NPL
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Measurement Note

DEPC-MN 047

Accelerated Weathering: Performance Testing of Polymer Matrix Composites

Summary

Polymer matrix composites (PMCs) are increasingly being used in a wide range of engineering applications, such as offshore and civil structures (e.g. bridges), where long-term service in hostile environments is required. Long-term performance under adverse conditions is an important issue from both a health and safety aspect and in terms of economic costs. The repair or replacement of a deteriorated part is both labour and capital intensive. As a consequence, there is a growing demand for manufacturers to guarantee the life expectancy of their products, particularly where inspection can be difficult or failure catastrophic.

Whilst the life expectancy of products in non-demanding applications have traditionally been predicted from previous in-service experience (i.e. service conditions considered identical or similar to those for which data already exists), long-term or critical applications require the use of accelerated ageing regimes to generate data in an attempt to simulate the engineering requirements and life expectancy of the component. A prime example is the use of accelerated weathering procedures to simulate natural weathering conditions. Various cyclic test methods involving exposure to salt spray, elevated and/or sub-zero temperatures, and ultraviolet (UV) radiation have been developed in an attempt to generate design data.

A major challenge is to ensure that performance testing for determination of chemical resistance is based upon a set of "quantitatively" measurable criteria. This Measurement Note presents the results of 6 months exposure of glass fibre-reinforced polyester sections to artificial weathering conducted in accordance with IS0 20340 "Paints and Varnishes - Performance Requirements for Protective Paint Systems for Offshore and Related Structures". Mechanical and physical measurements were conducted after 0, 1, 2, 3, 4 and 6 month duration in order to assess surface and bulk property degradation. The Measurement Note was prepared as a result of investigations undertaken within the DTI funded project "Measurements for Materials Performance (F04) - Accelerated Ageing Protocols".

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1 Introduction

Safe and reliable design of composite structures for long-term operation in hostile environments is dependent on the availability of reliable engineering data that can be used to predict structural integrity and life expectancy. It also requires the designer/ engineer to have a good understanding of chemical degradation of surface and bulk properties resulting from exposure to environmental conditions.

Whilst the life expectancy of products in non-demanding applications have traditionally been predicted from previous in-service experience (i.e. service conditions considered identical or similar to those for which data already exists), long-term or critical applications require the use of accelerated ageing regimes to generate data in an attempt to simulate the engineering requirements and life expectancy of the component. A prime example is the use of accelerated weathering procedures to simulate natural weathering conditions as experienced for example by offshore structures in the Persian Gulf or North Atlantic.

Accelerated weathering procedures [1-2] generally involve cyclic exposure to a combination of salt spray, elevated and/or sub-zero temperatures, and ultraviolet (UV) radiation. The environmentally conditioned material is subjected to a series of tests (i.e. performance testing) to determine the degree of degradation (i.e. chemical resistance) as a function of exposure time. The criteria used to assess chemical resistance include mechanical properties, such as hardness, flexural modulus and strength, dimensional stability (i.e. swelling), weight change and appearance (i.e. colour, gloss, crazing, fibre prominence, blister formation, loss of surface resin, etc) [3]. Whilst mechanical properties and dimensional stability are quantitatively measurable quantities, a number of the appearance criteria tend to be assessed in qualitative terms, and hence the question arises as to the reliability of the assessment.

A major challenge is to ensure that performance testing for determination of chemical resistance (level of degradation) is based upon a set of "quantitatively" measurable criteria; avoiding qualitative or subjective assessment. This Measurement Note presents the results of 6 months exposure of glass fibre-reinforced polyester rectangular beam sections to artificial weathering. Mechanical and physical measurements were conducted on composite rods after 0, 1, 2, 3, 4 and 6 month exposure in order to assess surface and bulk property degradation. Surface and bulk properties measured include:

- Barcol hardness
- Gloss
- Spectral reflectance (colour)
- Glass transition temperature ($\mathbf{T_g}$)
- Moisture content (wt %)
- Flexural properties
- Surface chemistry

Fourier transform infrared (FTIR) spectroscopy was used to observe surface chemistry changes.

