 PA may not cure fully and over 650 microns the gel coat may crack or contain excessive air entrapment. The gel coat may also pre-release if the thickness is excessive.

PIGMENTS AND FILLERS

The addition of fillers to NCS ULTRAGEL 31 P100 PA is not recommended since their use may adversely affect the weather resistant and water resistant properties of the cured gel coat.

It is recommended that, where mouldings are produced as sub-components of larger structures, or are simply large structures, that sufficient resin and pigment paste are mixed to enable the entire job to be completed, thus ensuring an exact colour match. Similarly, if pigmented gel coat is used, it is recommended that the same batch of material is used throughout the application as well as for sub-components. Thorough stirring of the mix shortly before use is recommended to ensure that the pigment is fully dispersed and that no separation has occurred. Care must be taken not to introduce air into the system. Users are reminded that the final colour of the cured gel coat and laminate can be affected by the curing system or the colour of the gel coat or resin to which the pigment paste is added, particularly when heavily filled systems are used. The colour card and/or colour swatch samples are intended purely for guidance and exact matching to the final laminate colour cannot be guaranteed. Users are advised to consult application bulletins which deal with the methods of use and scope of application of NCS Resins pigment pastes.

STORAGE AND HANDLING

To ensure maximum stability and maintain optimum properties, polyester resin should be stored in closed containers, maintained below 25°C and away from heat sources and sunlight. All storage should conform to local fire and building codes. Drum stock should be kept to a reasonable minimum with first-in, first-out stock rotation.
Where bung-in-head containers are stored outside, it is recommended that these be stored in a horizontal position to avoid the ingress of water.

STANDARD PACKAGE

Non-returnable metal drums. Bulk supplies can be delivered by road tanker.

MATERIAL SAFETY DATA SHEET

A Material Safety Data Sheet is available from your NCS Resins' representative. Make certain that you obtain a copy of this guide to the safe handling of unsaturated polyester resins and resin systems.

PLEASE READ AND UNDERSTAND THE MATERIAL SAFETY DATA SHEET BEFORE WORKING WITH THIS PRODUCT

WARNING:

CARE MUST BE TAKEN TO AVOID DIRECT MIXING OF ANY ORGANIC PEROXIDE (CATALYST) WITH METAL SOAPS, AMINE OR ANY OTHER POLYMERISATION ACCELERATOR OR PROMOTER, AS VIOLENT DECOMPOSITION WILL RESULT!

NCS RESINS BRANCHES AT:

JOHANNESBURG / DURBAN / CAPE TOWN / PORT ELIZABETH

A-3: NCS ULTRAGEL 21 P100 PA

NDS032/047
FAST CURE
LEVELLING BRUSH GELCOAT

DESCRIPTION

NCS ULTRAGEL 21 P100 PA is the product of an extensive development programme to identify and incorporate an optimum blend of properties, and has ample potlife coupled with the advantage of rapid cure.

NCS ULTRAGEL 21 P100 PA is an isophthalic white polyester gelcoat formulated to give good brushing and air release properties. The gelcoat is thixotropic and preaccelerated and its viscosity and thixotropy have been adjusted so that it flows evenly and minimises sag on inclined and vertical surfaces.

NCS ULTRAGEL 21 P100 PA is a resilient, impact resistant gelcoat suitable for general mouldings where excellent durability and weather resistance are a requirement. NCS ULTRAGEL 21 P100 PA is suitable for use on boat hulls that are subjected to long term immersion in water, and displays good resistance to a variety of chemical environments.

FEATURES and BENEFITS

Thixotropic
Eliminates drainage

Preaccelerated
Requires only the addition of the recommended catalyst

UV-stabilised
Improved weather resistance

Specially promoted
Rapid cure

New formulation
Excellent flow and levelling with low porosity.

Good colour
Readily pigmentable

Lloyds Approved
Meets international quality standards

NCS ULTRAGEL 31 P100 PA: Spray viscosity version
NCS ULTRAGEL 21 NAT PA: Clear brush viscosity version
NCS ULTRAGEL 21 P100 PA E: White brush export version (14 –22 min)
NCS ULTRAGEL 21 NAT PA E: Clear brush exports version
NCS ULTRAGEL 21 PA: Is available in a limited range of standard colours with excellent hiding power.

Table A-3: TYPICAL LIQUID PROPERTIES (NCS ULTRAGEL 21 P100 PA)

PROPERTY	**SPECIFICATION**	**NCS TEST METHOD**
Viscosity @ 25°C, mPa.s.	60 000 - 80 000	5.3
Geltime @ 25°C, 2 phg* BUTANOX M50, minutes NCS 21 P100 PAE	7 – 11 14 - 22	8
Tack-free time (film), hours	15 minimum	25
Liquid appearance	Opaque White	2
Stability in the dark @ 25°C, months	6 minimum	4.1

***phg = parts per hundred gelcoat, by mass**

CURING CHARACTERISTICS

NCS ULTRAGEL 21 P100 PA is supplied pre-accelerated, needing only the addition of catalyst to start the curing reaction.

The recommended catalyst for NCS ULTRAGEL 21 P100 PA is BUTANOX M50 (or equivalent 50% solution of medium reactivity MEKP). Low reactivity 30% MEKP catalysts are not recommended.

Curing should not be carried out at temperatures below 15°C. NCS ULTRAGEL 21 P100 PA must be allowed to attain workshop temperature (23°C) before being used. Catalyst levels below 1% and above 3% are not recommended.
The following formulation is recommended at an ambient temperature of 25°C.

COMPONENT PARTS BY WEIGHT

NCS ULTRAGEL 21 P100 PA: 100
BUTANOX M50: 2

The table below shows the pot life of 1 kg of NCS ULTRAGEL 21 P100 PA at various temperatures and catalyst levels:

Table A-4: Parts of BUTANOX M50 to 100 Parts of

NCS ULTRAGEL 21 P100 PA

Parts of BUTANOX M50 to 100 Parts of NCS ULTRAGEL 21 P100 PA	**Potlife in Minutes of NCS ULTRAGEL 21 P100 PA**				
	15°C	**20°C**	**25°C**	**30°C**	**35°C**
1,0	67	30	22	13	9
1,5	32	16	12	8	6
2,0	28	15	9	7	5
2,5	18	11	8	6	4
3,0	16	9	7	5	4

The above table is meant to serve only as a guide to the pot-life of NCS ULTRAGEL 21 P100 PA. The gel-time of the gelcoat film may vary and depends on several factors, including the material used to make the mould. It is recommended that the mould surface temperature be 1°C to 2°C higher than the gelcoat temperature

APPLICATION

NCS ULTRAGEL 21 P100 PA is designed for application by brush. For normal mouldings, the wet gel coat thickness should be controlled between 0,5 mm to 0,6 mm. As a guide, 550 g to 650 g/m^2 of NCS ULTRAGEL 21 P100 PA when applied will give the required thickness.

The use of glass or synthetic fibre surface tissues as the first layer of reinforcement will enhance the surface appearance and service life of the gel coat.

NCS ULTRAGEL 21 P100 NAT PA has been carefully formulated to give excellent brushing properties, designed to enhance levelling which promotes the uniformity of the gel coat film thickness which translates into efficient utilisation of material. The thixotropy has been adjusted to eliminate sag on inclined and vertical surfaces. NCS ULTRAGEL 21 P100 PA exhibits rapid film curing characteristics resulting in short backup times, typically one hour for a gel coat of cured film thickness of 0,5 mm cured with 2 phg BUTANOX M50 at 25°C. This short backup time facilitates achieving fast production rates and shorter overall mould turn-around times, without detracting from the smooth finish of the moulding.

The gel coat surface is important for proper adhesion of the backing laminate. Modification of the gel coat is not recommended as this will affect the properties which have been optimised.

PIGMENTS AND FILLERS

The addition of fillers to NCS ULTRAGEL 21 P100 PA is not recommended since their use may adversely affect the weather resistant and water resistant properties of the cured gelcoat. It is recommended that, where mouldings are produced as sub-components of larger structures, or are simply large structures, that sufficient resin and pigment paste are mixed to enable the entire job to be completed, thus ensuring an exact colour match. Similarly, if coloured gelcoat is used, it is recommended that the same batch of material is used throughout the application as well as for sub-components. Thorough stirring of the mix shortly before use is recommended to ensure that the pigment is fully dispersed and that no separation has occurred. Care must be taken not to introduce air into the system. Users are reminded that the final colour of the cured gelcoat and laminate can be affected by the curing system or the colour of the gelcoat or resin to which the pigment paste is added, particularly when heavily filled systems are used, and therefore the colour samples here are intended purely for guidance and exact matching to the final laminate colour cannot be guaranteed. Users are advised to consult application bulletins which deal with the methods of use and scope of application of NCS Resins pigment pastes.

STORAGE AND HANDLING

To ensure maximum stability and maintain optimum properties, polyester resin should be stored in closed containers, maintained below 25°C and away from heat sources and sunlight. All storage should conform to local fire and building codes. Drum stock should be kept to a reasonable minimum with first-in, first-out stock rotation. Where bung-in-head containers are stored outside, it is recommended that these be stored in a horizontal position to avoid the ingress of water.

STANDARD PACKAGE

Non-returnable metal drums. Bulk supplies can be delivered by road tanker.

MATERIAL SAFETY DATA SHEET

A Material Safety Data Sheet is available from your NCS Resins' representative. Make certain that you obtain a copy of this guide to the safe handling of unsaturated polyester resins and resin systems.

PLEASE READ AND UNDERSTAND THE MATERIAL SAFETY DATA SHEET BEFORE WORKING WITH THIS PRODUCT

WARNING

CARE MUST BE TAKEN TO AVOID DIRECT MIXING OF ANY ORGANIC PEROXIDE (CATALYST) WITH METAL SOAPS, AMINE OR ANY OTHER POLYMERISATION ACCELERATOR OR PROMOTER, AS VIOLENT DECOMPOSITION WILL RESULT!

NCS RESINS BRANCHES AT: JOHANNESBURG / DURBAN / CAPE TOWN / PORT ELIZABETH

A-4: Uvasorb® MET

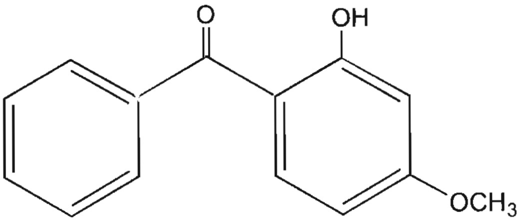


Figure A-3: Structure

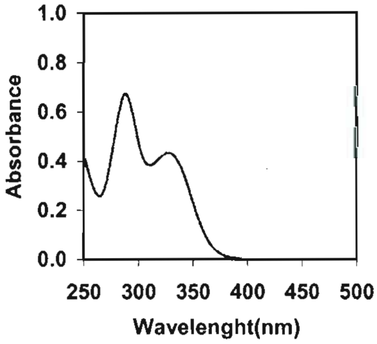


Figure A-4: Absorbance

Table A-5: Chemical and physical characteristics (Uvasorb® MET)

Chemical Name	2-hydroxy-4-methoxy benzophenone
Appearance	Yellow powder
CAS number	131-57-7
Molecular formula	$C_{14}H_{12}O_3$
Molecular weight	228.2
Melting point (°C)	63-64.5
Bulk density (g/cc)	0.65-0.75
Solubility (g/100ml 25°C)	
Acetone	>50
1-Butanol	4
Butyl acetate	38
Butyldiglycol	20
Ethanol	4
Ethyl acetate	>30
Methyl Alcohol	3
Methlylene Chloride	>50
Methyl ethyl ketone	>30
n-Hexane	<1
Solvesso 100	>25
Solvesso 150	>25
Styrene	>50
Toluene	>50
Xilene	>50
Water	insoluble

(*)Typical values not qualified for quality control purpose

PROPERTIES

Uvasorb® MET is an absorber of ultraviolet light , belonging to the class of compounds known as benzophenone derivatives; its absorption spectrum ranges from 270 to 380 nm with two maxima of absorbance at 288 and 327 nm. Uvasorb®METdoes not absorb in the visible region (Figure 1).

Fig.1 - Uvasorb®MET - Absorption curves;
Solvent Chloroform; Concentration 10 ppm

APPLICATIONS

Uvasorb® MET is thermally stable and is compatible with a broad range of binders, normally used in coating formulations such as:

Polyesters
Acrylics
Cellulosics
Polyurethanes.
Polystyrenes
Polyvinyl Acetate

Uvasorb®MET has an excellent solubility in aromatic solvents and in some polar solvents. It is slightly soluble in alcohols whereas it is practically insoluble in water. Uvasorb®MET protects against solar radiation improving the resistance of clear coating to sunlight modifications.

USE

The concentration of Uvasorb® MET depends on the required service life of the article, o thickness, presence of pigments etc. Typical addition level ranges from 0.10 to 1.0% of Uvasorb® MET. Any application should be thoroughly investigated according to the specific conditions of use.

TOXICOLOGICAL INFORMATION

LD_{50} (oral)	> 5000 mg/kg
Skin irritation	non irritant
Eye irritation	non irritant

(See also: C.I.R. - Final Report on the Safety Assessment of Benzophenones - Journal of the American College of Toxycology, Volume 2, Number 5, 1983)

TRANSPORT, STORAGE AND HANDLING

Labelling: product not classified as hazardous according to international transport regulations.

Do not breathe dust and avoid contact with skin, eyes and mucous membranes. In case of contact, wash immediately with plenty of water. Store this product in the original closed container in a dry and cool place. Protect from light. Avoid dust formation.

For further information please refer to safety data sheet.

A-5: ADEKIT H9940 STRUCTURAL EPOXY ADHESIVE

ADEKIT A 140

HIGH PERFORMANCES
PROPERTIES

The two-component epoxy adhesive for bonding structural assemblies must have good peeling and ageing resistances.

APPLICATIONS

- Bonding of body de carrosserie.
- Bonding metallic structures (racing vehicles, aeronautics)
- Bonding inserts and composite structure.

Table A-6: PHYSICAL PROPERTIES (H9940)

PHYSICAL PROPERTIES			
	RESIN	**HARDENER**	**MIXING**
Mixing ratio by weight	100	90	
Mixing ratio by volume	100	100	
Colour	grey, brown, black	beige	beige grey, brown, black
Density at 25°C	1.38	1.23	1.3
Brookfield RVT viscosity (sp6 1 rpm) (Pa.	400	450	4.3
Pot life at 25°C on 100 g (GEL TIMER) (min.)			30
Open time at 25°C (min)			40

Table A-7: MECHANICAL PROPERTIES ON ASSEMBLIES (H9940)

MECHANICAL PROPERTIES ON ASSEMBLIES			
Time to obtain 1 MPa lap shear strength at 25°C	ISO 4587-95	hour	4 hrs 30
Time to obtain 50% final lap shear strength at 25°C	ISO 4587-95	hour	20
Lap shear strength on aluminium (2)	ISO 4587-95	MPa	21 CF (3)
Floating roller peel resistance (2)	ISO 4578-97	kN/m	5 CF (3)

(1) Lap shear strength on aluminium2017A etched in sulfochromic bath
(2) Hardening conditions: 8 hrs at 80°C + 48 hrs at room temperature
(3) CF:Cohesive failure according to ISO 10365-95 norm

EQUIPMENT

ADEKIT A140 is packaged in 50 ml and 40 ml cartridges and requires a manual or pneumatic gun. Please consult our technical department for applications needing a machine.

PRECAUTIONS

It is recommended to use the product at a temperature between +18°C and +35°C. Normal health and safety precautions should be observed when handling these products:
☐ensure good ventilation
☐wear gloves and safety glasses
☐wear waterproof clothes
For further information, please consult the product safety data sheet.

