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A Comparison of Normal and Accelerated Ageing of GRP Laminates Immersed in Seawater

E.P. Gellert and D.M. Turley

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Maritime Platforms Division
Aeronautical and Maritime Research Laboratory

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ABSTRACT

Glass fibre reinforced plastic (GRP) materials for marine applications undergo losses to mechanical properties during ageing. This study examined a polyester, a phenolic and two vinylester GRP materials. Specimens were immersed in seawater, unloaded or loaded at a high service temperature of 30°C, or at 50°C as an accelerated ageing condition. Water uptake was monitored. After ageing to near saturation the losses in flexural strength ranged from 15 to 25% for the unloaded specimens. Loading in flexure at 20% of the strain to fail while ageing did not significantly affect the water uptake or losses to mechanical properties. Greater losses in mechanical properties from the 50°C immersion were accompanied by indications of abnormal degradation. The accelerated ageing condition therefore appears unsuitable for the assessment of these materials.

RELEASE LIMITATION

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Executive Summary

Glass fibre reinforced plastic (GRP) materials have been used for marine applications for over 50 years. They are increasingly being proposed and trialed for critical components such as masts, submarine control surfaces, transmission shafts and propellers.

Water absorption by the plastic matrix of GRP is considered to be a primary mechanism for degrading mechanical properties. The rate of absorption at service temperatures is quite low, taking many years to achieve saturation for typical thicknesses of marine GRP. A validated accelerated ageing process would be useful for assessing degradation likely for vessel or component lifetimes.

This study compared the mechanical properties of four GRP materials following immersion ageing at a high service temperature of 30°C and an accelerated ageing condition of 50°C. The materials examined were either in service, proposed for service or developmental and included a polyester, a phenolic and two vinylester GRPs.

All material types suffered decreases in flexural properties following 30°C ageing to near saturation. The vinylesters lost up to 20% and the phenolic 25% of initial strength. Degradation at the accelerated 50°C condition was more severe, and indications of damage mechanisms unrepresentative of the service temperature ageing were evident here.

The accelerated ageing condition appears unsuitable for life assessments for these materials. Design of GRP structures for Navy should include ageing losses in safety factor considerations. Ongoing work will attempt to correlate material degradation under laboratory ageing conditions with that under field exposure.

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Mr. Gellert graduated in Applied Science from the Footscray Institute of Technology. Since commencing with MRL in 1976 he has contributed to studies of polymer stabilization, the burning behaviour and the mechanics of polymeric materials, particularly fibre reinforced plastics. A three year term of work at AMRL Queensland involved environmental exposure trials on materials and equipment. Since returning to AMRL Maribyrnong in 1991 he has worked with polymeric materials for ship structures and GRP armour for land vehicles

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1. INTRODUCTION

Glass fibre reinforced plastic (GRP) materials have been used for marine applications for over 50 years. Their use has been directed more at the primary structures of hull, decks and structural bulkheads, and also to superstructure, framing members, non-structural bulkheads, submarine casings, sonar domes and radomes. Increasingly GRP is being proposed and trialed for critical components such as masts, submarine control surfaces, transmission shafts and propellers [1-4].

The application of GRP to naval and other vessels has often been accompanied by the application of conservative design safety factors [5, 6] due to limited durability data and to account for underwater shock loading (mine-countermeasure vessels). Design which seeks topside weight efficiency or component geometric efficiency may seek to minimise design safety factors, however, decreases in mechanical properties due to ageing should be included in safety factor considerations.

Laboratory studies have characterised water uptake and mechanical loss behaviour for immersed polymer matrix composites [7-11]. Degradation for such laminates can be severe [1, 7, 11], or can show aspects of improvement alongside degradation, such as increased energy to incipient damage under impact [9] or increased residual strength at high cycle counts for fatigued composites [10]. The impact study [9] however indicated overall losses in impact resistance with water uptake on the basis of the other indexes used.

Atmospheric ageing at high humidities has been shown to cause similar water uptake to immersion for epoxy composites [12-14] and Gutierrez has reported that ageing in sea air is as severe as in seawater for a range of marine composites [15]. This accords with the work of Pritchard who reported that the residual properties of an immersed polyester/glass composite were a function of absorbed water content [7]. For durability assessments the ageing of immersed composites may thus be regarded as indicative (albeit worst case) of ageing for composites in humid atmospheric applications. The water uptake profile for GRPs exposed under atmospheric service conditions may be complicated however, by drying cycles at times of low humidity.

Due to the long times required for typical marine GRP to approach water saturation at service temperatures, studies at these temperatures can be very slow. In order to hasten the absorption process some investigators have carried out accelerated ageing tests [7,8,12,16]. Bonniau and Bunsell [12] showed however, that acceleration of the effect of water vapour on ageing by immersion in hot boiling water was invalid as different absorption processes were found to occur. Dewimille and Bunsell [16] investigated the ageing of glass fibre reinforced composites over the temperature range 22 - 100°C. They found that the initial absorption was in accordance with Fick's law and the rate of water uptake increased with temperature. Increasing immersion times at high temperatures however, resulted in increasing amounts of cracking occuring in the specimens and water absorption became increasingly non-Fickian. Significant cracking occurred in specimens immersed in boiling water for 100 hours, whereas at 50°C cracking was not observed until 200 days and at 22°C no cracking was observed after nearly three years immersion. Dewimille and Bunsell also reported that at temperatures less than 50°C absorbed water had little significant effect on shear modulus and internal damping characteristics.

The purpose of the present work was to undertake laboratory water uptake studies at 30 and 50°C in seawater to investigate if immersion at 50°C could be used as an accelerated test. The standard immersion temperature was chosen as 30°C as this is representative of the maximum summer temperature of Australian tropical waters. A range of GRPs with different resin systems were investigated and the effect of temperature of immersion on diffusion rates, maximum water absorption and mechanical properties determined. Since in service composites are frequently exposed to the marine environment while subject to loading, tests were also carried out on stressed and unstressed specimens.

2. COMPOSITE SPECIMENS

The laminating resins used for specimen manufacture were as follows:

1. Cellobond A 2785CV, an isophthalic polyester originally supplied by Kemrez Chemicals Australia under licence from BP Chemicals Ltd, UK;
2. Hetron 922-6, an Ashland Chemicals thixotropic vinylester manufactured in Australia under licence by Huntsman Chemical Co. (formerly Chemplex);
3. Norpol 92-20, a vinylester supplied by A.C. Hatrick Chemicals, under licence to Jotun Polymer (Norway);
4. CL 1723, a developmental resole phenolic.