2 Accelerated Weathering

Accelerated weathering was performed using rectangular composite rods 8 mm wide, 9 mm thick (nominal) and 230 mm long cut from a pultruded glass fibre-reinforced polyester enclosure curved panel section. The composite panels, supplied to the project by Fibreforce Composites Ltd, were identical to the material used in a footbridge cladding system. The composite laminate contains several layers of 0°/90° stitched mat and unidirectional roving of varying areal weight with a surface veil on the top and bottom top surfaces. Solids (i.e. glass fibre and mineral filler) content: was 72 ± 1 wt% (measured by burn-off using ISO 1172 [4]).

Accelerated weathering was conducted at RAPRA in accordance with ISO 20340 "Paints and Varnishes - Performance Requirements for Protective Paint Systems for Offshore and Related Structures". This standard combines French AFNOR (NFT 34-600) and Norsok standards [1].

ISO 20340 consists of the following stages:

- 72 hrs exposure to UV radiation and water in accordance to ISO 11507 [5]. Alternating between:
  - 4 hrs exposure to UV (UVA 340 nm) at 60 °C; and
  - 4 hrs exposure to moisture condensation at 50 °C
- 72 hrs exposure to salt spray at 35 °C in accordance with ISO 7253 [6]
- 24 hrs exposure at -20 °C

Standard exposure procedures generally exclude the effect of sub-zero temperatures often experienced in practice or in external exposure testing. ISO 20340 was selected because it includes a freeze cycle in an attempt to produce more realistic results (see [1]). In order to simulate actual top-side service conditions, only one surface was exposed to salt spray and UV radiation. Surface measurements were restricted to exposed surfaces (i.e. top-side).

3 Performance Testing Results

This section presents the results of performance testing conducted on the conditioned specimens to determine the degree of degradation with exposure time.

3.1 Moisture Content and T_g

The moisture content (wt%) was measured before and after artificially weathering (see Table 1). The moisture content of the "as-received" material was approximately 0.23 wt% - equivalent to approximately one month of artificially weathering. Prior to artificially weathering, the rods were dried to a constant weight in an oven at 50 °C.

The moisture content reached an equilibrium level of ~0.55 w%. Variability in moisture content was most probably a result of partial drying occurring during transportation of samples to NPL. $\mathbf{T_g}$ remains relatively constant with moisture content (Table 1). Glass fibre-reinforced polyester systems when fully immersed in water at room temperature, or higher, have been observed to absorb far higher levels of moisture within the same timescale [7]. The increase in moisture content is also generally commensurate with a reduction in $\mathbf{T_g}$. The results shown in Table 1 may be indicative of moisture being mainly limited to the outer layers of the composite.

3.2 Barcol Hardness

The Barcol hardness was measured at ten locations on the surface of unconditioned material and on the top-side surface of the weathered specimens. Measurements were carried out using a Colman GYZJ 934-1 hand-held portable hardness tester. The results shown in Figure 1 indicate that hardness decreases with exposure time; asymptotically approaching a constant value after 3 - 6 months.

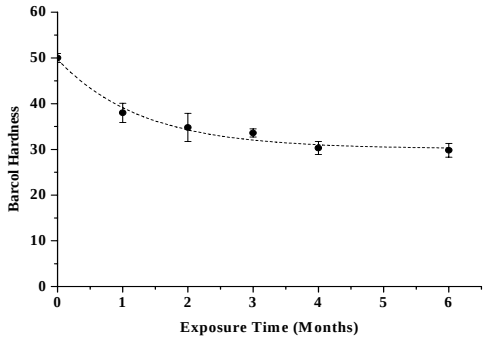

Figure 1: Barcol hardness versus exposure time.