ADEKIT A 140
ADEKIT H 9940
STRUCTURAL EPOXY ADHESIVE
HIGH PERFORMANCES

Table A-8: MECHANICAL PROPERTIES ON ASSEMBLES (H9940)

MECHANICAL PROPERTIES ON ASSEMBLES			
Lap shear strength after moist cataplasm 15 days at 80°C	ISO 4587-95	MPa	20 CF(3)
Lap shear strength after a thermal shock ageing cycle	ISO 4587-95	MPa	20 CF
15 cycles D3 (see annex)			16 CF
Lap shear strength after ageing in immersion for 3 weeks :			17 CF
• motor oil at 70°C			21 CF
• hydrochloric acid (0.1 N) at 23°C		MPa	21 CF
• soda (0.1 N) at 23°C	ISO 4587-95		19 CF
• seawater at 23°C	ISO 175-99		21 CF
• gasoil at 23°C			
• gas at 23°C			
Lap shear strength after thermal ageing 3 weeks at 100°C	ISO 4587-95	MPa	21 CF

Table A-9: THERMAL AND MECHANICAL PROPERTIES (H9940)

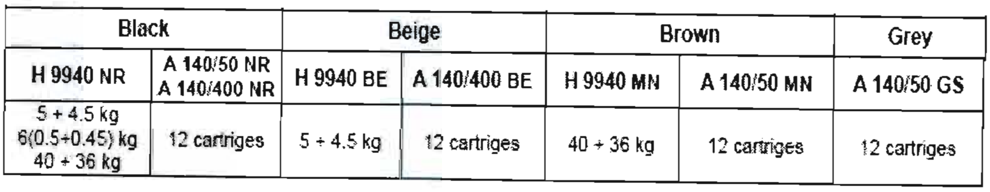
THERMAL AND MECHANICAL PROPERTIES			
Hardness	ISO 868-85	Shore D1 / D15	80/77
Elongation at break	ISO 527-96	MPa	30
Glass transition temperature	ISO 527-96	%	2
Thermal coefficient of expansion (CTE)	TMA-METTLER	°C	70
[-30;+60]°C	TMA-METTLER	10e-6 Ke-1	70
Working temperature	_	°C	-40 ; +100°C

SUBSTRATE PREPARATION

The item to be bonded must be free of all dirt, oil or other foreign matter. A clean, dry surface is a must. Consult our Technical Support and refer to the technical data sheet about surface preparations to choose adapted degreaser or cleaner.

PACKAGING

Table A-10: PACKAGING (H9940)



Black		Beige		Brown		Grey
H 9940 NR	A 140/50 NR A 140/400 NR	H 9940 BE	A 140/400 BE	H 9940 MN	A 140/50 MN	A 140/50 GS
5 + 4.5 kg 6(0.5+0.45) kg 40 + 36 kg	12 cartriges	5 + 4.5 kg	12 cartriges	40 + 36 kg	12 cartriges	12 cartriges

STORAGE CONDITIONS

Shelf life of ADEKIT A140 / H9940 is 12 months minimum stored in its original unopened packaging at a temperature between +15°C and +25°C.

GUARANTEE

The information contained in this technical data sheet result from research and tests conducted in our Laboratories under precise conditions. It is the responsibility of the user to determine the suitability of AXSON products, under their own conditions before commencing with the proposed application. AXSON guarantee the conformity of their products with their specifications but cannot guarantee the compatibility of a product with any particular application. AXSON disclaim all responsibility for damage from any incident which results from the use of these products. The responsibility of AXSON is strictly limited to reimbursement or replacement of products which do not comply with the published specifications.

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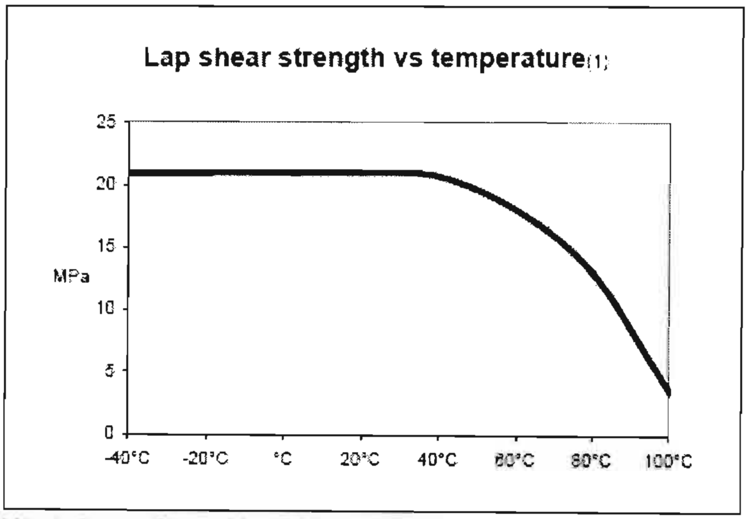

(1) Hardening conditions : 8 hrs at 80°C + 48 hours at room temperature

Figure A-5: Lap shear

THERMAL SHOCK TEST ACCORDING TO ISO 9142-93 NORM

D3 cycle

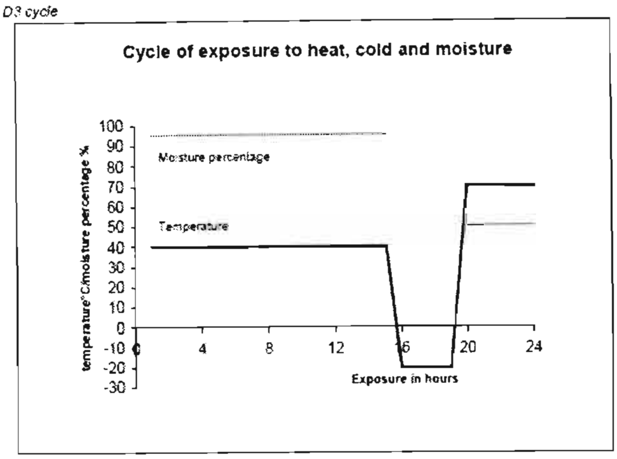

Figure A-6: Exposure Cycle

ADEKIT H 9940

STRUCTURAL EPOXY ADHESIVE

HIGH PERFORMANCES

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A-6 N C S: 901 PA Resin

FAST WET-OUT, GENERAL-PURPOSE, POLYESTER RESIN
LLOYDS APPROVED

DESCRIPTION

NCS 901 PA is a rigid, medium reactivity, thixotropic, orthophthalic unsaturated polyester resin. NCS 901 PA is pre-accelerated and of medium cure rate. NCS 901 PA is designed for hand lay-up and spray applications. This resin is ideal for use in marine applications, automotive components and general industrial mouldings.

Table A-11: Features and Benefits

FEATURES	**BENEFITS**
Low viscosity	Excellent glassfibre wet-out
Thixotropic	Minimal drainage
Non air-inhibited	Cures to a tack-free finish
Specially promoted	Predictable geltime and cure rate
Lloyds approved	Meets international quality standards
SABS 713-1999 approved	Meets national quality standards
Heat Distortion Temperature above 80°C	Good heat resistance
Good colour	Readily pigmentable

OTHER RELATED VERSIONS

NCS 901 P100 PA
White Pigmented version of
NCS 901 PA
NCS 901 P100 PAE
White pigmented version of NCS 901 PA, for export.

NCS 901 P919 PA

Grey pigmented version of NCS 901 PA

NCS 948 PA

Summer (longer geltime) version of NCS 901 PA with a gel-time of 25-35 minutes

Table A-12: TYPICAL LIQUID PROPERTIES

PROPERTY	SPECIFICATION	NCS TEST METHOD
Relative density 25°/25°C	1,09 - 1,11	14
Viscosity @ 25°C, mPa.s	230 - 330	5.2
Thixotropic index, ratio	1.25 minimum	
Acid value, mg KOH/g	19.5 – 24.5	13
Volatile content, %	43 - 46	7
Geltime @ 25°C, using 2 phr* BUTANOX M50, minutes	10 - 13	8
Liquid appearance	Opaque pink	2
Stability in the dark @ 25°C, months	6 minimum	4.1
***phr = parts per hundred resin, by mass.**		

CURING CHARACTERISTICS

NCS 901 PA needs only the addition of catalyst to start the curing reaction. The resin must be allowed to attain workshop temperature (23°C) before being formulated for use. The correct amount of catalyst is therefore added and thoroughly stirred into the resin shortly before use.

The ambient temperature and the amount of catalyst control the gel-time of the resin formulation. This can be approximately determined from the table below which shows the gel-time of 100 parts by mass of NCS 901 PA, containing 1 to 2 phr BUTANOX M50.

Table A-13: Gel-time (minutes)

Parts of BUTANOX M50 to 100 Parts NCS 901 PA	**1**	**1.5**	**2**
Geltime @ 15°C, minutes	>75	45	33
Geltime @ 20°C, minutes	42	25	19
Geltime @ 25°C, minutes	23	14	11
Geltime @ 30°C, minutes	14	9	7

Curing should not be carried out at temperatures below 15°C. Ideally, the catalyst level should range between 1 and 2 phr.

POST-CURING

Many satisfactory laminates can be made from NCS 901 PA by curing at ambient temperature (but not less than 15°C). When optimum properties and long-term performance are required however, the laminate should be post-cured.

After release from the mould, laminates should be allowed to mature for 24 hours at workshop temperature (23°C). They should then be post-cured for 3 hours at 80°C, although a longer period at a lower temperature will give almost the same result. The post-cure is most effective if it is carried out immediately after the 24 hour maturing period.

PIGMENTS AND FILLERS

NCS 901 PA can be pigmented by the addition of up to 5% NCS POLYCHROME PIGMENT PASTE, but lower quantities consistent with achieving adequate hiding power are preferred if the physical properties of the cured laminate are to be maintained.The addition of fillers to NCS 901 PA is likely to change the hardening characteristics of the resin and will affect the properties of the laminate. Fillers should be accurately checked for moisture content and effect on geltime and cure rate before use.

Table A-14: TYPICAL PHYSICAL PROPERTIES

Typical Properties of NCS 901 PA (unfilled castings) Prepared, post-cured and tested in accordance with SABS 713-1974, as amended	
Temperature of deflection - under load (1,80 MPa), °C	90
Water absorption:	
a) Increase in mass after 28 days immersion, mg	100
b) Loss in mass after drying, mg	45
Barcol (GYZJ 934-1) hardness	45
Tensile strength, MPa	76
Flexural strength, MPa	84
Flexural modulus, MPa	3 930
Compressive strength, MPa	152

Table A-15: Typical Properties of Cured NCS 901 PA

Standard Glass Cloth Laminate Prepared, post-cured and tested in accordance with SABS 713-1974, as amended	
Glass content, % m/m	60-65
Flexural Strength:	
a) At 23°C - original, MPa	600
b) At temperature of deflection - after ageing, MPa	500

STORAGE AND HANDLING

To ensure maximum stability and maintain optimum properties, polyester resin should be stored in closed containers, maintained below 25°C and away from heat sources and sunlight. All storage should conform to local fire and building codes. Drum stock should be kept to a reasonable minimum with first-in, first-out stock rotation. Where bung-in-head containers are stored outside, it is recommended that these be stored in a horizontal position to avoid the ingress of water.

STANDARD PACKAGE

Non-returnable metal drums.
Bulk supplies can be delivered by road tanker.

MATERIAL SAFETY

DATA SHEET

A Material Safety Data Sheet is available from your NCS Resins' representative. Make certain that you obtain a copy of this guide to the safe handling of unsaturated polyester resins and resin systems.

PLEASE READ AND UNDERSTAND THE MATERIAL SAFETY DATA SHEET BEFORE WORKING WITH THIS PRODUCT

WARNING

CARE MUST BE TAKEN TO AVOID DIRECT MIXING OF ANY ORGANIC PEROXIDE (CATALYST) WITH METAL SOAPS, AMINE OR ANY OTHER POLYMERISATION ACCELERATOR OR PROMOTER, AS VIOLENT DECOMPOSITION WILL RESULT!

NCS RESINS BRANCHES AT:
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A-7 UPE1280

ISOPHTHALIC CHEMICAL AND WATER
RESISTANT MARINE LAMINATING
LLOYDS APPROVED

DESCRIPTION

UPE1280 is a clear, pre-accelerated, un-waxed, thixotropic, rigid, medium-reactivity, isophthalic unsaturated polyester resin. UPE1280 has excellent glass-fibre wetting properties and produces laminates with good mechanical properties and good chemical resistance.

UPE1280 is suitable for a wide range of critical applications where high structural performance and maximum durability are required.

UPE1280 carries approval by the Lloyds Register of Shipping, which makes it ideal for marine applications.

APPLICATIONS

UPE1280 is designed for lamination by hand or spray lay-up for the construction of high performance boats, swimming pools, tanks, car bodies, road tankers, ducting, chemical plant and food containers where good chemical and water resistance are required. It forms a complimentary boat manufacturing system when used in conjunction with POLYCOR® GC5S1000 or GC6S1000 gel-coat.

The low level of residual styrene in fully cured laminates makes this resin ideal for the manufacture of non-toxic, non-tainting food containers.

CHARACTERISTICS

Thixotropic
Limited drainage on inclined surfaces.

Lloyds approved

Meets international quality standards.

Low water absorption.

Good mechanical properties.

Isophthalic based

Good chemical and water resistance.

Good hydrolytic stability.

Good heat resistance.

Crisp cure in thin laminates.

Unwaxed

Good inter-laminar adhesion.

Cures basically tack-free.

Pre-accelerated

Requires addition of catalyst only

Table A-16: Liquid Properties

Version: 23/02/2004

PROPERTY	SPECIFICATION
Stability in the dark @ 25°C (months)	6
Viscosity @ 25°C (Cone & Plate, poise)	2.3 – 2.7
Geltime @ 25°C (2% m/m Curox M-200, minutes)	15 – 20
Cure time (minutes)	24 – 29
Peak Exotherm (°C)	180 – 190
Thixotropic Index	2.3 – 2.7
Specific gravity (g/cm^3)	1.10 – 1.12
Non-volatile content (%)	50 – 54
Acid value (mg KOH/g)	20 – 27
Liquid appearance	Hazy blue

Ref: C_PES00081

VARIANTS

UPE1143 is the semi-flexible version.
UPE1371 is the semi-flexible, non-thixotropic version.
UPE1517 is the semi-flexible, unaccelerated version.

CURING CHARACTERISTICS

UPE1280 should be allowed to attain workshop temperature (18 - 25°C) before use. Drums should be rolled or mixed before use, in case any settlement of the thixotrope has taken place. The recommended catalyst is Curox M-200 (MEKP NA2) at 2% by resin mass to start the curing reaction. The ambient temperature and amount of catalyst will control the gel time of the resin.

Under no circumstances should less than 1% MEKP be used to cure this unsaturated polyester. Ensure that the catalyst is thoroughly dispersed in the resin to prevent uneven or under-cured areas which may lead to product failure. Curing should not be carried out below 15°C.

POST-CURING

Curing at ambient temperatures renders laminates suitable for most applications. For optimum performance however, post-curing can be performed on the laminates. Allow for a maturing period of 24 hours. Thereafter perform standard post-curing for 3 hours at 80°C or alternatively 16 hours at 40°C.

To obtain non-toxic, non-tainting laminates for foodstuff containers, it is essential to post-cure the laminates for at least 3 hours at 90°C followed by wet steam cleaning for at least 1 hour.

PHYSICAL PROPERTIES

Properties of a Cured UPE1280 Unfilled Casting

Performed on a 3 mm unfilled casting, post-cured for 3 hours at 80°C, and tested in accordance with SANS 713-2000, ISO R62 and BS 2782.

Deflection temperature under load (264 psi, °C)	95
Tensile strength (MPa)	65
Tensile modulus (MPa)	3 770
Flexural strength (MPa)	108
Specific gravity @ 20°C (g/cm^3)	1.20
Volumetric shrinkage (%)	7.4
Elongation at break (%)	1.3
Water absorption after 7 days (mg)	50
Barcol (GYZJ 934-1) hardness	48

Properties of a Cured UPE1280 CSM Laminate

Performed on a 3 x 450 g/cm^2 chopped strand glass mat laminate tested in accordance with SANS 141-1992. The laminate was cured for 7 days at 23°C before testing.

Tensile strength (MPa)	108
Tensile modulus (MPa)	9 600
Flexural strength (MPa)	204
Glass content (%)	30.0
Barcol (GYZJ 934-1) hardness	48

Performed on a 4 x 450 g/cm^2 chopped strand glass mat laminate. The laminate was cured for 16 hours at 40°C before testing.