Using these resins, ~ 4mm thick GRP panels were fabricated by hand layup techniques. The E-glass ply sequence was symmetric with woven roving (WR ~600g/m^2) as both outer plies, and WR alternating with chopped strand mat (CSM ~300g/m^2) for the inner plies. An exception to this was that for the phenolic specimens where a powder bound CSM of 450g/m^2 was used instead of the emulsion bound CSM, for reasons of resin compatibility with the binder. The 4mm specimens were thus constructed of 4 WR alternating with 3 CSM.

Following lamination the lay-ups were compressed between aluminium plates and vacuum bagged at 20kPa pressure to minimise variations in surface topography. This is not representative of most current marine fabrication but was used in the laboratory to minimise variations in fabrication of the panels.

Beam specimens 150mm x 15mm were cut from the panels with the principal axis parallel to the warp direction of the woven roving. The specimens were then machined on a tensilkut router using a diamond faced grinding bit to ensure parallel sides and then edge-finished using emery paper on a flat-bed. The edges of all specimens were painted with vinylester resin prior to post-curing at 70°C for 20 hours (80°C for 2 hours for the phenolic) in an air oven, before drying to constant weight at 50°C. The edge coating was to minimise any absorption along fibre interfaces from the exposed edge and the post-cure was to minimise any curing effects from immersing at 50°C. Temperature measurements of GRP exposed to sunlight [17] have indicated that 70°C would not be an unrealistic service temperature for structures above the waterline.

3. EXPERIMENTAL DETAILS

3.1 Environmental Loading and Immersion

All water uptake and mechanical test data is reported for samples of 5-8 specimens. Unloaded specimens were immersed in seawater tanks at 30°C or 50°C and periodically withdrawn for weighing to monitor water uptake. The loaded specimens were installed in stainless steel 4 point bending fixtures, loaded at quarter-points, with a support span of 120mm. The loading roller radii were 5mm. The loading rollers were displaced toward the support rollers by tightening bolts down to the displacement required to achieve outer fibre strains in the test specimens of 20% ultimate strain as determined in control tests on dry specimens. This is a condition of stress-relaxation with material creep occurring at the set beam deflection. These loaded specimens were installed in the same seawater at 30°C or 50°C. Specimens were periodically withdrawn, weighed for water uptake and returned.

3.2 Mechanical Testing

Flexure testing for flexural modulus, strength and strain to failure was carried out according to ASTM D790M-84 [18]. The testing parameters are given below.

All specimens were tested to Method I, Procedure A, which is 3 point loading at a straining rate of 0.01±0.005 min^{-1}.

Support Span L (mm)	60
Support Roller diameter (mm)	10
Loading Roller diameter (mm)	25
Crosshead speed (mm/min)	2
Strain rate (approx.) min^{-1}	0.012

All specimens were tested at the standard laboratory temperature of 23±2°C. The withdrawn immersion specimens were conditioned in water at this test temperature for 2 hours then surface dried and immediately tested.

Flexural strength $$S = \frac{3PL}{2bd^2} \text{ (Mpa)} \quad (1)$$

where P = maximum load (N)
L = support span (min)
b = specimen width (mm)
d = specimen thickness (mm)

Tangent Modulus of Elasticity $$E = \frac{L^3M}{4bd^3} \text{ (Mpa)} \quad (2)$$

where M = slope of the tangent to the initial straight-line portion of the load-deflection curve, N/mm of deflection

Ultimate strain $$\varepsilon_f = \frac{6\delta d}{L^2} \text{ (mm/mm)} \quad (3)$$

where δ = deflection at the centre of the specimen at maximum load (mm).

4. RESULTS

4.1 Water Uptake

The weight uptake (%) is given at selected intervals for the specimens in Table 1. These data are usually not measured data points but are taken from the graphs of the experimental data points to enable convenient tabling. They are unadjusted for any weight loss from material leaching. Plots of weight uptake vs √time are given in Figures 1-6 and 9-12 which give the experimental data points. Classical Fickian absorption is characterised by a nearly linear relationship between weight uptake and √time up to about half the saturation uptake, which then asymtotes to a constant saturation level [10, 19]. This can be described by

$$\frac{Mt}{M\infty} = \frac{4}{\sqrt{\Pi}}\left(\frac{Dt}{d^2}\right)^{½} \quad (4)$$

where Mt and M∞ are the weight uptakes at time = t and ∞ respectively, D is the measured diffusion coefficient, and d is the specimen thickness.

Examination of Figures 1-6 and 9-12 shows that the absorption kinetics deviated to various extents from classical Fickian behaviour. The initial part of the water uptake graphs were not always linear and at long exposure times they did not always asymtote to a plateau indicating that saturation had not occurred. Measurements of the initial gradients were estimated to give the greatest error (±5%) in determining the measured diffusion coefficient D. Despite these deviations from classical diffusion behaviour, indicating that non-diffusion processes are contributing to water uptake, the diffusion coefficients D have been calculated from equation (4) at time t when $\frac{Mt}{M\infty}$

= 0.3. For finite specimen size where edge absorption is significant the apparent diffusion coefficient D^1 for homogeneous material is given by [14].

$$D^1 = \frac{D}{\left[1+\frac{d}{b}+\frac{d}{x}\right]^2} \qquad (5)$$

where D = measured diffusion coefficient for the finite specimen (mm^2/s)

x = specimen length (mm)

b = specimen width (mm)

This correction does not strictly apply for composite materials which are not homogeneous and where diffusivity may differ for the 3 principal axes, however, it has been applied in the present study and values for the apparent diffusion coefficient D^1 are given in Table 2 together with the estimated saturation water uptake M_∞.