Table 1: Moisture Content and Glass Transition Temperature (T_g)

Material	Moisture Content (%)	Glass Transition Temperature (°C)
As-received	0.23 ± 0.01	94.7
Dry	0	97.0
Exposure (Months)		
1	0.27 ± 0.02	92.2
2	0.34 ± 0.04	95.5
3	0.56 ± 0.04	92.3
4	0.39 ± 0.10	95.2
6	0.54 ± 0.02	96.9

3.3 Gloss

A Novo-Gloss meter was used to measure surface reflectivity of the weathered and "as-received" materials at a fixed angle of 60º. This instrument projects a collimated beam of white light (filtered to give a spectrum response similar to that of the human eye) onto the target surface at a specific angle and measures the amount of specular reflected light. Surface degradation (e.g. micro-cracking, loss of surface resin and fibre prominence, etc.) causes the incident light to be scattered at other angles, such that the scatter increases with the level of degradation.

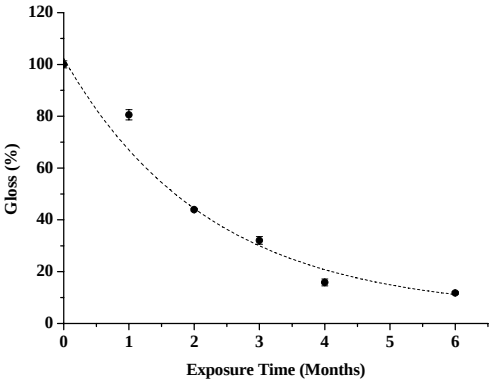

Figure 2: Gloss versus exposure time (60º angle measurements).

Table 2 presents the 60º angle gloss measurements for different periods of artificially weathering. The gloss measurements clearly show a strong relationship between gloss and exposure time (see also Figure 2). Gloss decreases rapidly with exposure time. After 6 months of artificial weathering, gloss has been reduced by a factor of almost 10.

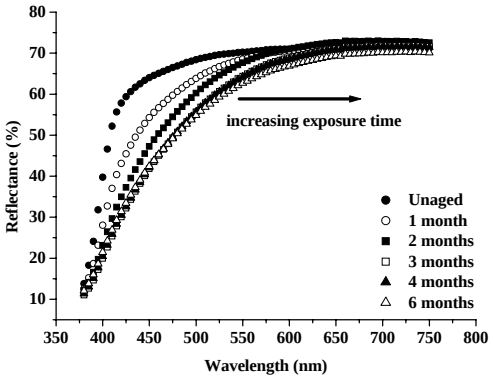

Figure 3: Spectral reflectance plots for different exposure times.

4 Colorimetry

The spectral reflectance of conditioned and "as-received" materials was measured using a Datacolor Spectraflash 500 spectrophotometer. The spectrophotometer exposes a 10 mm diameter circular area on the surface to a light source with a daylight colour temperature and compares the percentage reflectance within the visible spectrum (360 – 750 nm wavelength) to that of reference white and black colour tiles [8].

The reflectance of the sample was measured at 1 nm wavelength intervals over the spectral range 380 nm to 780 nm. Two sets of measurements were made on separate occasions on the test specimens and the average recorded. The degree of reflectance decreases with exposure time (see Figure 3), mirroring the changes in gloss. Figure 4 shows a normalised plot of total reflectance over the spectral range 380 nm to 780 nm. The total reflectance data for each specimen (i.e. exposure time) was normalised with respect to the total reflectance data obtained for the unconditioned material.