Tensile strength (MPa) BS EN ISO 527-4 100
Tensile modulus (MPa) BS EN ISO 527-4 7 900
Flexural strength (MPa) BS EN ISO 14125 166
Flexural modulus (MPa) BS EN ISO 14125 6 800
Compressive strength (MPa) ISO 604 201
Compressive modulus (MPa) ISO 604 7 700
Water absorption after 7 days (mg) ISO 62 54
Glass content (%) ISO 1172 28.4

PIGMENTS AAND FILLERS

UPE1280 can be pigmented with up to 5% Cray Valley POLYCOL Pigment Paste. It is advisable to use lower quantities to have the minimum affect on laminate properties, while still achieving adequate hiding power. Where foodstuffs are involved and when resistance to chemicals is required, incorporation of pigment pastes should be minimised and simulation tests carried out to determine its influence on the performance of laminates. The affect of fillers on the geltime and cure rate of the resin should be determined before commencing with full-scale production. Fillers will also affect the physical properties of the laminate.

CHEMICAL RESISTANCE

A chemical resistance table can be obtained through your Harvey's Composites representative. The table provides the recommended maximum service temperatures for laminates of UPE1280 immersed in various chemical environments. Where a combination of chemicals is involved, please consult with a Cray Valley Resins technical service representative. For resistance to oils we would rather recommend UPE1679.

STORAGE

UPE1280 should be stored in closed containers away from direct sunlight and other heat sources. The recommended storage temperature is below 25°C. In case of outside storage, containers should be stacked horizontally to avoid the ingress of water.

PACKAGING

UPE1280 is supplied in 230kg non-returnable drums.

HEALTH AND SAFETY

A Material Safety Data Sheet can be obtained through your Harvey's SAFETYComposites representative.

POLYESTER SAFETY INFORMATION

All sales of products manufactured by Cray Valley Resins South Africa and described herein are made solely on condition that our customers comply with applicable health and safety laws, regulations and orders relating to the safe handling of our products in the workplace. Before using, read the following information and both the product label and Material Safety Data Sheet pertaining to each product.

Most polyester products contain styrene. Styrene can cause eye, skin and respiratory tract irritation. Avoid contact with eyes, skin and clothing. Impermeable gloves, safety eyewear and protective clothing should be worn during use to avoid skin and eye contact. Wash personal protective equipment thoroughly after use.

Styrene is a solvent and may be harmful if inhaled. Reports have associated repeated and prolonged occupational overexposure to solvents with permanent brain and nervous system damage. Extended exposure to styrene at concentrations above the recommended exposure limits may cause central nervous system depression causing dizziness, headaches or nausea and if overexposure is continued indefinitely, loss of consciousness, liver and kidney damage.

Do not breathe or ingest vapour, spray mists and dusts caused by applying, sanding, grinding and sawing polyester products. Wear an appropriate OHSA approved, properly fitted respirator during application and use of these products until vapours, mists and dusts are exhausted, unless air monitoring demonstrates vapours, mists and dusts are below applicable exposure limits. Follow respirator manufacturer's directions for respirator use.

The International Agency for Research on Cancer (IARC) has reclassified styrene as Group 2B "possibly carcinogenic to humans". This new classification is not based on new health data relating to either humans or animals, but on a change in the IARC classification system. The Styrene Information and Research Center does not agree with the reclassification and has published the following statement: Recently published studies tracing 50 000 workers exposed to high occupational levels of styrene over a period of 45 years showed no association between styrene and cancer, no increase in cancer among styrene workers (as opposed to the average among all workers), and no increase in mortality related to styrene.

Styrene is classified by OHSA and the Department of Transport as a flammable liquid. Flammable polyester products should be kept away from heat, sparks and flame. Lighting and other electrical systems in the workplace should be vapour-proof and protected from breakage.

Vapours from styrene may cause flash fire. Styrene vapours are heavier than air and may concentrate in the lower levels of moulds and the work area. General clean air dilution or local exhaust ventilation should be provided in volume and pattern to keep vapours well below the lower explosion limit and all air contaminants (vapour, mists, dusts) below the current permissible exposure limits in the mixing, application, curing and repair areas.

Some polyester products may contain additional hazardous ingredients. To determine the hazardous ingredients present, their applicable exposure limits and other safety information, read the Material Safety Data Sheet for each product (identified by product code) before using.

FIRST AID: In case of eye contact, flush immediately with plenty of water for at least 15 minutes and get medical attention; for skin, wash thoroughly with soap and water. If affected by inhalation of vapours or spray mist, remove to fresh air. If swallowed, get medical attention.

Polyester products have at least two components that must be mixed before use. Any mixture of components will have hazards of all components. Before opening the packages, read all warning labels. Observe all precautions.

Keep polyester containers closed when not in use. In case of spillage, absorb with inert material and dispose of in accordance with applicable regulations. Emptied containers may retain hazardous residue. Do not cut, puncture or weld on or near these containers. Follow container label warnings until containers are thoroughly cleaned or destroyed.

DISCLAIMER AND LIMITATION OF LIABILITY

The products sold hereunder shall meet Seller's applicable specifications at the time of shipment. Seller's specifications may be subject to change at any time without notice to Buyer. Buyer must give Seller notice in writing of any alleged defect covered by this warranty (together with all identifying details, including the product code(s), description and date of purchase) within thirty (30) days of the date of shipment of the product or prior to the expiration of the shipment's quality life, whichever occurs first. The warranty described herein shall be in lieu of any other warranty, express or implied, including but not limited to, any implied warranty or merchantability or fitness for a particular purpose. There are no warranties that extend beyond the description on the face hereof.

The Buyer's sole and exclusive remedy against Seller shall be for the replacement of the product or refund of the purchase price in the event that a defective condition of the product should be found to exist by Seller. No other remedy (including, but not limited to, incidental or consequential damages for lost profits, lost sales, injury to person or property, or any other incidental or consequential loss) shall be available to the Buyer.

The sole purpose of this exclusive remedy shall be to provide Buyer with replacement of the product or refund of the purchase price of the product if any defect in material or workmanship is found to exist. This exclusive remedy shall not be deemed to have failed its essential purpose so long as Seller is willing and able to replace the defective products or refund the purchase price.

Final determination of the suitability of the material for the use contemplated, the manner of use and whether the suggested use infringes any patents is the sole responsibility of the Buyer.

A-8: NCS SUPREME 101 P1075 PA

(S0112/4)

NDS032/035

HIGH PERFORMANCE MARINE BRUSH GELCOAT

DESCRIPTION

NCS SUPREME 101 P1075 PA is a white, thixotropic, pre-accelerated unsaturated polyester gelcoat. It is especially formulated using chemistry and raw matrials selection to provide superior weathering performance and blister resistance

NCS SUPREME 101 P1075 PA is highly recommended for applications which require long term outdoor weather resistance and blister resistance. This makes this product ideal for ocean going yatchs and power boats.

FEATURES and BENEFITS

Thixotropic
Minimal drainage with good flow

Pre-accelerated
Requires only the addition of suitable catalyst

UV-stabilized
Improved weather resistance

New Chemistry
Improved durability and property retention

Specially promoted
Minimal gel time drift with improved cure characteristics

Pigmented White

High opacity

OTHER VERSIONS

NCS SUPREME 101 NAT PA Clear Brush Marine Gel coat
NCS SUPREME 101 PA Clear Spray Marine Gel coat
NCS SUPREME 101 NAT PA White Spray Marine Gel coat.

Table A-17: TYPICAL LIQUID PROPERTIES

PROPERTY	SPECIFICATION	NCS TEST METHOD
Viscosity @ 25°C, MPa.s	55 000 - 65 000	5.3
Gel time @ 25°C, 2 phg* BUTANOX M50, minutes	12 - 16	8
Liquid appearance	Opaque White	2
Stability in the dark, months	6 minimum	4.1
***phg = parts per hundred gel coat**		

CURING CHARACTERISTICS

NCS ULTRAGEL 31 P100 PA is supplied pre-accelerated, needing only the addition of catalyst to start the curing reaction.

The recommended catalyst for NCS SUPREME 101 P1075 PA is BUTANOX M50. BUTANOX M50 disperses readily in a gel coat, but must nevertheless be mixed in thoroughly. Low reactivity 30% MEKP must not be used. Under normal conditions, it is advisable to use two parts of BUTANOX M50 per one hundred part of gelcoat by mass.

Curing should not be carried out at temperatures below 15°C.SUPREME 101 P1075 PA must be allowed to attain workshop temperature (>20°C) before being formulated for use.

NCS SUPREME 101 P1075 PA requires only the addition of catalyst to start the curing reaction. The catalyst is therefore added and thoroughly stirred into the gel coat resin shortly before use. The time taken for the gel coat film to harden will depend on several factors, including the thickness of the gel coat layer applied and the material from which the mould is constructed.

It should be noted that this gel coat is not as forgiving as standard is gel coats. With respect to low temperature, low catalyst level and lo film thickness. Precautions should be taken to ensure that the gel coat temperature is above 15°C, the catalyst level above 1,5 pgh and the film thickness above 400 microns.

The following formulation is recommended.

COMPONENT PARTS BY MASS

NCS ULTRAGEL 31 P100 PA: 100
BUTANOX M50: 2

The table below shows the potlife of 1kg of NCS SUPREME 101 P1075 P1 PA at various temperatures and catalyst levels:

Table A-18: Parts of BUTANOX M50 to 100 parts SUPREME 101 P1075 PA

Parts of BUTANOX M50 to 100 parts ULTRAGEL 31 P100 PA	**1**	**1,5**	**2**	**2,5**	**3**
Potlife @ 15°C, minutes	86	48	35	29	14
Potlife @ 20°C, minutes	43	23	19	15	12
Potlife @ 25°C, minutes	27	17	13	10	9
Potlife @ 30°C, minutes	17	12	9	8	7
Potlife @ 35°C, minutes	11	8	6	5	4

APPLICATION

NCS SUPREME 101 P1075 PA is designed for application by brush. For normal mouldings, the gelcoat thickness should be controlled to about 0,45-0,65 mm. As a guide, 500-700g.m^{-2} of NCS SUPREME 101 P1075 PA, when evenly applied, will give the required thickness.

PIGMENTS AND FILLERS

NCS SUPREME 101 P1075 PA is supplied pre-pigmented white with excellent opacity and does not require further addition of pigment.

The addition of fillers to NCS SUPREME 101 P1075 PA is not recommended since their use may adversely affect the weather resistant and water resistant properties of the cured gelcoat.

It is recommended that, where mouldings are produced as sub-components of larger structures, or are simply large structures, that sufficient resin and pigment paste are mixed to enable the entire job to be completed, thus ensuring an exact colour match. Similarly, if pigmented gelcoat is used, it is recommended that the same batch of material is used throughout the application as well as for sub-components. Thorough stirring of the mix shortly before use is recommended to ensure that the pigment is fully dispersed and that no separation has occurred. Care must be taken not to introduce air into the system. Users are advised to consult application bulletins which deal with the methods of use and scope of application of NCS Resins gelcoats.

STORAGE AND HANDLING

To ensure maximum stability and maintain optimum properties, polyester resin should be stored in closed containers, maintained below 25°C and away from heat sources and sunlight. All storage should conform to local fire and building codes. Drum stock should be kept to a reasonable minimum with first-in, first-out stock rotation.

Where bung-in-head containers are stored outside, it is recommended that these be stored in a horizontal position to avoid the ingress of water.

STANDARD PACKAGE

Non-returnable metal drums.

MATERIAL SAFETY DATA SHEET

A Material Safety Data Sheet is available from your NCS Resins' representative.

PLEASE READ AND UNDERSTAND THE MATERIAL SAFETY DATA SHEET BEFORE WORKING WITH THIS PRODUCT

WARNING:

CARE MUST BE TAKEN TO AVOID DIRECT MIXING OF ANY ORGANIC PEROXIDE (CATALYST) WITH METAL SOAPS, AMINE OR ANY OTHER POLYMERISATION ACCELERATOR OR PROMOTER, AS VIOLENT DECOMPOSITION WILL RESULT!

NCS RESINS BRANCHES AT:

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B Appendix B

Tables of Modulus, Stress, Strain, Load and Stress-Strain Graphs of each Tested Specimen

Table B-1: Modulus, Stress, Strain, and Load of each tested NUV 2 specimen

NUV 2 (exposed)	Maximum Load (N)	Load @ Failure (N)	Strain @ Failure (%)	Max. Comp. Stress (MPa)	Modulus
1	-6799.59	6531.752	20.51	421.811	4516.9
2	-6226.99	6226.985	20.55	419.326	4927.3
3	-7731.84	7728.858	24.07	487.505	5236.5
4	-65.96.94	6564.559	17.91	430.048	5545.4
5	-5635.05	5635.05	22.21	355.3	1464.9
mean	-6598.08	6537.441	21.05	422.798	4338.2
S.D	773.17	763.37	2.28	46.927	1650.6
Minimum	-7731.05	5635.050	17.91	355.3	1464.9
Maximum	-5635.05	7728.858	24.07	487.505	5545.4
Range	2096.79	2093.808	6.16	132.206	4080.4

Table B-2: Modulus, Stress, Strain, and Load of each tested NUV 17 specimen

NUV 17 (unexposed)	Maximum Load (N)	Load @ Failure (N)	Strain @ Failure (%)	Max. Comp. Stress (MPa)	Modulus
1	-4735.8	4733.021	25.64	365.416	2395.4
2	-5615.3	5480.168	32.62	389.951	1582.2
3	-6316.37	6282.256	44.94	503.698	1262.9
4	-6163.96	6163.959	39.88	428.053	1320.4
mean	-57.07.86	5664.851	35.77	421.78	1640.2
S.D	714.56	714.775	8.43	60.387	522.2
Minimum	-6316.37	4733.021	25.64	365.416	1262.9
Maximum	-4735.8	6282.256	44.94	503.698	2395.4
Range	1580.57	1549.234	19.29	138.281	1132.4

Table B-3: Modulus, Stress, Strain, and Load of each tested TIN 3 specimens

TIN 3 (exposed)	Maximum Load (N)	Load @ Failure (N)	Strain @ Failure (%)	Max. Comp. Stress (MPa)	Modulus
1	-6077.73	5321.075	38.76	452.886	1555.0
2	-5522.46	5247.784	31.99	418.368	2392.4
3	-4294.07	4289.258	45.98	298.199	858.4
mean	-5298.09	4952.706	38.91	389.818	1601.9
S.D	912.75	575.73	6.99	81.199	768.0
Minimum	-6077.73	4289.258	31.99	298.199	858.4
Maximum	-4294.07	5321.075	45.98	452.886	2392.4
Range	1783.66	1031.816	13.99	154.687	1534.0

Table B-4: Modulus, Stress, Strain, and Load of each tested TIN 47 specimens

TIN 47 (unexposed)	Maximum Load (N)	Load @ Failure (N)	Strain @ Failure (%)	Max. Comp. Stress (MPa)	Modulus
1	-4552.86	4475.872	19.28	303.524	3125.4
2	-5188.13	4899.673	17.25	366.393	5377.0
3	-5074.33	5071.708	27.81	352.384	1367.4
4	-4199.62	4163.69	21.39	277.752	1350.5
Mean	-4753.3	4652.736	21.43	325.013	2805.1
S.D	461.48	411.081	4.58	41.46	1906.1
Minimum	-5188.13	4163.69	17.25	277.752	1350.5
Maximum	-4199.62	5071.708	27.81	366.393	5377.0
Range	988.51	908.018	10.56	88.641	4026.5

Table B-5: **Modulus, Stress, Strain, Load of each tested MET 23 specimen**

MET 23 (unexposed)	Maximum Load (N)	Load @ Failure (N)	Strain @ Failure (%)	Max. Comp. Stress (MPa)	Modulus
1	-5947.64	5947.635	36.63	495.636	1494.8
*2	6.94	-8.368	0.02	-0.525	
*3	-108.87	108.871	1.54	8.248	534.9
4	-4623.66	3535.858	84.48	350.277	782.1
5	-1330.96	934.045	11.19	114.738	1626.3
mean	-3967.42	3472.513	44.1	320.217	1301.1
S.D	2377.37	25.07.395	37.21	192.22	454.2
Minimum	-5447.64	934.045	11.19	114.738	782.1
Maximum	-1330.96	5947.635	84.48	495.636	1626.3
Range	4616.67	5013.59	73.29	380.898	844.2