4.1.1 Effect of Temperature on Water Uptake

The effect of temperature on water uptake is shown in Figures. 5 and 6 for the Cellobond, Hetron and Norpol, with discrete data given in Tables 1 and 2. The estimated saturation uptakes M_∞ and the apparent diffusion coefficients D^1 are illustrated for both immersion temperatures in Figures 7 and 8 respectively. From Table 2 the apparent diffusion coefficients D^1 indicate that the initial rate of uptake at least doubled with an increase in water temperature from 30°C to 50°C, see also Figure 8. For all materials except the phenolic GRP (where degradation was evident) the higher immersion temperature increased the estimated saturation uptakes M_∞ by about 10-20%, see Table 2 and Figure 7. The phenolic GRP specimens lost weight beyond their peak water uptake with more severe losses occurring for the 50°C immersion. Peak absorption for the phenolics occurred after about 150 days at 30°C (Fig. 2) and after about 70 days at 50°C (Fig. 4). The weight losses were manifested as material exudation from the edges of the specimens confirming degradation. Analysis of the exudate using infra-red (IR) spectroscopy indicated that residue from the binder of the chopped-strand-mat was a component. The isophthalic polyester was also beginning to lose weight at 50°C when the specimens were withdrawn for mechanical testing after 400 days immersion (Fig. 3).

At 30°C both vinylesters showed similar water uptake approaching a saturation level of about 0.44 weight % after 800 days immersion. At this time the isophthalic polyester uptake was approaching 0.85 weight % and the phenolic had passed its peak water uptake of 8.8 weight % (Figures. 1 and 2). In comparison the estimated saturation uptakes at 50°C were ~0.49% for the vinylesters, with the polyester and phenolic having passed their respective peak uptakes of 1.01 and 8.4 weight % prior to the withdrawal at 400 days (Figures 3 and 4).

4.1.2 Effect of Loading on Water Uptake

The effect of loading on water uptake is shown in Figures. 2, 4 and 7-12, and in Tables 1 and 2. At 30°C no consistent differences were observed between the water uptake behaviour of the flexure-loaded and unloaded specimens. The uptake kinetics as described by the water uptake versus $\sqrt{t}$ curves were similar (Figures. 2, 4 and 9-12). No consistent effect of loading on M_∞ or D^1 was evident at 30°C, see Figures 7 and 8. This is consistent with the results reported by Kasturiarachchi for a glass/epoxy composite [20]. Comparisons at 50°C suggest that the saturation levels M_∞ were higher for all stressed specimens except the Norpol, whereas the apparent diffusion coefficients D^1 are greater for all stressed specimens except the Cellobond isophthalic polyester (Table 2). While the apparent diffusion coefficient D^1 is probably the less reliable index for these comparisons, the 6-7% higher saturation levels apparent for the loaded Cellobond and Hetron may not be significant either, and the 13% higher equilibrium water uptake for the loaded phenolic appears anomalous in that uptake continued beyond the time where losses occurred for the unloaded specimens, see Figure 4.

4.2 Mechanical Properties

The first withdrawal of the 4mm thick 30°C flexure specimens occurred at either 140 or 210 days immersion when water uptake was generally over 9/10 of the level expected at saturation. Flexural properties for the unimmersed control specimens are given in Table 3 and properties at the first and second withdrawals at 30°C in Tables 4 and 5 respectively.

At the first 30 °C withdrawal the Cellobond lost 5% of modulus and 9% of strength relative to the controls. The vinylesters Hetron and Norpol suffered no significant modulus loss, but did lose ~ 7-14% in strength. For the phenolic GRP the fall in strength was significant at 25% whereas the modulus was reduced by only 3%.

At the second 30°C withdrawal after 800 days immersion (close to saturation) the unloaded polyester and vinylesters had lost 15-20% of their original strength and up to 10% of their original modulus, while the phenolic had lost 25% of strength and 6% of the original modulus. These changes in strength and modulus are illustrated in Figures 13 and 14. The immersion period between the first and second 30°C withdrawals saw the water uptake figures for the unloaded phenolic, Cellobond, Hetron and Norpol change from 8.9 to 8.4, 0.71 to 0.85, 0.41 to 0.44 and 0.40 to 0.43 respectively.

The 50°C specimens were withdrawn for testing at either 400 or 490 days immersion where moisture uptake was over 9/10 of the expected level at saturation. The results are given in Table 6. Regarding the unloaded specimens, Cellobond and phenolic suffered large reductions of modulus (22 and 26%) and strength (37 and 35%). The two vinylesters Hetron and Norpol suffered lower modulus losses (11 and 9%) and strength losses of 35 and 43% respectively. These lower mechanical properties following 50°C immersion are illustrated in Figures 13 and 14.

Considering the effect of loading (at 20% of ultimate flexure strain) on mechanical properties, greater losses were evident for some 30°C loaded than for unloaded specimens but the correlations were not consistent. However for the 50°C immersions loading exacerbated the mechanical losses for all specimens except the Cellobond isophthalic polyester, see Figures 15 and 16 and Tables 4-6.

The mechanical losses for the Cellobond and phenolic were accompanied by weight losses in the later stages of immersion suggesting that material loss may have been a contributing factor. The strength losses for the Hetron and Norpol were of similar severity, but any indication of material loss will not be available until accompanying untested specimens have been redried and weighed.

5. DISCUSSION

The diffusion of water into polymers is usually modelled according to Fick's law. This law assumes one-dimensional diffusion with the rate of liquid diffusion being proportional to the concentration gradient in the diffusion direction.. The present study with GRP showed some departures from classical Fickian behaviour (discussed in section 4.1 earlier), suggesting that the uptake processes are more complex. Such departures have been reported by other investigators [7,11,12,19,21-22].

For the phenolic resin laminate at 30°C, saturation uptake $M\infty$ was much greater than for the polyester and vinylester laminates while the apparent rate of diffusion D^1 was smaller. The higher saturation uptake can be attributed to the microporosity of the phenolic matrix as seen in Figure 17. The microporosity could be expected to present a large free volume for the accumulation of significantly more water than can be accommodated within the polymer network of the matrix.

Immersion at 50°C resulted in D^1 and $M\infty$ increasing for all laminates except the phenolic, compared with values obtained at 30°C. The exception with the lower apparent saturation uptake for phenolic would be due to the earlier material degradation at 50°C. These increased rates of water uptake with increased immersion temperature are consistent with known behaviour for polymers [7, 8, 12, 14, 16, 19, 23]. Examination by scanning electron microscopy of polished sections of specimens subject to immersion at 30°C and 50°C did not provide evidence of interface effects caused by the higher temperature, see Fig. 18. However visual inspection of the polyester revealed an enhanced visual prominence of glass fibres following 50°C immersion suggesting interface effects not evident for the 30°C specimens, see Fig. 19.