Table 2: Gloss Measurements

Material	Gloss
As received	22.1 ± 0.1
Exposure (Months)	
1	17.8 ± 0.4
2	9.7 ± 0.1
3	7.1 ± 0.3
4	3.5 ± 0.3
6	2.6 ± 0.1

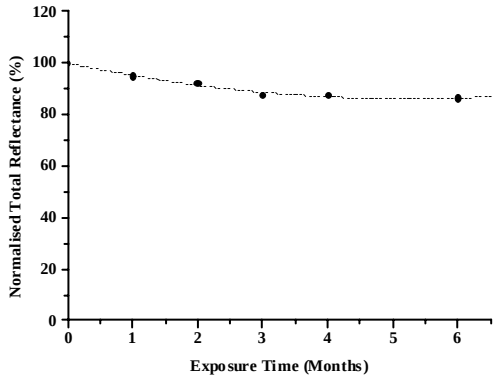

Figure 4: Total reflectance of artificially weathered specimens normalised with respect to the "as-received" material.

The spectral reflectance results presented in Figure 3 also show that the composite discolours as a result of artificially weathering. The discolouration (i.e. yellowing) observed with exposure time as shown in Figure 5 is due to a reduction in spectral reflectance over the spectral range 380 nm to 600 nm (i.e. blue component). Discolouration can be mainly attributed to exposure to UV radiation (UVA 340 nm).

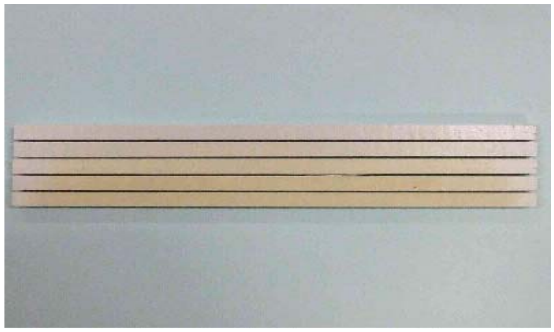

Figure 5: Discolouration of GRP rods due to artificial weathering: 0 (top), 1, 2, 3 and 6 (bottom) months exposure.

3.5 Flexure Tests

Four-point flexure tests were carried out on the unconditioned and artificially weathered composite rods, which were 8 mm wide, 9 mm thick (nominal) and 230 mm long. Although a non-standard specimen geometry was employed, testing generally conformed to BS EN ISO 14125 [9]. The geometry was selected for convenience of conditioning and to enable direct comparison with other flexure data obtained for GRP pultruded rods of similar dimensions exposed to deionised water and caustic solution.

The specimens were tested using an Instron 4507 screw-driven test machine at a cross-head displacement rate of 5 mm/min under standard laboratory conditions of. 23 °C and 50% relative humidity (RH). Load and displacement were recorded during the tests. The inner and outer span lengths were 51 mm and 153 mm, respectively. The support and loading rollers had a diameter of 10 mm. GRP woven fabric shims (2 mm thick) were placed between the loading rollers and the test specimen to distribute local stresses and prevent crushing. Displacement at the beam mid-section was measured using a linear voltage displacement transducer (LVDT).

Four-point flexure modulus and strength data measured for the "as-received", dried and artificial weathered material are presented in Table 3. Additional flexural tests were conducted on 15 mm wide specimens (as specified in BS EN ISO 14125) for the "dry" material in order to check that edge effects were minimal for the narrow beam specimens (i.e. no reduction in flexural properties).

Table 3: Four-Point Flexure Results

Material	Flexural Modulus (GPa)	Flexural Strength (MPa)
As-received	22.5 ± 0.5	442 ± 23
Dry	23.8 ± 1.1	490 ± 11
Exposure (Months)		
1	23.3 ± 1.3	416 ± 38
2	22.7 ± 1.3	404 ± 56
3	21.7 ± 1.3	377 ± 23
4	22.1 ± 1.2	377 ± 24
6	21.3 ± 0.8	371 ± 35

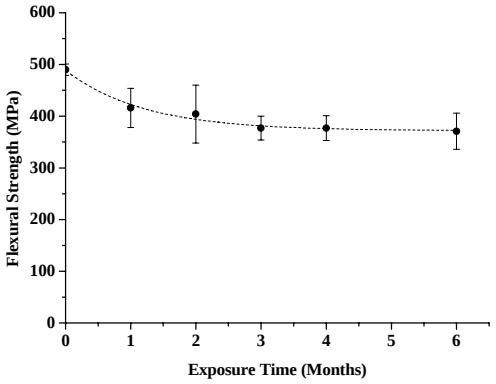

Figure 6: Flexural strength versus exposure time.