(*) – Results are spoilt due to load cell not being balanced

Table B-6: Modulus, Stress, Strain, and Load of each tested MET 16 specimen

MET 16 (exposed)	Maximum Load (N)	Load @ Failure (N)	Strain @ Failure (%)	Max. Comp. Stress (MPa)	Modulus (MPa)
1	-4487.84	4209.839	23.41	392.294	2950.2
2	-4777.74	4497.138	47.52	361.95	901.1
3	-5264.1	3778.136	24.81	378.168	2533.7
4	-5443.05	5279.655	37.08	391.023	1229.5
Mean	-4993.18	4441.192	33.21	380.859	1903.6
S.D	438.77	632.276	11.35	14.129	991.9
Minimum	-5443.05	3778.136	23.41	361.65	901.1
Maximum	-4487.84	5279.655	47.52	392.294	2950.2
Range	955.2	1501.52	24.11	30.344	2049.1

Table B-7: **Modulus, Stress, Strain, and Load of each tested MET 16 specimen**

MET 4 (unexposed)	Maximum Load (N)	Yield Strength (0.2 % Offset) (Mpa)	Max. Comp. Stress (MPa)	Failure Type
1	5910.78		388.152	same as before
2	7046.56	246.55	403.269	same as before
3	6890.49		423.363	same as before
Mean	6615.94	249.55	404.928	0
S.D	615.65	0	17.664	0
Minimum	5910.78	249.55	388.152	0
Maximum	7046.56	249.55	423.363	0
Range	1135.78	0	35.211	0

Table B-8: **Modulus, Stress, Strain, and Load of each tested MET 31 specimen**

MET 31	Maximum Load (N)	Load @ Failure (N)	Strain @ Failure (%)	Max. Comp. Stress (MPa)	Modulus
1	-7017.2	7003.649	16.98	504.109	3487.969
2	-6728.26	6607.088	14.81	485.269	19341.279
3	-6892.47	6456.551	17.79	552.281	3483.296
Mean	-6879.31	6689.096	16.53	513.887	8770.848
S.D	144.92	282.618	1.54	34.559	9154.262
Minimum	-7017.2	6456.551	4.81	485.269	3483.296
Maximum	-6728.26	7003.649	17.79	552.281	19341.279
Range	288.95	547.099	2.98	67.012	15857.983

Table B-9: Modulus, Stress, Strain, and Load of each tested NUV 26 specimen

NUV 26	Maximum Load (N)	Load @ Failure (N)	Strain @ Failure (%)	Max. Comp. Stress (MPa)	Modulus
1	-7146.68	7144.054	15.21	513.411	5128.144
2	-5677.49	5465.627	11.18	423.851	4899.294
3	-6547.53	6544.853	13.97	489.078	4586.284
mean	-6457.23	6384.845	13.45	475.447	4871.241
S.D	738.75	850.777	2.07	46.31	272.017
Minimum	-1746.68	5465.627	11.18	423.851	4586.284
Maximum	-5677.49	7144.054	15.21	513.411	5128.144
Range	1469.19	1678.427	4.03	89.56	541.86

Table B-10: Modulus, Stress, Strain, and Load of each tested K 100 specimen

K 100	Maximum Load (N)	Load @ Failure (N)	Strain @ Failure (%)	Max. Comp. Stress (MPa)	Modulus
1	-4997.4	4912.219	8.2	323.77	4583.771
2	-6956.53	6758.566	10.95	429.415	4405.554
3	-5530.6	5237.32	9.33	365.78	5340.757
mean	-5828.17	5636.035	9.49	372.989	4776.694
S.D	1012.9	985.637	1.38	53.19	496.554
Minimum	-6956.63	4912.219	8.2	323.77	4405.554
Maximum	-4997.4	6758.566	10.95	429.415	5340.757
Range	1959.13	1846.347	2.75	105.645	935.203

Table B-11: Modulus, Stress, Strain, and Load of each tested NUV 1 specimen

NUV 1	Max. Comp. Stress (MPa)	Strain @ Failure (%)	Maximum Load (N)	Failure Type
1	391.8	0.13	6213.93	Shear
2	392.37	0.15	6427.07	Shear
*3	88.74	0.03	1402.725	exclude
4	515.42	0.13	8147.8	Shear
5	533.44	0.19	8710.017	Shear
Mean	458.26	0.15	7374.704	
S.D	76.76	0.03	1241.792	
Minimum	391.8	0.13	6213.93	
Maximum	533.44	0.19	8710.017	
Range	141.64	0.06	2496.086	

Table B-12: Modulus, Stress, Strain, and Load of each tested I TIN 53 specimens

I TIN 53	Maximum Load (N)	Load @ Failure (N)	Strain @ Failure (%)	Max. Comp. Stress (MPa)	Modulus
2	-6564.36	6418.094	12.61	518.922	5539.933
3	-5232.55	5229.205	11.01	379.72	4392.611
4	-5214.01	5035.45	17.47	440.931	2927.934
mean	-5670.31	5560.916	13.7	446.525	4286.826
S.D	774.33	748.633	3.36	69.769	1309.209
Minimum	-6564.36	5035.45	11.01	379.72	2927.934
Maximum	-5214.01	6418.094	17.47	518.922	5539.933
Range	1350.35	1382.645	6.46	139.202	2611.999

Table B-13: Modulus, Stress, Strain, and Load of each tested K 404 specimen

K 404	Max. Comp. Stress (MPa)	Strain @ Failure (%)	Maximum Load (N)	Failure Type
1	405.77	0.22	7205.507	tabs debonded
2	284.02	0.34	5214.534	tabs debonded
3	323.83	0.14	6198.16	failure at tabs
4	364.69	0.12	7122.42	failure at tabs
mean	344.58	0.2	6435.155	
S.D	52.43	0.1	933.07	
Minimum	284.02	0.12	5214.534	
Maximum	405.77	0.34	7205.507	
Range	121.75	0.22	1990.973	

Table B-14: Modulus, Stress, Strain, and Load of each tested I TIN 1specimen

I TIN 1	Maximum Load (N)	Load @ Failure (N)	Strain @ Failure (%)	Max. Comp. Stress (MPa)	Modulus
*1	-967.5	967.499	9.95	55.022	2293.667
2	-6047.98	6034.231	28.95	348.933	1819.507
3	-6943.14	6699.661	15.06	391.118	3107.718
4	-5987.44	5987.437	15.08	377.138	2535.34
5	-6592.89	5384.153	21.1	374.937	4002.402
mean	-6392.86	6026.37	20.2	373.031	2866.242
S.D	456.85	537.693	6.43	17.591	922.735
Minimum	-6943.14	5384.153	15.06	348.933	1819.507
Maximum	-5987.44	6699.661	28.95	391.118	4002.402
Range	955.7	1315.508	13.89	42.186	2182.895

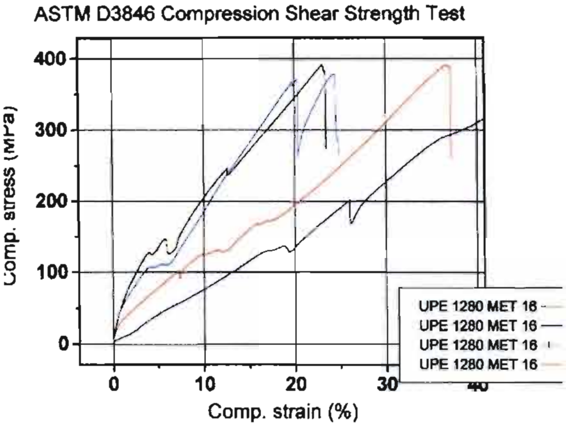


Figure B-1: Stress vs. Strain (MET 16)

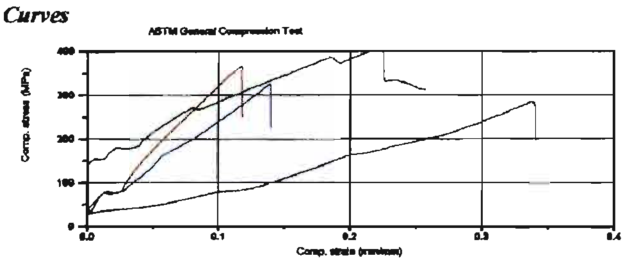


Figure B-2: Stress vs. Strain (K 404)

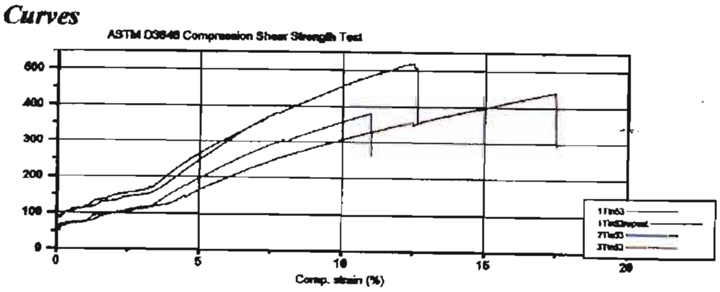


Figure B-3: Stress vs. Strain (I TIN 53)

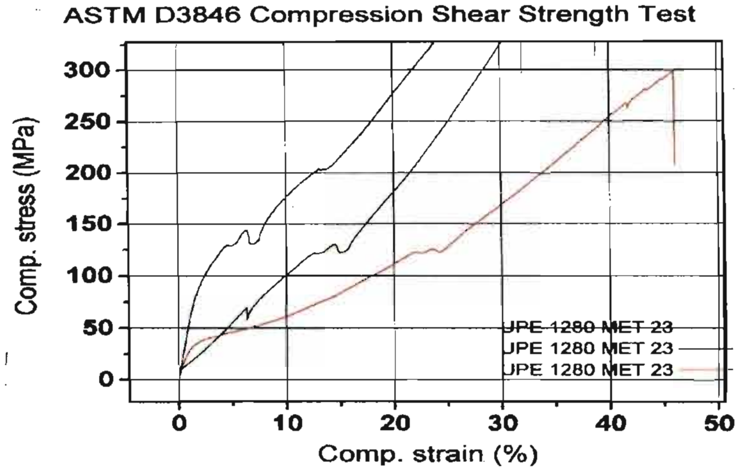


Figure B-4: Stress vs. Strain (MET 23)

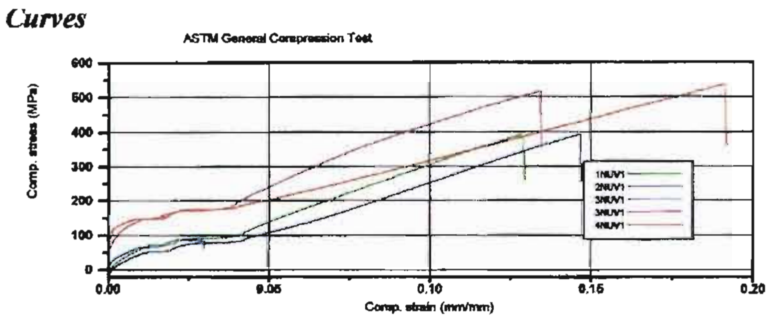


Figure B-5: Stress vs. Strain (NUV 1)

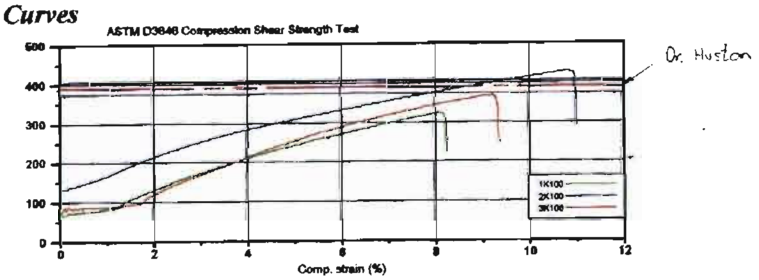


Figure B-6: Stress vs. Strain (K 100)

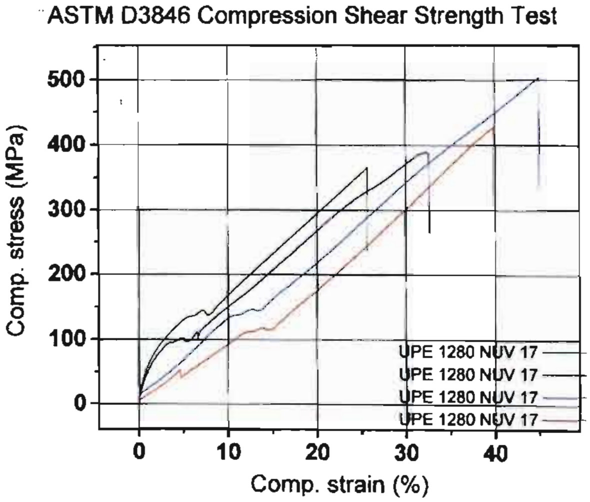


Figure B-7: Stress vs. Strain (NUV 17)

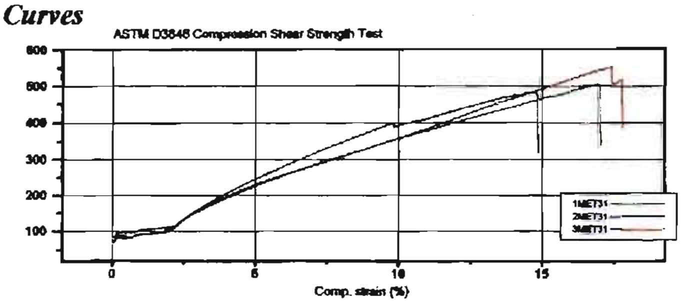


Figure B-8: Stress vs. Strain (MET 31)

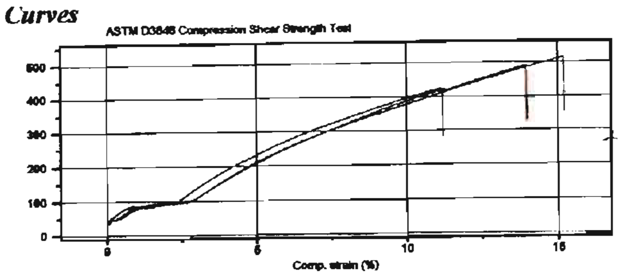


Figure B-9: Stress vs. Strain (NUV 26)

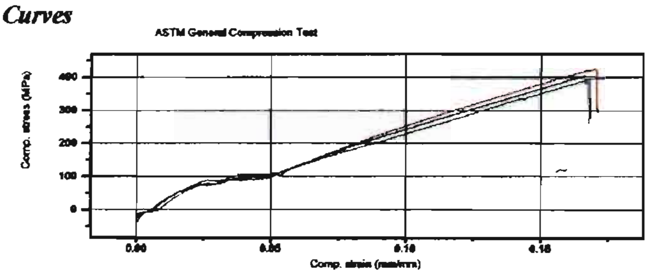


Figure B-10: Stress vs. Strain (MET 4)

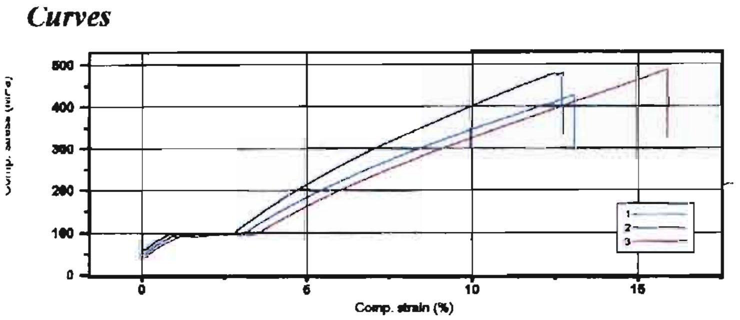
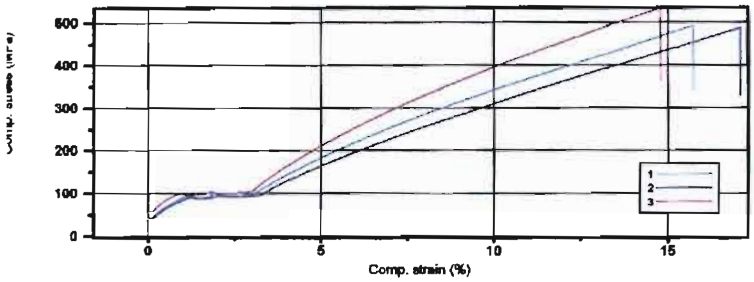
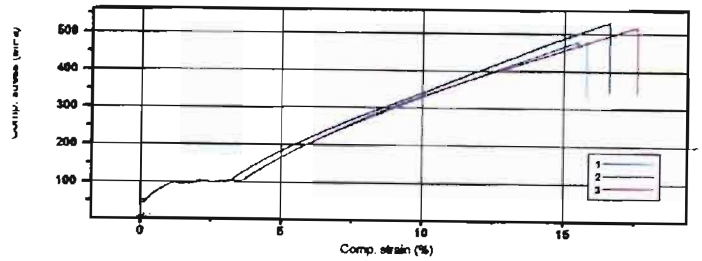