The apparent decrease in water uptake measured after long immersion times at 50°C for the Cellobond and phenolic specimens can be attributed to a loss of material from within the specimens. Leaching of low molecular weight species from resin has previously been reported to occur [8,12,20] particularly at higher temperatures. In the present work material exuding from the edges of the phenolic GRP specimens which was found by IR analysis to derive from the binder of the chopped-strand-mat.

The much greater loss in flexural strength and modulus for specimens immersed at 50°C (Figures 13 and 14) indicates that the material damage occurring at this higher temperature is adversely affecting material properties.

The greater decreases in flexural strength and modulus after immersion at 50°C compared with 30°C are significant. These results together with the higher saturation uptakes M_∞ at 50°C immersion, the weight losses for Cellobond and phenolic, the interaction with loading to increase uptake and the visual prominence of fibres following 50°C immersion raise serious doubts concerning the validity of accelerated ageing at 50°C to represent true service durability. To enable early indications of strength loss it may be useful to immerse specimens at 30°C until ~90% of the estimated saturation level before testing. At the significantly shorter immersion time here of 210 vs. 810 days this ageing was indicative of about half the strength loss at saturation, for the unloaded polyester and vinylesters, see Tables 4 and 5.

The effect of flexural loading (at the levels used here) on the water uptake behaviour has not been unequivocally established. However, a more consistent relationship was noted between loading and mechanical losses for the 50°C than for the 30°C immersed specimens. Given that the greater losses in flexural properties for unloaded 50°C compared to 30°C specimens is associated with increased material damage evident as weight loss, it seems likely that the specimens at 50°C had a lower threshold to damage from loading, so the cumulative effect of thermal-water damage and loading became more significant.

No effect was reported for flexurally loaded glass/epoxies by Kasturiarachchi [20], but other work [5, 24-25] has demonstrated increased water uptake with increased tensile stress, and related water uptake to the angle between the principal fibre axis and the applied stress [24,25]. This suggests that flexurally loaded GRP specimens will experience increased water uptake on the tensile loaded side of the beam and decreased water uptake on the compressive loaded side which would tend to conceal the effect of loading on weight uptake.

6. CONCLUSIONS

Although water absorption showed some departures from Fickian diffusion behaviour the diffusion coefficients calculated assuming Fickian behaviour are considered to be reasonably accurate.

All GRP specimens studied suffered decreases in flexural properties with immersion in seawater at 30°C under the laboratory conditions used. The phenolic suffered severe decreases in properties rendering it unsuitable for immersion or water contact applications.

Loading immersed specimens at 30°C under conditions of set-strain with stress relaxation at $0.2\varepsilon_f$ did not significantly affect the water uptake or the losses in flexural strength and modulus.

The 50°C accelerated ageing test appears to be unsuitable for evaluating the ageing of composites due to damage mechanisms occurring, which are supplementary to service temperature diffusion related effects. Nevertheless this accelerated test may serve as an indicator of worst-case losses to mechanical properties.

A useful truncated ageing test may be to withdraw 30°C immersion specimens before the saturation plateau, eg. at $0.9\ M_\infty$. Such ageing can be indicative of about half the loss of strength at less than half the ageing time to saturation.

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Appendix: Tables

Table 1: Weight uptake (%) for loaded and unloaded 4mm thick beam specimens immersed at 30 °C and 50 °C, for selected intervals up to 800 days. Uptake data has not been adjusted for material loss due to leaching

	UNLOADED Weight Uptake (%)							
Immersion Time (days)	30°C				50°C			
	Cellobond (Isophthalic polyester)	CL 1723 (phenolic)	Hetron (vinylester)	Norpol (vinylester)	Cellobond	Phenolic	Hetron	Norpol
1	-	-	-	-	0.22	1.7	0.11	0.11
4	0.20	1.9	0.13	0.12	0.40	3.9	0.21	0.21
9	0.31	3.1	0.18	0.17	0.52	5.7	0.28	0.28
25	0.46	5.5	0.26	0.25	0.71	7.9	0.38	0.38
100	0.67	8.6	0.37	0.37	0.91	8.3	0.44	0.44
210	0.73	8.9	0.41	0.40	-	-	-	-
400	-	-	-	-	0.98	7.8	0.47	0.46
800	0.85	8.4	0.44	0.43	-	-	-	-
	LOADED							
	30°C				50°C			
1	-	-	-	-	0.22	2.2	0.12	0.11
4	0.22	2.2	0.13	0.12	0.40	4.5	0.23	0.21
9	0.32	3.50	0.18	0.17	0.57	6.6	0.31	0.29
25	0.48	5.8	0.26	0.25	0.76	8.6	0.40	0.38
100	0.69	8.6	0.38	0.37	0.98	9.4	0.47	0.45
400	-	-	-	-	1.06	9.2	0.51	0.48
800	0.85	8.5	0.44	0.44	-	-	-	-

Note: These data are usually not measured data points but are inferred from the measured points which describe the plots.

Table 2: Estimated saturation uptakes M∞ (%) and apparent diffusion coefficients D^1 ($mm^2/s \times 10^{-7}$) adjusted for finite specimen dimensions, for loaded and unloaded 4mm thick beams at 30 ℃ and 50 ℃.

(a) 4mm beams at 30°C								
	Unloaded				Loaded			
	Cellobond	Phenolic	Hetron	Norpol	Cellobond	Phenolic	Hetron	Norpol
M∞ (%)	0.85	8.8	0.44	0.44	0.85	8.9	0.43	0.43
D^1 ($mm^2/s \times 10^{-7}$)	2.5	2.3	4.3	4.3	3.1	2.9	3.8	3.5
(b) 4mm beams at 50°C								
	Unloaded				Loaded			
M∞ (%)	1.01	8.4	0.49	0.48	1.07	9.5	0.52	0.49
D^1 ($mm^2/s \times 10^{-7}$)	7.4	8.9	8.5	9.3	6.7	10.8	9.3	9.7

Table 3: Flexural properties of 4mm thick unimmersed control specimens

Laminate	Flexural Strength (MPa)	Flexural Modulus (GPa)	Strain at failure (mm/mm)	Failure mode
(4mm)				
Cellobond (Isophthalic polyester)	365	17.7	0.029	mixed compressive/tensile
CL1723 (phenolic)	206	16.8	0.019	mixed compressive/delamination
Hetron (vinylester)	497	16.8	0.032	tensile
Norpol (vinylester)	483	16.1	0.033	tensile