Flexural modulus for the narrow and standard width beams for the "dry" material was 23.8 ± 1.1 GPa and 23.9 ± 0.2 GPa, respectively. The corresponding flexural strengths for the two specimen widths were 490 ± 11 MPa and 460 ± 25 MPa. Thus, edge effects seem to have minimal effect on the flexural properties obtained for the narrow specimens.

The flexure modulus remains relatively unaffected by artificial weathering. Whereas, flexure strength decreases with exposure time (see Figure 6). Tensile initiated failure was observed to occur for the majority of flexure tests. A decrease in flexural strength with exposure time is not unexpected as any degradation involving the outer layers of the composite will have an amplified effect on load-bearing capacity under flexural loading conditions. The influence of layers on flexural strength increases proportionally to the cube of the distance of the layer from the neutral axis of the beam.

The reduction in flexural strength is commensurate with the reduction in surface hardness, gloss and spectral reflectance observed. The results also indicate that the flexural strength decreases with increasing moisture content. The question arises as to the use of non-destructive surface measurements, such as Barcol hardness, gloss and spectral reflectance, as possible indicators of mechanical property (i.e. flexural strength) reduction.

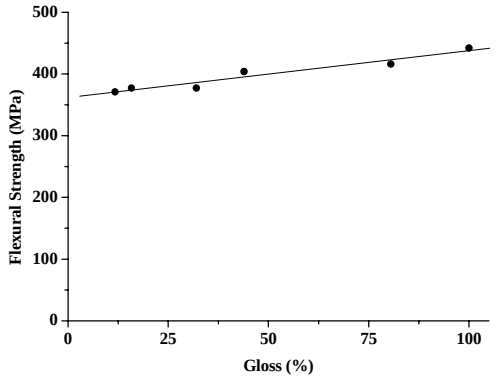

Figure 7: Flexural strength versus gloss for weathered and "as-received" materials (—- linear curve fit).

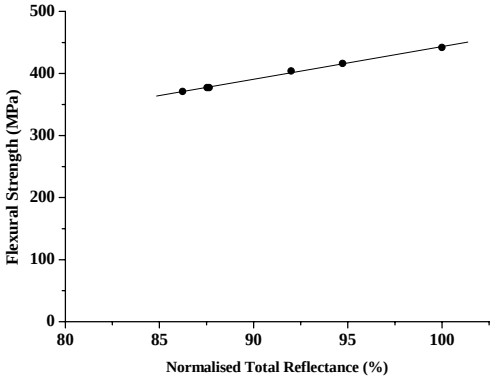

Figure 8: Flexural strength versus normalised total reflectance for weathered and "as-received" material (—- linear curve fit).

It is possible to estimate the flexural strength of the composite based on reflectance data. Figures 7 and 8 show that flexural strength tends to decrease linearly with a reduction in both gloss and normalised total reflectance (increased degradation). The curves incorporate flexural strength and reflectance data for the "as-received" material and not the "dry" material. The correlation coefficient for the linear curve fit to the flexural strength and gloss and normalised total reflectance was 0.9690 and 0.9985, respectively. Although spectral reflectance (i.e. colorimetry) measurements are intrinsically more accurate than gloss measurements, the latter can be obtained using a portable hand-held device.