Figure B-11: Stress vs. Strain (I TIN 48)



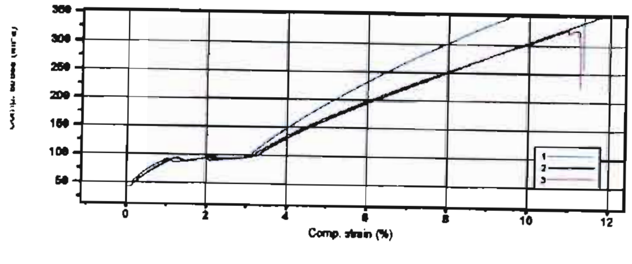
Curves

Figure B-12: Stress vs. Strain (I TIN 8)



Curves

Figure B-13: Stress vs. Strain (I TIN 4)



Curves

Figure B-14: Stress vs. Strain (I TIN 61)

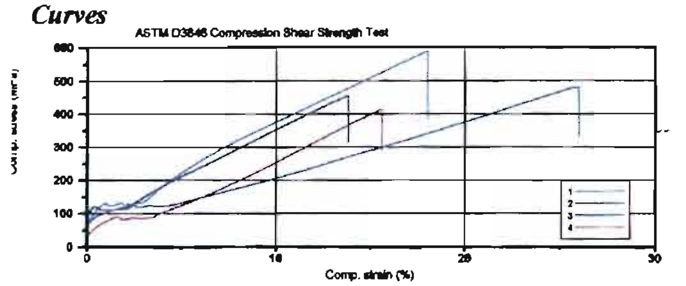


Figure B-15: Stress vs. Strain (MET 2)

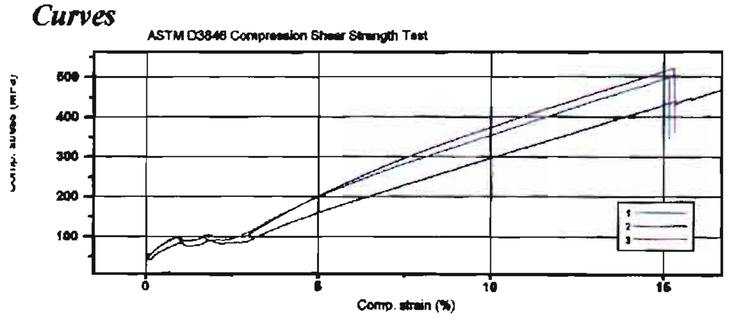


Figure B-16: Stress vs. Strain (I TIN 5)

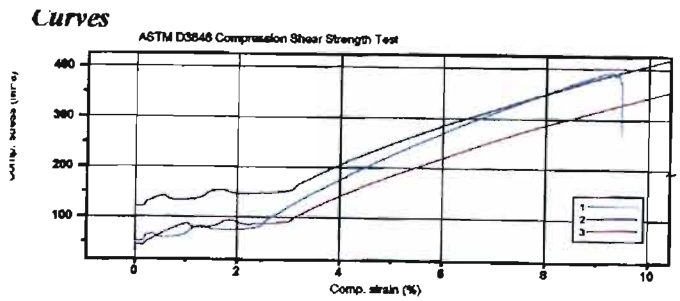


Figure B-17: Stress vs. Strain (MET 17)

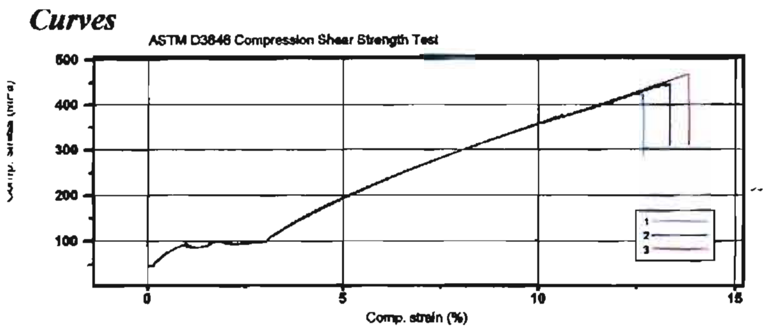


Figure B-18: Stress vs. Strain (MET 33)

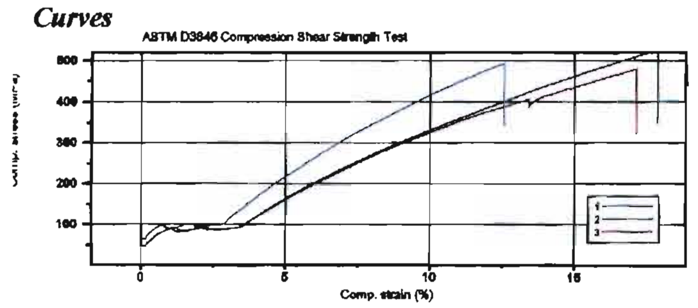


Figure B-19: Stress vs. Strain (MET 8)

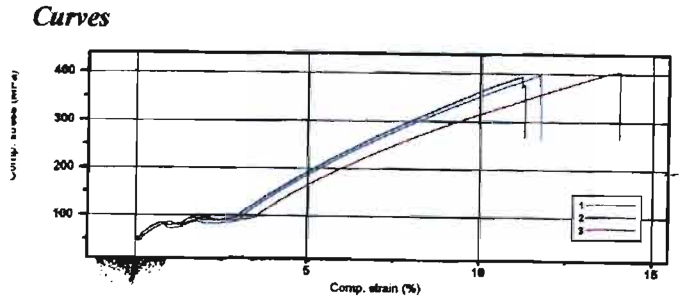


Figure B-20: Stress vs. Strain (I TIN 48)

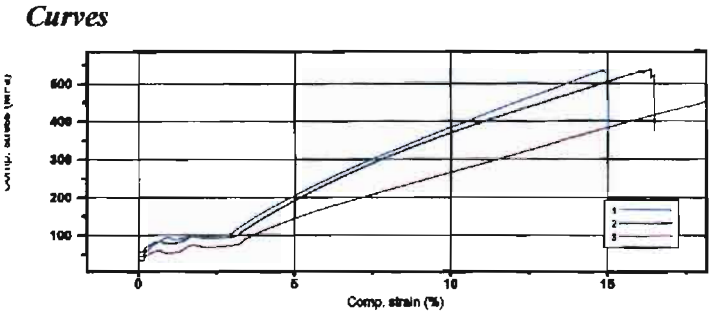


Figure B-21: Stress vs. Strain (MET 6)

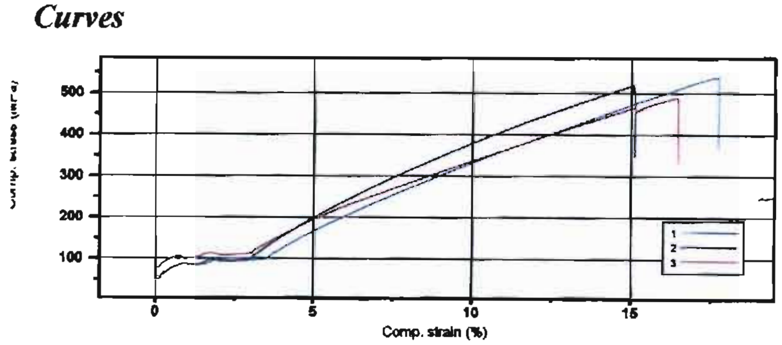


Figure B-22: Stress vs. Strain (NUV 8)

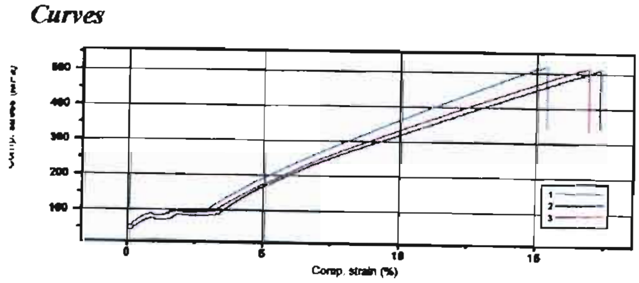


Figure B-23: Stress vs. Strain (NUV 4)

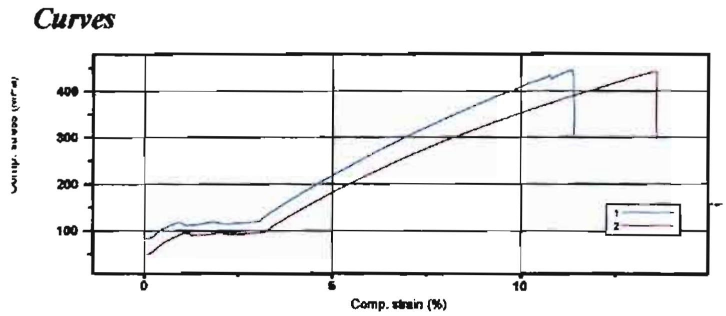


Figure B-24: Stress vs. Strain (NUV 28)

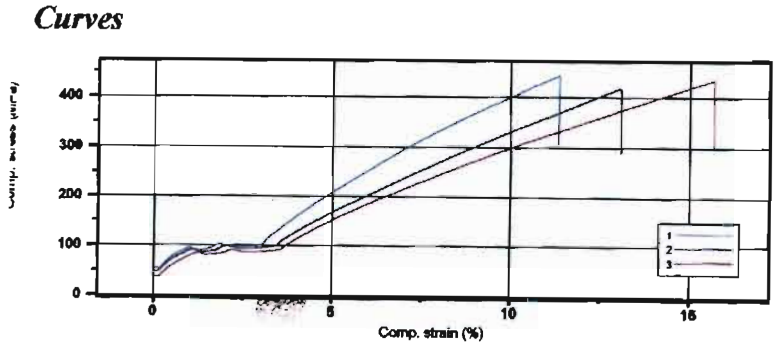


Figure B-25: Stress vs. Strain (NUV 32)

C Appendix C

The Colour Analysis Graphs

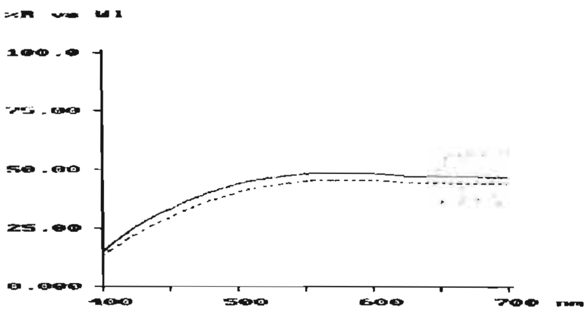


Figure C-1: (Wavelength vs. Index) MET 6 vs. MET

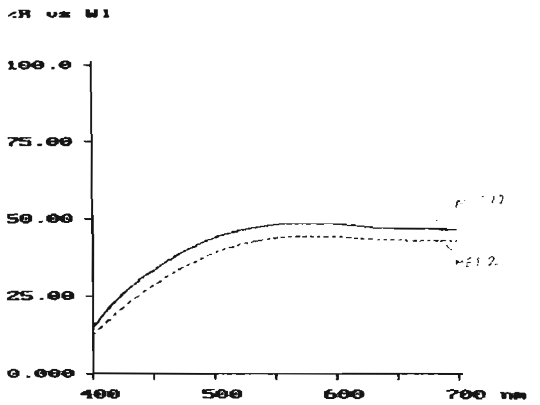


Figure C-2: (Wavelength vs. Index) MET 2 vs. MET 17

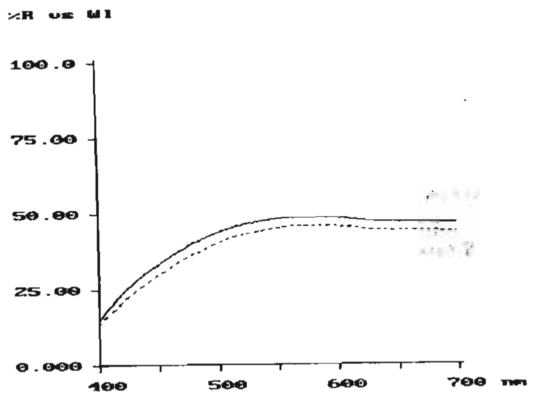


Figure C-3: (Wavelength vs. Index) MET 8 vs. MET 17

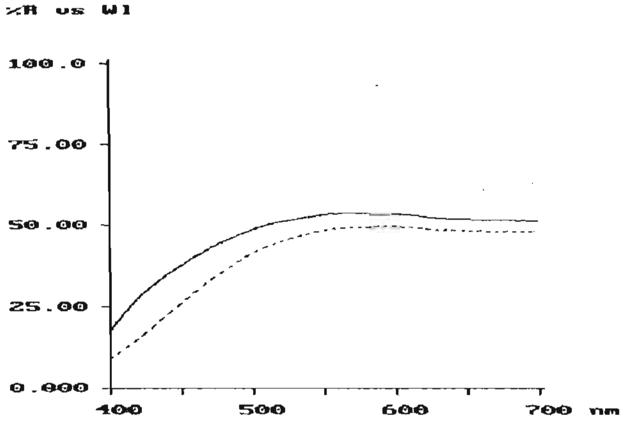


Figure C-4: (Wavelength vs. Index) NUV 8 vs. NUV 16

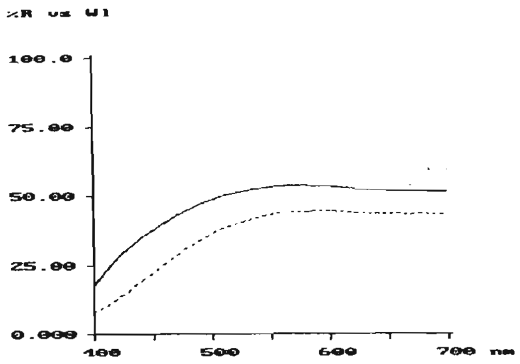


Figure C-5: (Wavelength vs. Index) NUV 16 vs. NUV 3

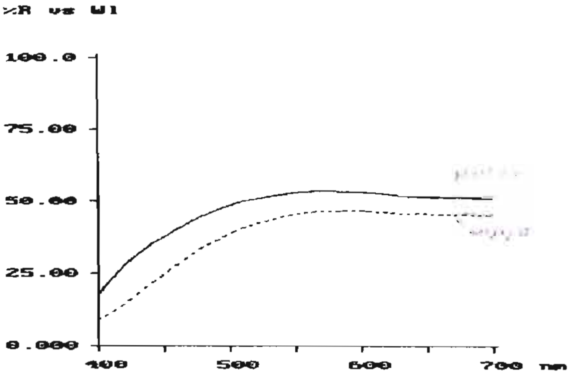


Figure C-6: (Wavelength vs. Index) NUV 4 vs. NUV 16

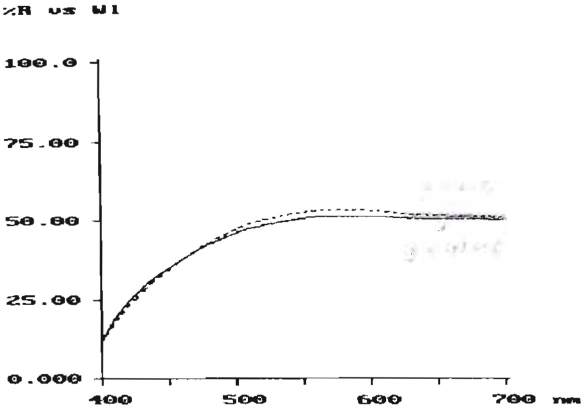


Figure C-7: (Wavelength vs. Index) I TIN 5 vs. I TIN 48

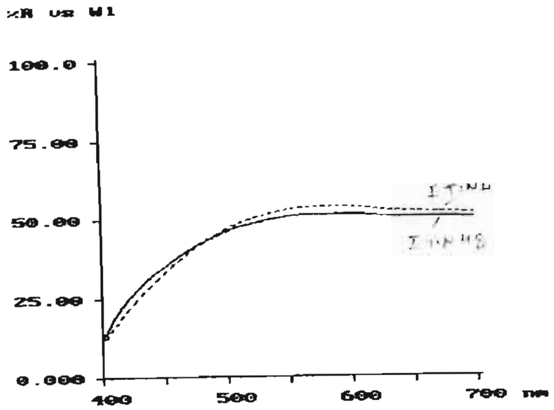


Figure C-8: (Wavelength vs. Index) I TIN 4 vs. I TIN 48

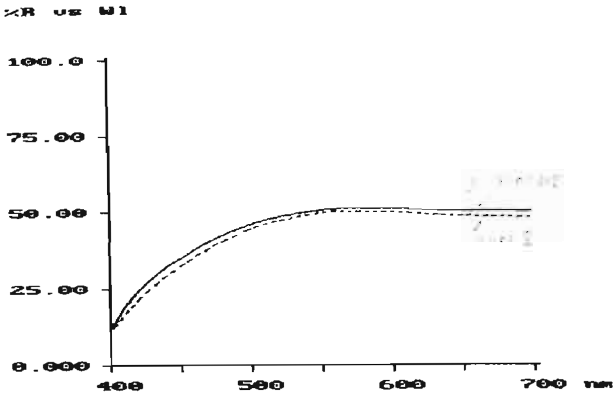


Figure C-9: (Wavelength vs. Index) I TIN 8 vs. I TIN 48

D Appendix D

Table of sizes of all tested specimens

1280 UPE Polyester (Gel coated specimens)

Table D-1: MET 31 (unexposed)