Table 4: Flexural properties of the first 30℃ withdrawal of immersed 4mm laminate beams: Cellobond after 140 days, Phenolic, Hetron and Norpol after 210 days immersion (change in property given in brackets)

Unloaded specimens					
Laminate	Flexural Strength (MPa)	Flexural Modulus (GPa)	Strain at failure (mm/mm)	Weight uptake (%)	Failure mode
Cellobond (Isophthalic polyester)	333 (-9%)	16.8 (-5%)	0.027 (-7%)	0.71	compressive and c/t
CL1723 (phenolic)	154 (-25%)	16.3 (-3%)	0.015 (-21%)	8.9	compressive buckle/delamination
Hetron (vinylester)	464 (-7%)	17.1 (+2%)	0.030 (-6%)	0.41	tensile
Norpol (vinylester)	418 (-14%)	16.6 (+3%)	0.029 (-12%)	0.40	tensile
Loaded Specimens					
Cellobond	329 (-10%)	15.2 (-13%)	0.024 (-14%)	0.72	compressive and c/t
Phenolic	152 (-26%)	14.9 (-11%)	0.018 (-5%)	8.8	compressive buckle/delamination
Hetron	469 (-6%)	16.0 (-5%)	0.032 (0)	0.41	tensile
Norpol	445 (-8%)	16.3 (+1%)	0.031 (-6%)	0.40	tensile

Table 5: Flexural properties of the second 30 °C withdrawal of immersed 4mm laminate beams after 810 days immersion
(Change in property compared to controls given in brackets)

Unloaded					
Laminate	Flexural Strength (MPa)	Flexural Modulus (GPa)	Strain at failure (mm/mm)	Weight uptake (%)	Failure mode
Cellobond	304 (-17%)	16.5 (-6%)	0.024 (-17%)	0.85	compressive, then tensile/delam.
Phenolic	154 (-25%)	15.7 (-6%)	0.017 (-11%)	8.37	compressive
Hetron	422 (-15%)	16.6 (-10%)	0.028 (-13%)	0.44	tensile/delamination
Norpol	382 (-21%)	16.5 (+2%)	0.025 (-24%)	0.43	tensile/delamination
Loaded					
Cellobond	325 (-11%)	16.6 (-6%)	0.025 (-14%)	0.85	compressive, then tensile/delam.
Phenolic	131 (-36%)	14.3 (-15%)	0.016 (-16%)	8.53	compressive, then delamination
Hetron	414 (-17%)	15.7 (-6%)	0.029 (-9%)	0.44	tensile/delamination
Norpol	381 (-21%)	16.1 (0%)	0.026 (-21%)	0.44	tensile/delamination

Table 6: Flexural properties of 50 °C immersed 4mm laminate beams: Cellobond and Phenolic after 400 days, Hetron and Norpol after 490 days immersion (Change in property given in brackets)

Unloaded					
Laminate	Flexural Strength (MPa)	Flexural Modulus (GPa)	Strain at failure (mm/mm)	Weight uptake (%)	Failure mode
Cellobond	229 (-37%)	13.0 (-22%)	0.021 (-28%)	0.98	compressive and tensile
Phenolic	135 (-35%)	12.3 (-26%)	0.016 (-16%)	7.81	compressive and tensile
Hetron	322 (-35%)	14.9 (-11%)	0.021 (-34%)	0.48	tensile
Norpol	276 (-43%)	14.7 (-9%)	0.019 (-42%)	0.47	tensile
Loaded					
Cellobond	219 (-40%)	14.1 (-20%)	0.018 (-38%)	1.06	compressive and tensile
Phenolic	104 (-50%)	8.3 (-51%)	0.017 (-11%)	9.21	compressive and tensile
Hetron	272 (-45%)	14.4 (-14%)	0.019 (-41%)	0.51	tensile
Norpol	238 (-51%)	13.7 (-15%)	0.017 (-48%)	0.48	tensile

Appendix: Figures

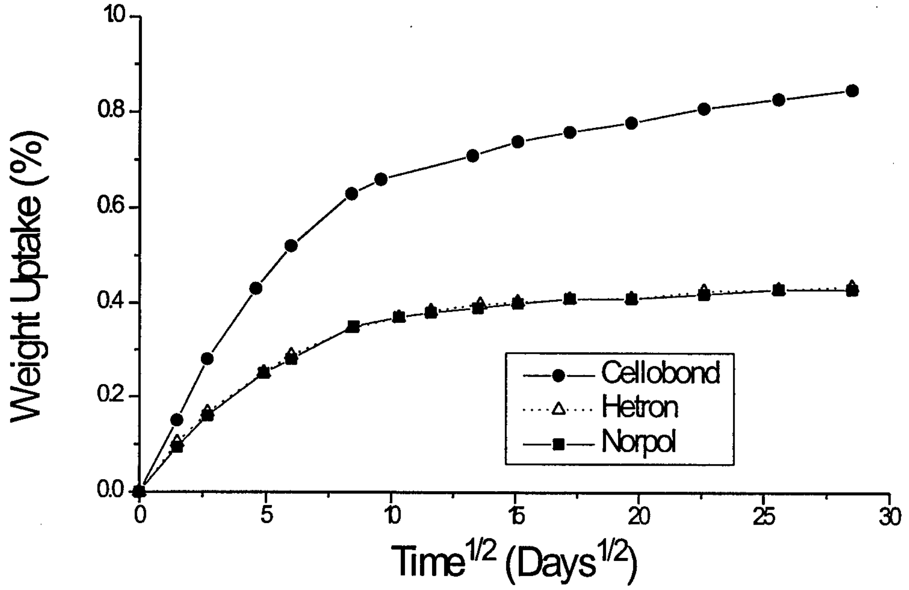


Figure 1: Water uptake in Cellobond, Hetron and Norpol specimens immersed at 30℃, unloaded.