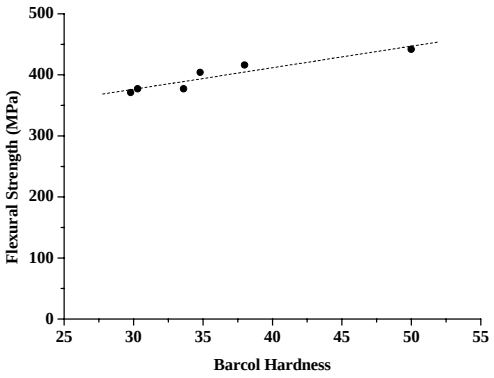

Figure 9: Flexural strength versus Barcol hardness for weathered and "as-received" materials (- - - trend line).

The relationship between flexural strength and Barcol hardness (Figure 9) also tends to follow a linear relationship. The correlation coefficient for a linear regression fit to the data is lower, hence Figure 9 shows only a trend line. However, Barcol hardness can provide an indication as to the level of flexural strength reduction. The disadvantage using Barcol hardness is that it leaves small permanent imprints on the surface; a possible source of environmental ingress and surface damage. The surface also needs to be smooth. The technique is not suited to rough surfaces.

3.6 Fourier Transform Infrared Spectroscopy (FTIR)

The surfaces of the weathered samples were analysed by PerkinElmer using a PerkinElmer Spectrum 100 FTIR Spectrometer and Universal Attenuated Total Reflectance Accessory (UATR). The FTIR spectra were recorded for all exposure times from 0 to 6 months exposure. The set of spectra showed gradual, consistent changes indicating that significant chemical changes have taken place (see Figure 10).

Some of the more obvious changes are the relative increase in intensity of the absorbance at ~3500 cm and 1640 cm. There are also more subtle changes with an increase in absorbance at ~1775 cm and a change in the absorbance maxima wave number for the absorbance band at ~1725 cm (C-O ester group).

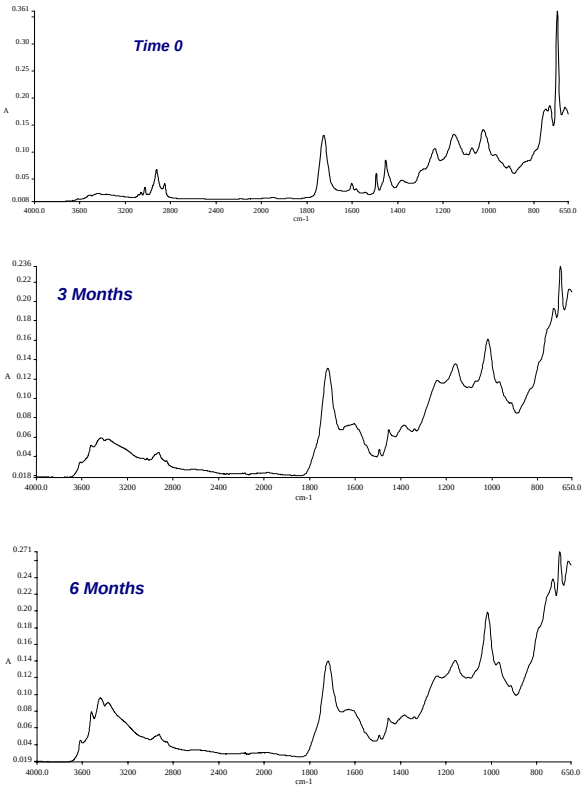

Figure 10: FTIR spectra for 0, 3 and 6 months weathering (courtesy of ElmerPerkin).

The increase in intensity of the absorbance at ~3500 cm and 1640 cm may possibly be attributed to a combination of moisture ingress and oxidation due to UVA radiation.

4 Conclusions

The results clearly demonstrate that suitable non-invasive test methods are available that can provide reliable and accurate quantitative data relating the degree of surface degradation to mechanical performance. These test methods make it possible to produce measurable criteria for performance testing for determination of chemical resistance of composite materials.

Gloss and Barcol hardness measurements could possibly be used to monitor the detrimental effects of service environments on flexural strength. It may also be possible to use these techniques to quantify the level of degradation (i.e. a graduated scale) and provide realistic weighting factors (see [3]).

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