Specimen	Width (mm)	Thickness (mm)	Gauge length (mm)
1 MET 31	5.8	2.40	8.53
2 MET 31	5.9	2.35	8.65
3 MET 31	5.2	2.40	9.0

Table D-2: MET 4 (exposed)

Specimens	Gauge length (mm)	Width (mm)	Thickness (mm)
1MET 4	10.35	5.64	2.7
2MET 4	10.59	6.52	2.68
3MET 4	10.47	5.94	2.74
4MET 4	10.41	6.36	2.78

Table D-3: NUV 26 (unexposed)

Specimen	Width (mm)	Thickness (mm)	Gauge length (mm)
1 NUV 26	5.80	2.40	9.45
2 NUV 26	5.70	2.35	10.30
3 NUV 26	5.95	2.35	9.35

Table D-4: NUV 1 (exposed)

Specimens	Gauge length (mm)	Width (mm)	Thickness (mm)
1NUV 1	10.5	6.1	2.6
2NUV 1	10.65	6.3	2.6
3NUV 1	10.5	6.08	2.6
4NUV 1	10.43	6.28	2.6

Table D-5: I TIN 53 (unexposed)

Specimen	Width (mm)	Thickness (mm)	Gauge length (mm)
1 TIN 53	5.75	2.20	9.20
2 TIN 53	5.30	2.60	9.13
3 TIN 53	5.50	2.15	8.70

Table D-6: I TIN 1: (exposed)

Specimens	Gauge length (mm)	Width (mm)	Thickness (mm)
1Tin 1	10.66	6.28	2.8
2Tin 1	10.4	6.28	2.76
3Tin 1	10.25	6.34	2.8

Table D-7: K 100 (unexposed)

Specimen	Width (mm)	Thickness (mm)	Gauge length (mm)
1 K100	6.3	2.45	10.15
2 K100	6.0	2.7	9.90
3 K100	5.6	2.7	10.40

Table D-8: K 404 (exposed)

Specimens	Gauge length (mm)	Width (mm)	Thickness (mm)
1K404	8.99	6.04	2.94
2K404	10.12	6.12	3
3K404	10.55	6.38	3
4K404	10.65	6.3	3.1

Table D-9: MET 16 (exposed)

UV MET 16	Width (mm)	Thickness (mm)	Gauge length (mm)
1	5.2	2.2	9.13
2	6.0	2.2	9.75
3	5.8	2.4	10.2
4	6.8	2.4	9.7

Table D-10: MET 23 (unexposed)

UV MET 23	Width (mm)	Thickness (mm)	Gauge length (mm)
1	6.1	2.2	10.3
2	5.8	2.2	10.6
3	6.0	2.2	10.45
4	5.8	2.4	10.75

Table D-11: NUV 2 (exposed)

NUV 2	Width (mm)	Thickness (mm)	Gauge length (mm)
1	6.0	2.6	10.8
2	6.1	2.6	11.2
3	5.9	2.6	10.3
4	6.1	2.6	11.1

Table D-12: NUV 17 (unexposed)

NUV 17	Width (mm)	Thickness (mm)	Gauge length (mm)
1	5.4	2.4	10.35
2	6.0	2.4	10.7
3	5.9	2.2	10.65
4	6.0	2.4	10.33

Table D-13: I TIN 47 (unexposed)

(I Tin 47)	Width (mm)	Thickness (mm)	Gauge length (mm)
1	6.0	2.5	11.6
2	5.9	2.4	10.25
3	6.0	2.4	10.4
4	6.3	2.4	11.15

Table D-14: I TIN 3 (exposed)

Specimen	Width (mm)	Thickness (mm)	Gauge length (mm)
1 TIN 3	6.0	2.0	9.83
2 TIN 3	6.0	2.2	9.7
3 TIN 3	5.8	2.0	10.3
4 TIN 3	*	*	*

*Dimensions of this sample have been left out because the tabs de-bonded before testing.

Table D-15: NUV 3 (exposed)

Specimen	**Thickness (mm)**	**Width (mm)**	**Gauge length (mm)**
NUV 3 (1)	2.6	6.6	11.5
NUV 3 (2)	2.7	6.5	12
NUV 3 (3)	2.7	6.5	10.4

Table D-16: I TIN 5 (exposed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
I TIN 5 (1)	2.6	6.6	11.5
I TIN 5 (2)	2.7	6.7	11.6
I TIN 5 (3)	2.5	6.5	11.6

Table D-17: MET 17 (unexposed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
MET 17 (1)	2.7	6.5	12.2
MET 17 (2)	2.75	6.4	10.2
MET 17 (3)	2.7	6.35	12

Table D-18: MET 2 (exposed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
MET 2 (1)	2.7	6.35	10.7
MET 2 (2)	2.8	6.5	11.9
MET 2 (3)	2.7	6.4	11.3
MET 2 (4)	2.8	6.6	11.5

Table D-19: NUV 16 (unexposed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
NUV 16 (1)	2.65	6.5	11.1
NUV 16 (2)	2.6	6.5	11.4
NUV 16 (3)	2.6	6.5	11.5

Table D-20: NUV 4 (exposed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
NUV 4 (1)	2.6	6.5	11.75
NUV 4 (2)	2.5	6.45	9.9
NUV 4 (3)	2.6	6.6	10.3

Table D-21: NUV 8 (exposed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
NUV 8 (1)	2.6	6.6	9.65
NUV 8 (2)	2.6	6.5	11.7
NUV 8 (3)	2.7	6.6	10.5

Table D-22: NUV 32 (water immersed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
NUV 32 (1)	2.55	6.3	11.6
NUV 32 (2)	2.6	6.3	10.4
NUV 32 (3)	2.65	6.55	10.45

Table D-23: NUV 28 (water immersed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
NUV 28 (1)	2.55	6.6	10.9
NUV 28 (2)	2.6	6.6	10.9

Table D-24: MET 8 (exposed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
MET 8 (1)	2.65	6.55	10.9
MET 8 (2)	2.75	6.6	9.55
MET 8 (3)	2.65	6.4	9.6

Table D-25: MET 33 (water immersed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
MET 33 (1)	2.7	6.4	11.4
MET 33 (2)	2.7	6.4	11.7
MET 33 (3)	2.75	6.45	11.2

Table D-26: MET 6 (exposed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
MET 6 (1)	2.6	6.45	11.9
MET 6 (2)	2.6	6.55	10.05
MET 6 (3)	2.7	6.55	10.3

Table D-27: I TIN 48 (unexposed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
I TIN 48 (1)	2.75	6.4	11.55
I TIN 48 (2)	2.65	6.5	11.65
I TIN 48 (3)	2.6	6.5	10.1

Table D-28: I TIN 4 (exposed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
I TIN 4 (1)	2.5	6.5	10
I TIN 4 (2)	2.45	6.5	11.85
I TIN 4 (3)	2.5	6.5	9.8

Table D-29: I TIN 8 (exposed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
I TIN 8 (1)	2.7	6.5	12.15
I TIN 8 (2)	2.7	6.45	11.6
I TIN 8 (3)	2.5	6.45	11.3

Table D-30: I TIN 61 (water immersed)

Specimen	Thickness (mm)	Width (mm)	Gauge length (mm)
I TIN 61 (1)	2.6	6.35	11.5
I TIN 61 (2)	2.6	6.5	11.8
I TIN 61 (3)	2.7	6.5	12.4

E Appendix E

Log Sheet for Environmental Exposure Cycles

Table E-1: Login Sheet for Accelerated Exposure

Number of cycles	**Total Time**		**Date**	**Notes**	**Temperature**
1	98.05	*			
2	98.05	*			
3	98.05	*			
4	98.05	*			
5	98.05	*			
6	98.05	*			
7	98.05	*			
8	98.05	*			
9	98.05	*		20.33 for K	**Report**
10	98.05	*	**10/7/2003**		
11	99.05	*		**21.11**	
12	99	*			
13	99	*			
14	99	*			
15	98	*			
16	49.44	*	5/9/2003		48.56 b4
17	81.6	*			**1605.59**
18	80.74	*			
19	77.68	*	**25-Sep**		
20	89.46	*	**29-Sep**		
21	95.79	*	**3-Oct**		
	80.92	*	**6-Oct**		
	89.92	*	**14-Oct**		
	99	*	**21-Oct**		
	99	*	**1-Nov**		
	99	*		**2417.1**	**15-Nov**
	82.9	*			
		for Ken	**1617.55**	**sum**	
	4	*	**2-Dec**	Fog	30 degrees

	4	*	**2-Dec**	UV	30 degrees
	4	*	3-Dec	Fog	30 degrees
	8	*	3-Dec	UV	30 degrees
	8	*	4-Dec	Fog	30 degrees
	8	*	4-Dec	UV	30 degrees
	8	*		Fog	
	8	*		UV	
	8	*		Fog	
	8	*		UV	
	8	*		Fog	
	8	*		UV	
	8	*	10-Dec	Fog	40 degrees
	8	*	11-Dec	fog + UV	40 degrees
			13-Dec	100	Sum
	8	*	7-Jan		40 degrees
	8	*	2-Feb	fog	
	8	*	5-Jan	UV	
	8	*	6-Jan	Fog	
	8	*			
	8	*	23-Jan	UV	
	8	*	24-Feb	Fog	
	8	*	24-Feb	UV	
	16	*	1-Mar	UV	
	8	*	2-Mar	Fog	
	8	*	9-Mar	UV	
	8	*	10-Mar	Spray	
	8	*	11-Mar	UV	
	8	*	13-Mar	Spray	
	8	*	17-Mar	UV	
	8	*	18-Mar	Spray	
	8	*	25-Mar	UV	

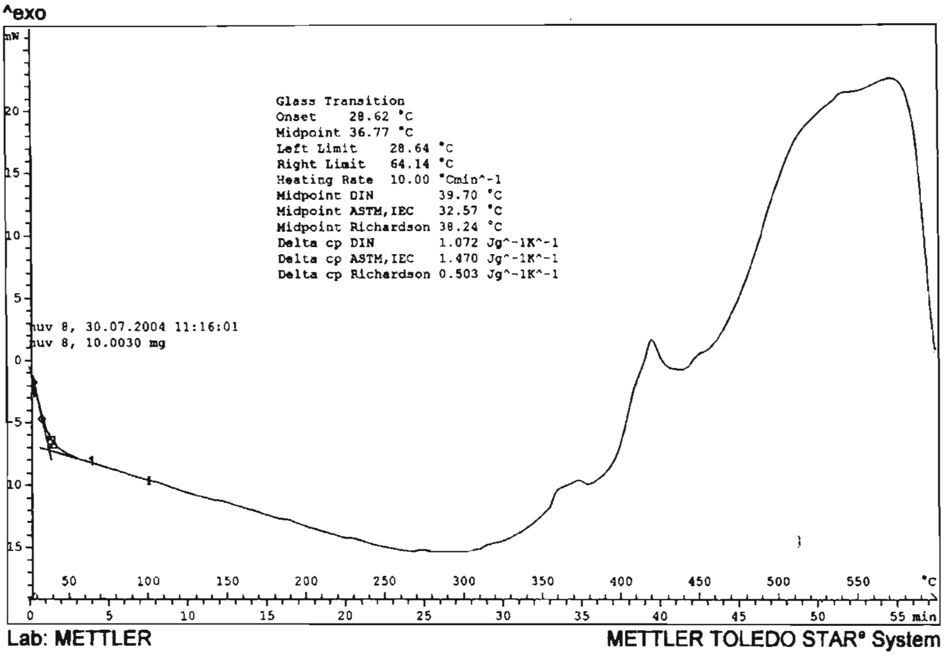
	8	*	26-Mar	Spray	
	8	*	29-Mar	UV	
	8	*	31-Mar	Spray	
	8	*	1-Apr	UV	
	8	*	1-Apr	Spray	
	8	*	15-Apr	UV	
		Sum	15-Apr	192	Sum
	8	*	16-Apr	Spray	
	8	*	20-Apr	UV	
	8	*	22-Apr	Spray	
	8	*	28-Apr	UV	
	8	*	4-May	Spray	
	8	*	5-May	UV	
	8	*	8-May	Spray	
	8	*	10-May	UV	
	8	*	11-May	Spray	
	8	*	12-May	UV	
	8	*	13-May	Spray	
	8	*	15-May	UV	
	8	*	19-May	Spray	50 degrees
			Sum	**2896**	
	8	*	20-May	Spray	50 degrees
	8	*	25-May	Heat	70 degrees
	8	*	1-Jun	UV	70 degrees
	8	*	2-Jun	Spray	60 degrees
			Sum	**2928**	
	8	*	24-Jun	UV	60 degrees
	8	*	28-Jun	Spray	60 degrees
	8	*	29-Jun	UV	60 degrees
	8	*	30-Jun	Spray	60 degrees
	8	*	1-Jul	UV	60 degrees
	8	*	2-Jul	Spray	60 degrees

	8	*	5-Jul	UV	60 degrees
	8	*	6-Jul	Spray	60 degrees
	8	*	7-Jul	UV	60 degrees
			Sum	**3000**	

*** Completed Cycles**

F Appendix F

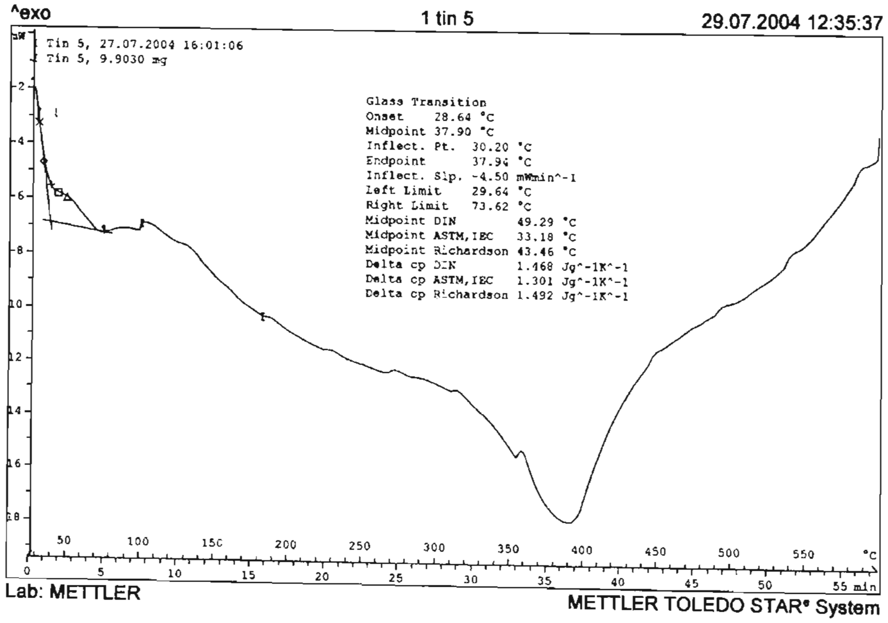
Differential Scanning Calorimetry (DSC) Scans



```
Glass Transition
Onset     28.62 °C
Midpoint 36.77 °C
Left Limit     28.64 °C
Right Limit    64.14 °C
Heating Rate   10.00 °Cmin^-1
Midpoint DIN           39.70 °C
Midpoint ASTM,IEC      32.57 °C
Midpoint Richardson 38.24 °C
Delta cp DIN           1.072 Jg^-1K^-1
Delta cp ASTM,IEC      1.470 Jg^-1K^-1
Delta cp Richardson 0.503 Jg^-1K^-1
```

```
nuv 8, 30.07.2004 11:16:01
nuv 8, 10.0030 mg
```