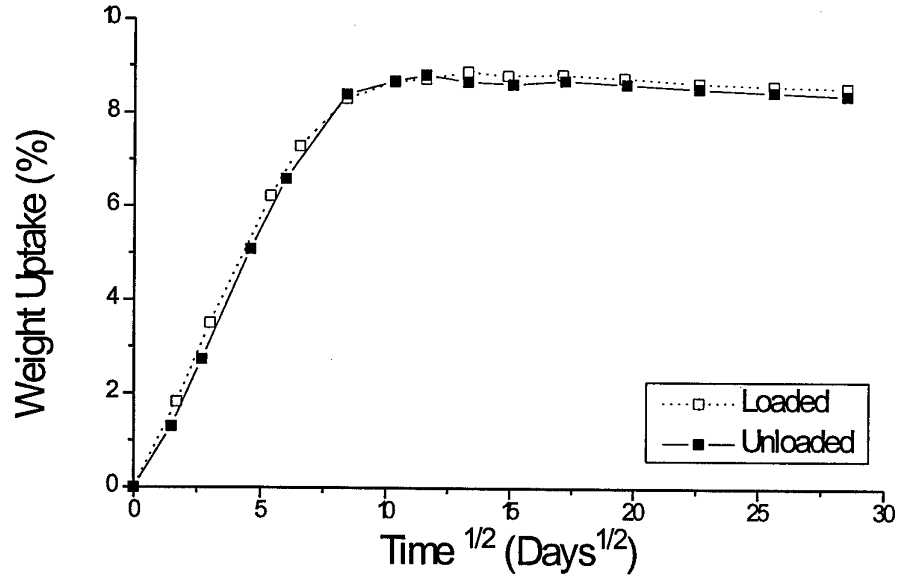


Figure 2: Water uptake in phenolic specimens immersed at 30℃, unloaded and loaded.

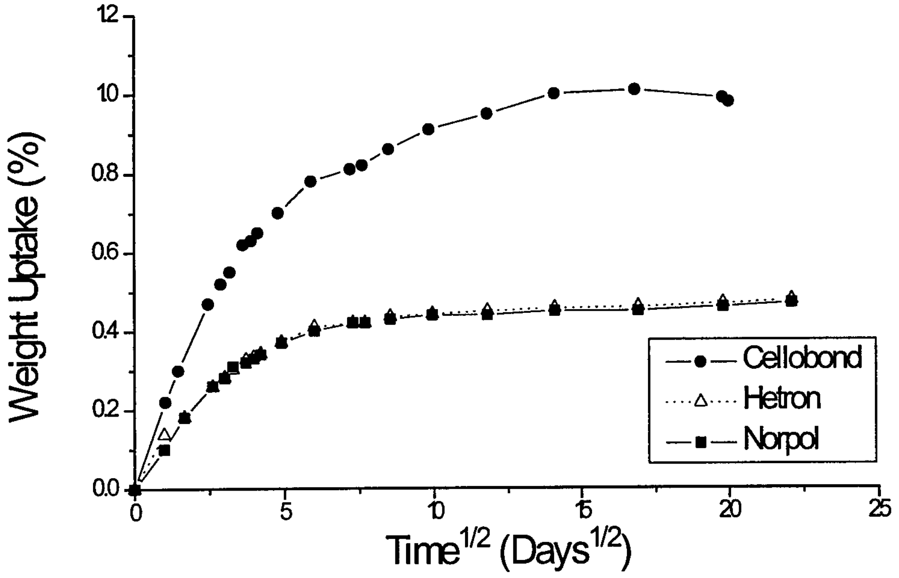


Figure 3: Water uptake in Cellobond, Hetron and Norpol specimens immersed at 50°C unloaded.

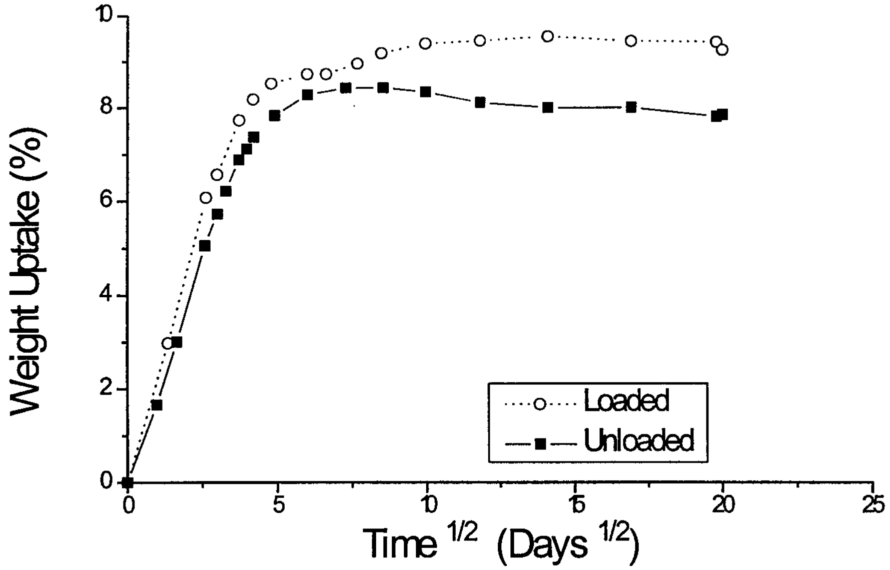


Figure 4: Water uptake in phenolic specimens immersed at 50°C, unloaded and loaded.

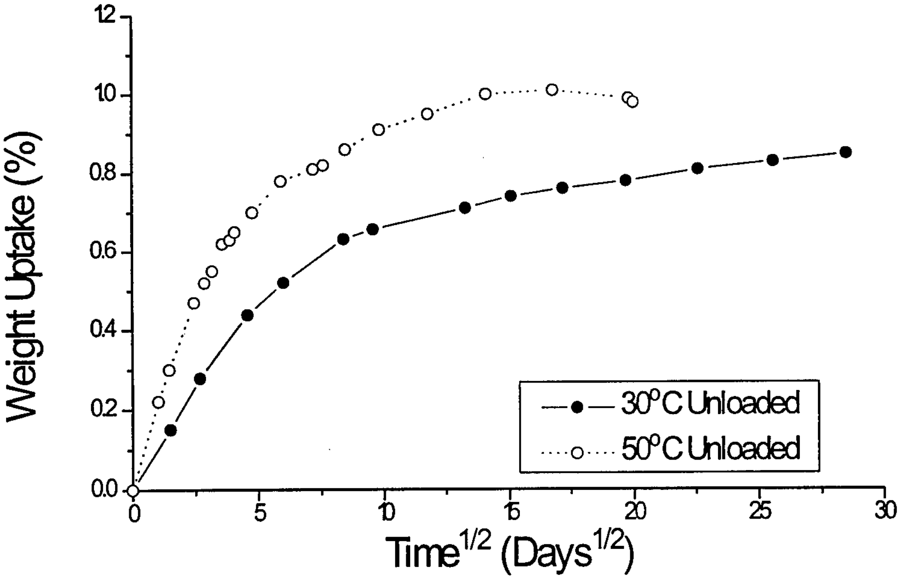


Figure 5: Water uptake in Cellobond specimens immersed at 30 ℃ and 50 ℃, unloaded.