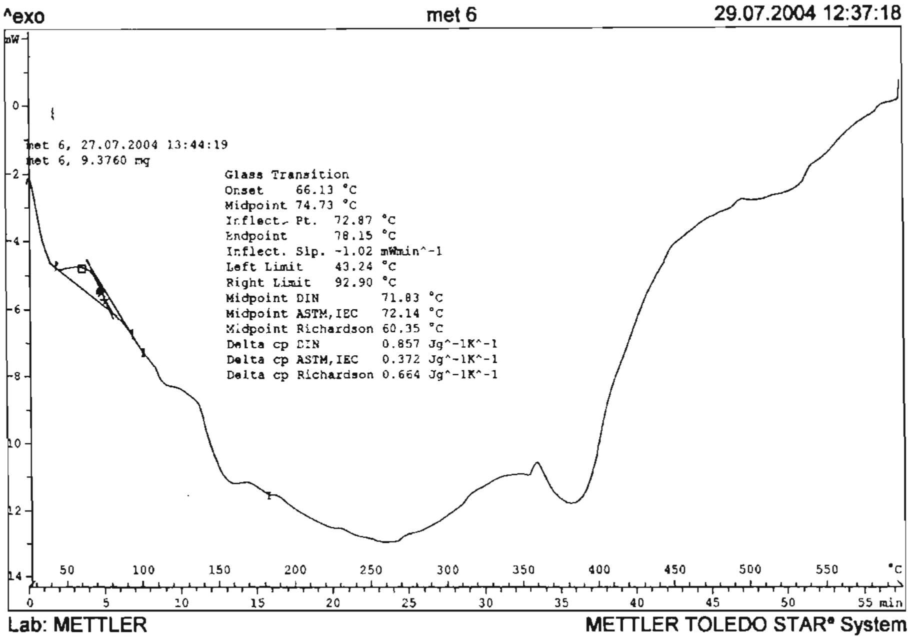
Figure F-1: DCS scans showing Tg (NUV 8)



```
Tin 5, 27.07.2004 16:01:06
Tin 5, 9.9030 mg
```

```
Glass Transition
Onset     28.64 °C
Midpoint 37.90 °C
Inflect. Pt.   30.20 °C
Endpoint       37.94 °C
Inflect. Slp. -4.50 mWmin^-1
Left Limit     29.64 °C
Right Limit    73.62 °C
Midpoint DIN           49.29 °C
Midpoint ASTM,IEC      33.18 °C
Midpoint Richardson 43.46 °C
Delta cp DIN           1.468 Jg^-1K^-1
Delta cp ASTM,IEC      1.301 Jg^-1K^-1
Delta cp Richardson 1.492 Jg^-1K^-1
```

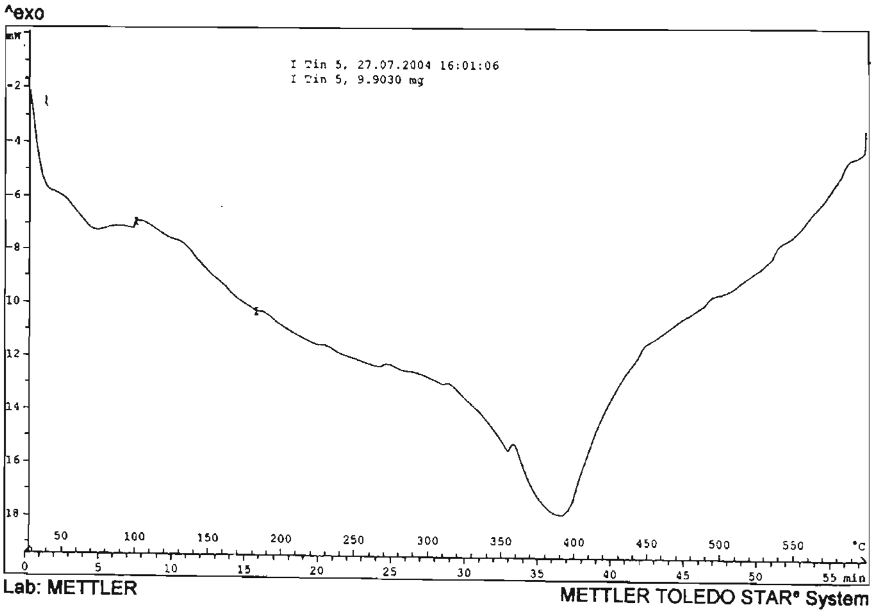
Figure F-2: DCS scans showing Tg (I TIN 5)



met 6, 27.07.2004 13:44:19
met 6, 9.3760 mg

Glass Transition
Onset 66.13 °C
Midpoint 74.73 °C
Inflect. Pt. 72.87 °C
Endpoint 78.15 °C
Inflect. Slp. -1.02 mWmin^-1
Left Limit 43.24 °C
Right Limit 92.90 °C
Midpoint DIN 71.83 °C
Midpoint ASTM,IEC 72.14 °C
Midpoint Richardson 60.35 °C
Delta cp DIN 0.857 Jg^-1K^-1
Delta cp ASTM,IEC 0.372 Jg^-1K^-1
Delta cp Richardson 0.664 Jg^-1K^-1

Figure F-3: DCS scans showing Tg (MET 6)



I Tin 5, 27.07.2004 16:01:06
I Tin 5, 9.9030 mg

Figure F-4: DCS scans not showing Tg (I TIN 5)

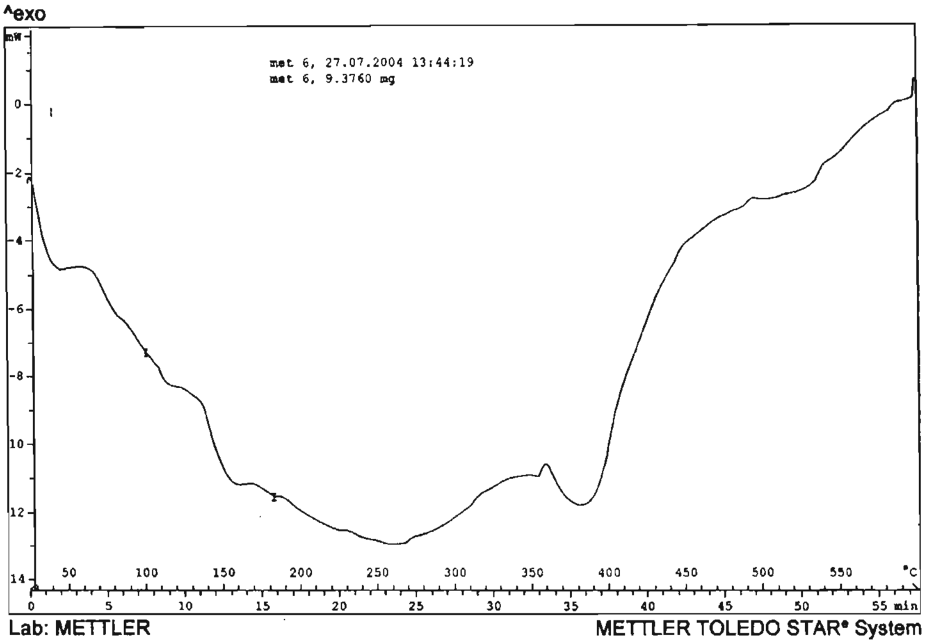


Figure F-5: DCS scans not showing Tg (MET 6)