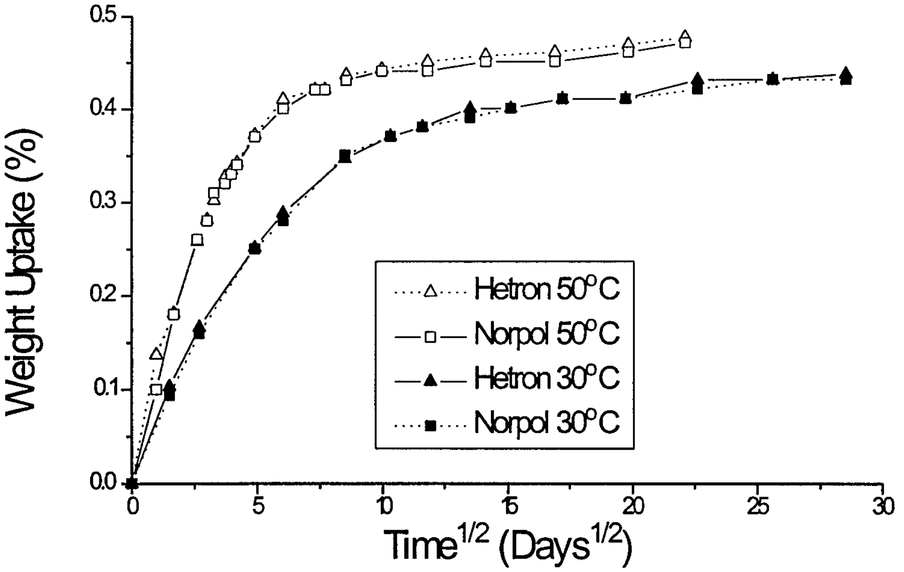


Figure 6: Water uptake in Hetron and Norpol specimens immersed at 30 ℃ and 50 ℃, unloaded.

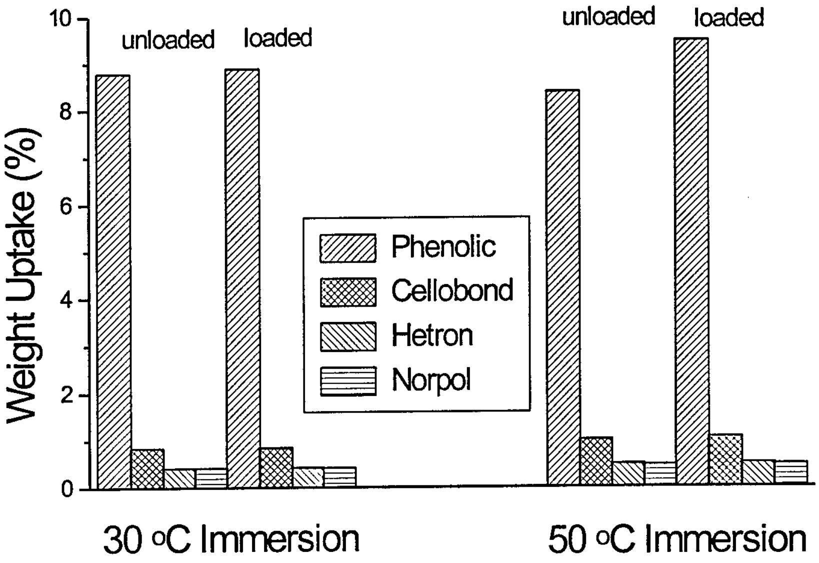


Figure 7: Estimated saturation uptakes M∞ (weight uptake %) at 30 °C and 50 °C for unloaded and loaded phenolic, Cellobond, Hetron and Norpol specimens.

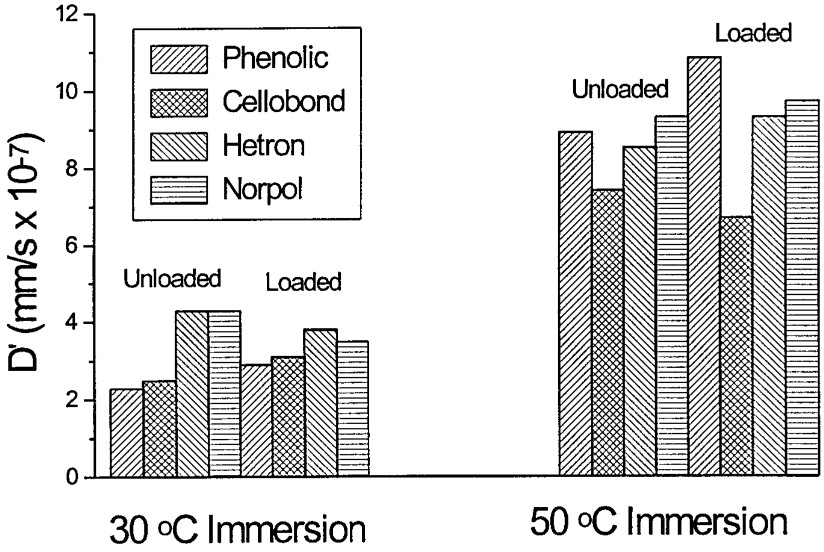


Figure 8: Apparent diffusion coefficients D^1 (mm/s x 10^{-7}) at 30 °C and 50 °C for unloaded and loaded phenolic, Cellobond, Hetron and Norpol.