G Appendix G

Lloyds Machine Test Details

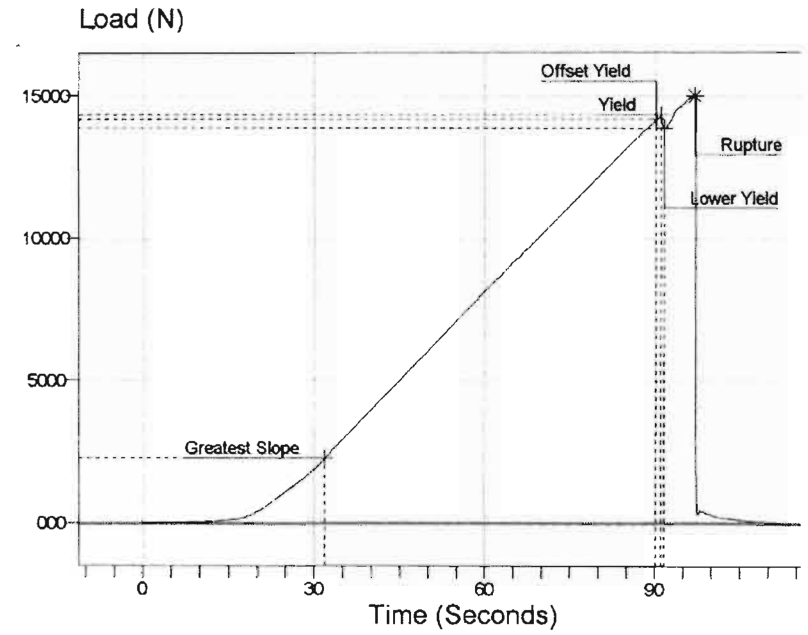


Figure G-1: 1 NUV 9

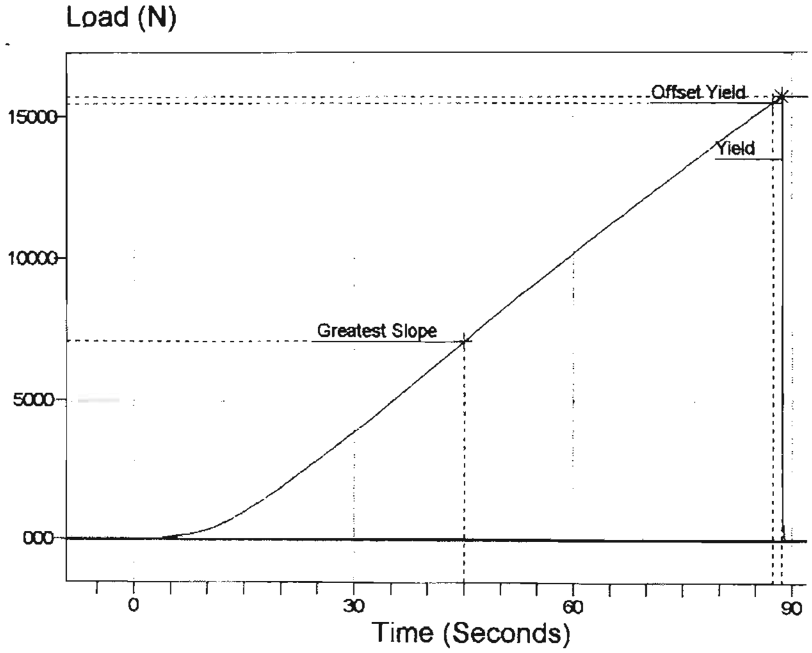


Figure G-2: 2 NUV 9

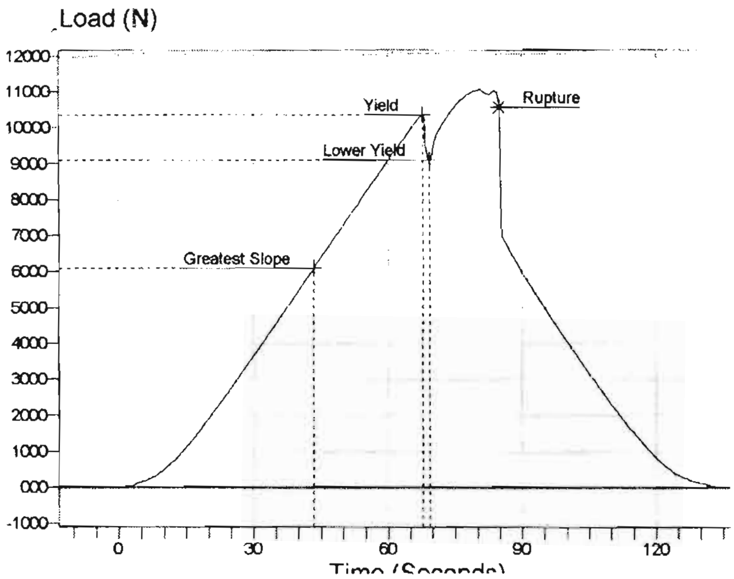


Figure G-3: 1 I TIN 58

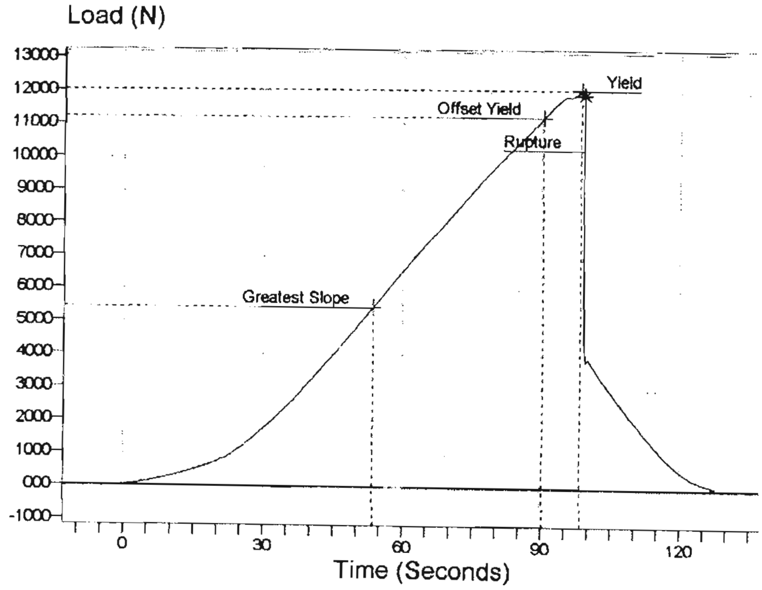


Figure G-4: 1 MET 30

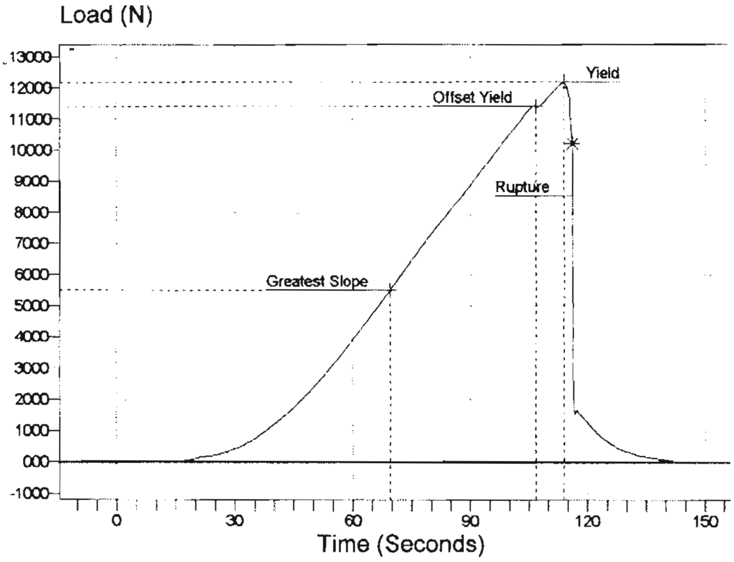


Figure G-5: 2 I TIN 58

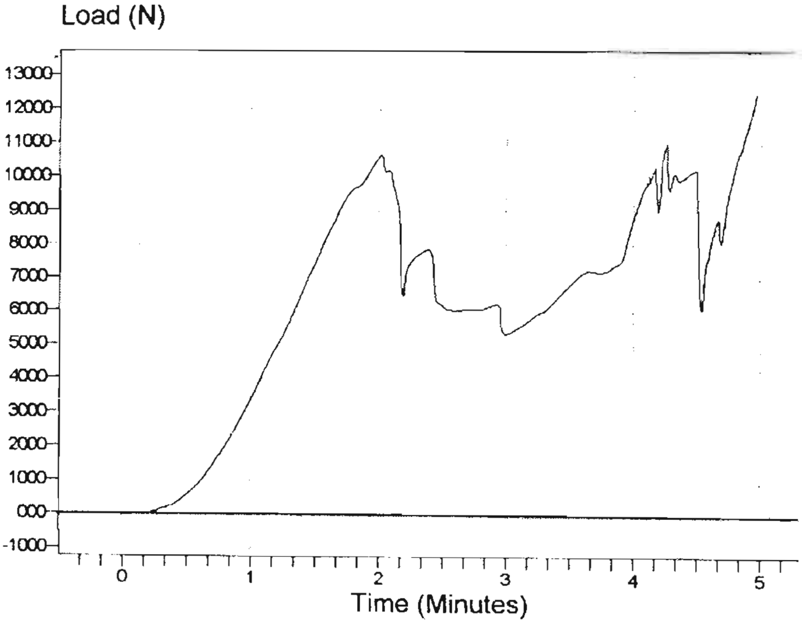
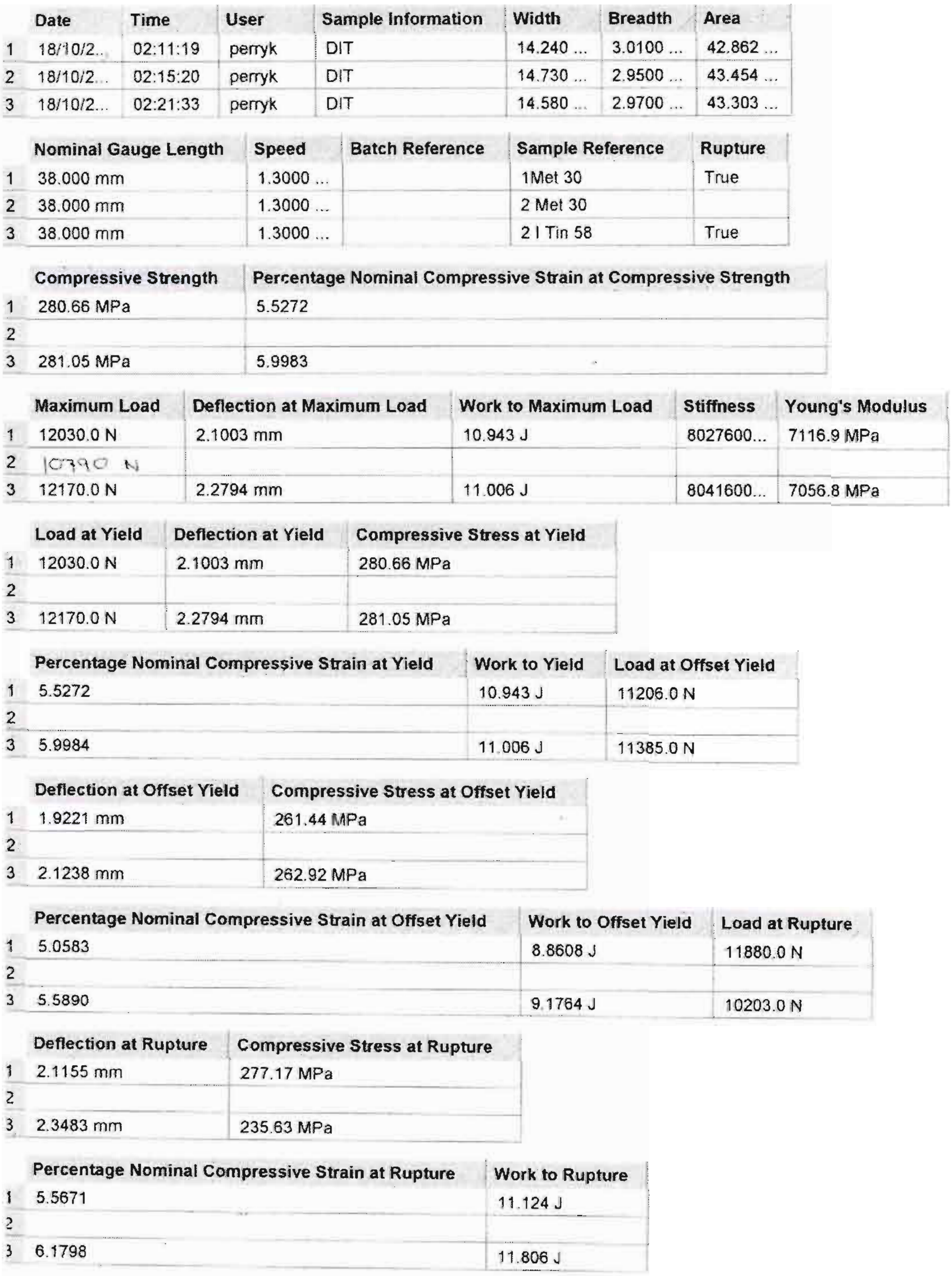


Figure G-6: 2 MET 30

Table G-1: Tables showing detailed Lloyds test results



	Date	Time	User	Sample Information	Width	Breadth	Area
1	18/10/2...	02:11:19	perryk	DIT	14.240 ...	3.0100 ...	42.862 ...
2	18/10/2...	02:15:20	perryk	DIT	14.730 ...	2.9500 ...	43.454 ...
3	18/10/2...	02:21:33	perryk	DIT	14.580 ...	2.9700 ...	43.303 ...

	Nominal Gauge Length	Speed	Batch Reference	Sample Reference	Rupture
1	38.000 mm	1.3000 ...		1Met 30	True
2	38.000 mm	1.3000 ...		2 Met 30	
3	38.000 mm	1.3000 ...		2 I Tin 58	True

	Compressive Strength	Percentage Nominal Compressive Strain at Compressive Strength
1	280.66 MPa	5.5272
2		
3	281.05 MPa	5.9983

	Maximum Load	Deflection at Maximum Load	Work to Maximum Load	Stiffness	Young's Modulus
1	12030.0 N	2.1003 mm	10.943 J	8027600...	7116.9 MPa
2	10790 N				
3	12170.0 N	2.2794 mm	11.006 J	8041600...	7056.8 MPa

	Load at Yield	Deflection at Yield	Compressive Stress at Yield
1	12030.0 N	2.1003 mm	280.66 MPa
2			
3	12170.0 N	2.2794 mm	281.05 MPa

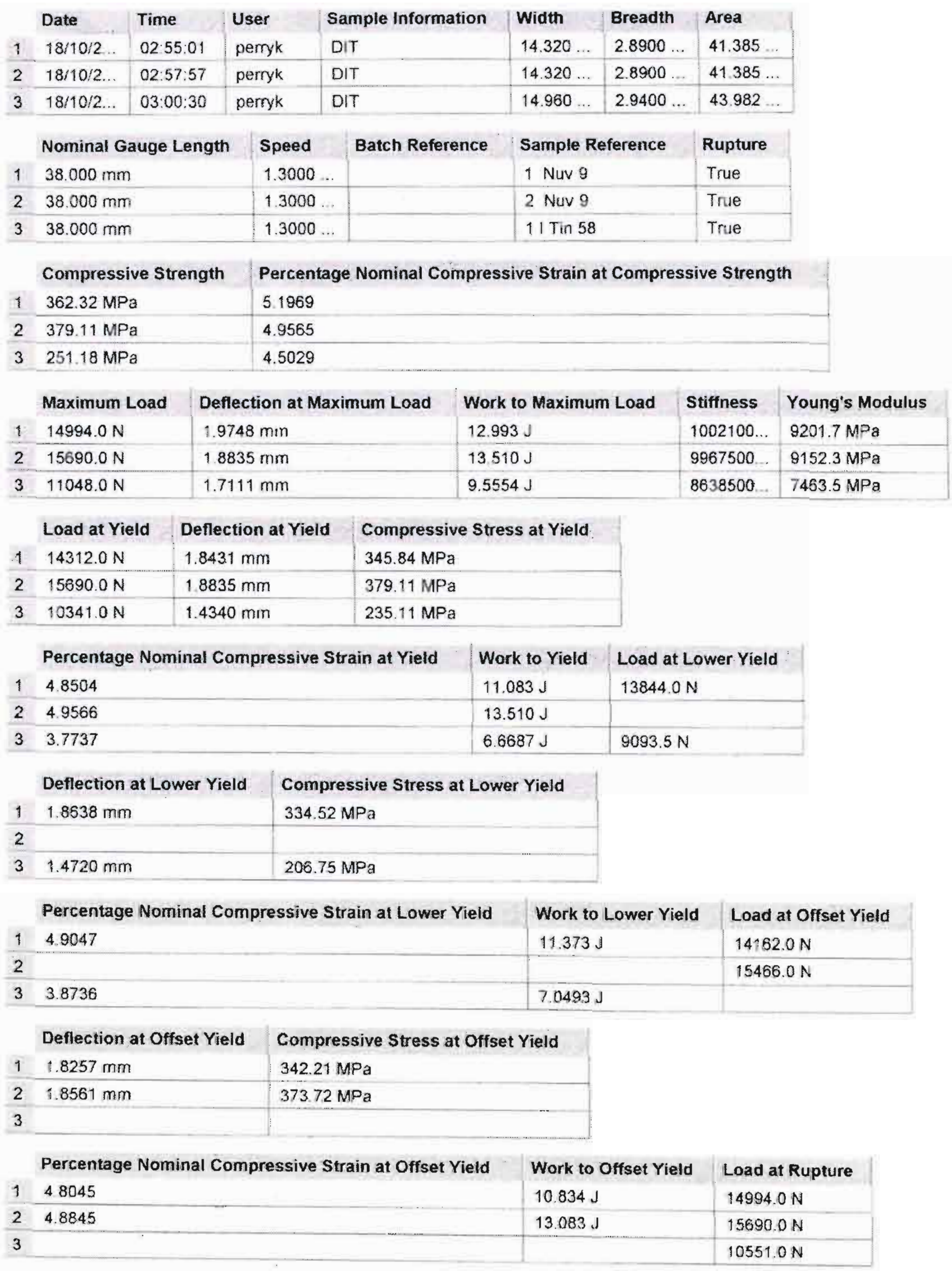
	Percentage Nominal Compressive Strain at Yield	Work to Yield	Load at Offset Yield
1	5.5272	10.943 J	11206.0 N
2			
3	5.9984	11.006 J	11385.0 N

	Deflection at Offset Yield	Compressive Stress at Offset Yield
1	1.9221 mm	261.44 MPa
2		
3	2.1238 mm	262.92 MPa

	Percentage Nominal Compressive Strain at Offset Yield	Work to Offset Yield	Load at Rupture
1	5.0583	8.8608 J	11880.0 N
2			
3	5.5890	9.1764 J	10203.0 N

	Deflection at Rupture	Compressive Stress at Rupture
1	2.1155 mm	277.17 MPa
2		
3	2.3483 mm	235.63 MPa

	Percentage Nominal Compressive Strain at Rupture	Work to Rupture
1	5.5671	11.124 J
2		
3	6.1798	11.806 J



	Date	Time	User	Sample Information	Width	Breadth	Area
1	18/10/2...	02:55:01	perryk	DIT	14.320 ...	2.8900 ...	41.385 ...
2	18/10/2...	02:57:57	perryk	DIT	14.320 ...	2.8900 ...	41.385 ...
3	18/10/2...	03:00:30	perryk	DIT	14.960 ...	2.9400 ...	43.982 ...

	Nominal Gauge Length	Speed	Batch Reference	Sample Reference	Rupture
1	38.000 mm	1.3000 ...		1 Nuv 9	True
2	38.000 mm	1.3000 ...		2 Nuv 9	True
3	38.000 mm	1.3000 ...		1 I Tin 58	True

	Compressive Strength	Percentage Nominal Compressive Strain at Compressive Strength
1	362.32 MPa	5.1969
2	379.11 MPa	4.9565
3	251.18 MPa	4.5029

	Maximum Load	Deflection at Maximum Load	Work to Maximum Load	Stiffness	Young's Modulus
1	14994.0 N	1.9748 mm	12.993 J	1002100...	9201.7 MPa
2	15690.0 N	1.8835 mm	13.510 J	9967500...	9152.3 MPa
3	11048.0 N	1.7111 mm	9.5554 J	8638500...	7463.5 MPa

	Load at Yield	Deflection at Yield	Compressive Stress at Yield
1	14312.0 N	1.8431 mm	345.84 MPa
2	15690.0 N	1.8835 mm	379.11 MPa
3	10341.0 N	1.4340 mm	235.11 MPa

	Percentage Nominal Compressive Strain at Yield	Work to Yield	Load at Lower Yield
1	4.8504	11.083 J	13844.0 N
2	4.9566	13.510 J	
3	3.7737	6.6687 J	9093.5 N

	Deflection at Lower Yield	Compressive Stress at Lower Yield
1	1.8638 mm	334.52 MPa
2		
3	1.4720 mm	206.75 MPa

	Percentage Nominal Compressive Strain at Lower Yield	Work to Lower Yield	Load at Offset Yield
1	4.9047	11.373 J	14162.0 N
2			15466.0 N
3	3.8736	7.0493 J	

	Deflection at Offset Yield	Compressive Stress at Offset Yield
1	1.8257 mm	342.21 MPa
2	1.8561 mm	373.72 MPa
3		

	Percentage Nominal Compressive Strain at Offset Yield	Work to Offset Yield	Load at Rupture
1	4.8045	10.834 J	14994.0 N
2	4.8845	13.083 J	15690.0 N
3			10551.0 N

H Appendix H

(Specifications and Features of the HOBO)

HOBO Specifications

HOBO H8 (Temperature and Relative Humidity, Light and external input Data Logger);

- Minature datalogger with internal temperature, RH and Lux sensors
- Temperature range (sensor in case) -20°C to +70°C
- NIST traceable temperature certification - accurate to ±0.7°C
- Humidity range 25 - 95% to an accuracy of ±5%
- Lux Range: 2 to 600 footcandles (lumens/ft2)
- Memory capacity over 7000 temperature records
- User-selectable sampling interval
- Data can either stop or wrap when full
- Time accurate to ±1 minute per week at 20°C
- User-replaceable battery lasts 1 year
- Requires software and cable to connect to PC or use data Shuttle to return data to a PC
- Size: 68 x 48 x 19 mm ;
- Weight: 29 gms

BoxCar Pro 4.3 Starter Software [55]

BoxCar Pro 4 is the software that collects the data from the HOBO logger
and allows you to manipulate the data in charts and graphs.

Logger Setup

Launch (Start) Hobos and Stowaway Loggers
Set start time and memory modes (e.g., stop when full, wrap-around when full)
Verify logger operation before launching
Synchronizes logger and data shuttle clocks to computer clock

Graphing

Add new data series from stored files or drag-and-drop from one plot onto another
Multiple value axis on one graph, such as temperature and RH
View data from successive deployments on one graph to see long-term trends

Overlay data from different deployments, to compare month-to-month, or before-and-after
Focus on data of interest with powerful zoom and drag tools
Set axis ranges
Use cursor to display specific plot values
Display series data and details such as launch parameters and series statistics
Add limit lines to the graph
Copy and paste graphs into other Windows programs
Control axis, series and legend properties

Analysis Functions

Min, max and average values per interval
On/off and State logger data:
  Run time and off time (closed time and open time) in seconds
  Percent on and percent off (percent closed and percent open)
  Number of ons and offs (number of opens and closes)
  Rainfall per time interval
  Number of events

Export Data to other Programs

Control bar tool for Microsoft Excel export (.TXT format)
Lotus 1-2-3 and custom export
International data format options
Batch export utility

Other Features

Print graphs and series details
Print preview
Multiple logger launches
Long file names (up to 255 characters)
International data format options
Thumbnail view for showing many plots on screen at once