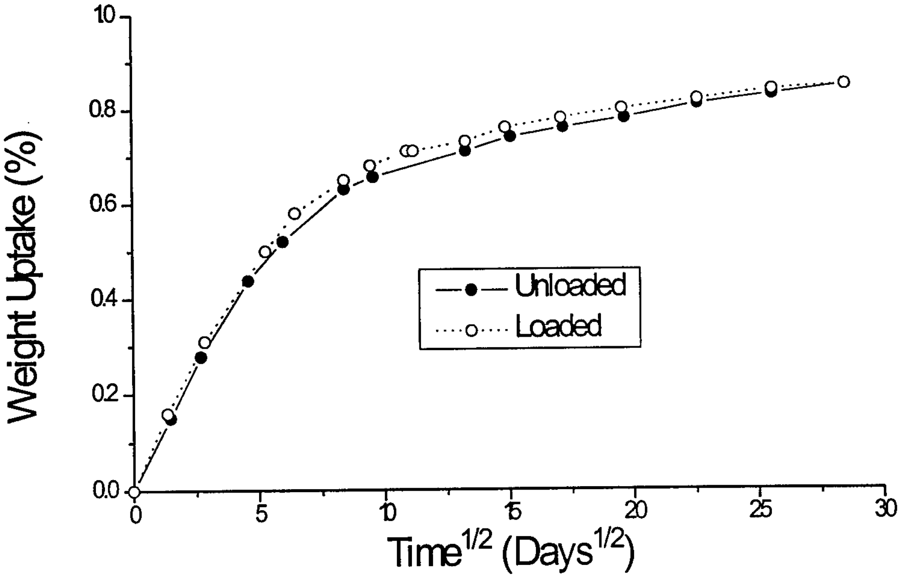


Figure 9: Water uptake in Cellobond specimens immersed at 30 °C, unloaded and loaded.

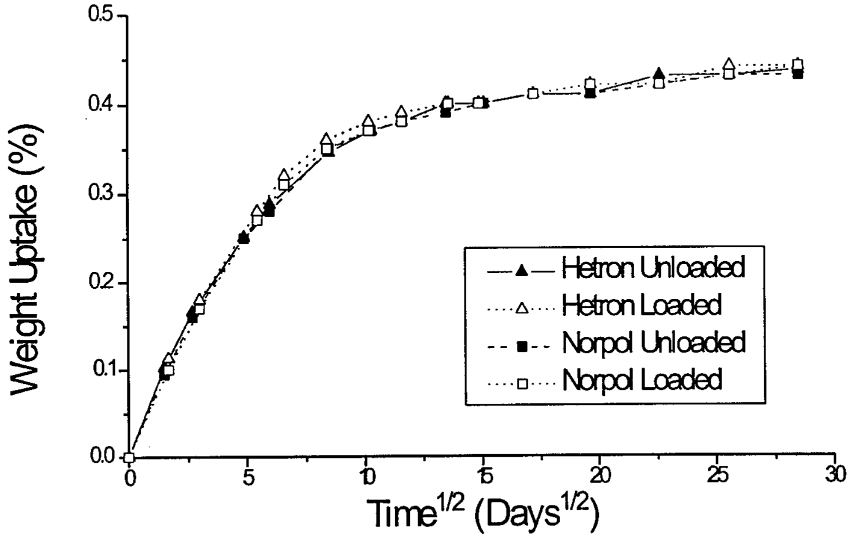


Figure 10: Water uptake in Hetron and Norpol specimens immersed at 30 °C, unloaded and loaded.

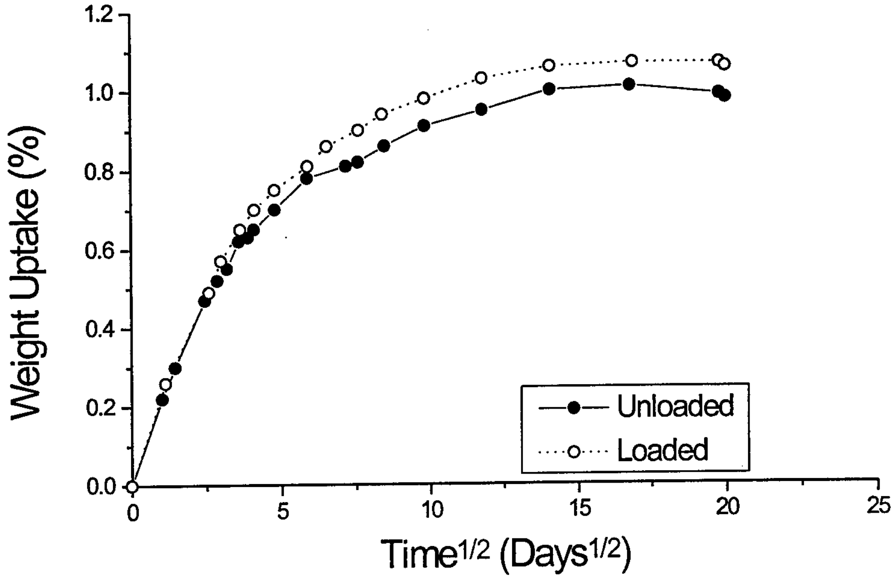


Figure 11: Water uptake in Cellobond specimens immersed at 50 ℃, unloaded and loaded.

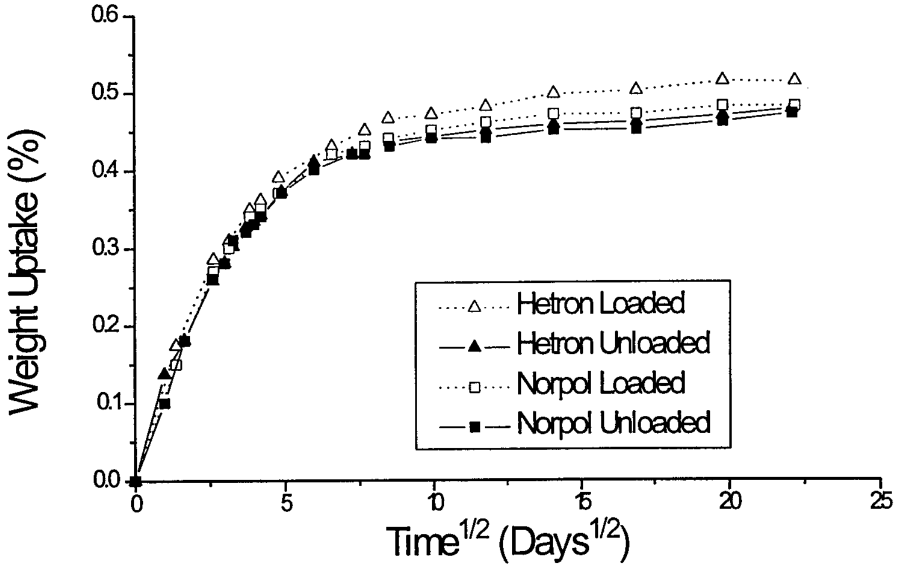


Figure 12: Water uptake in Hetron and Norpol specimens immersed at 50 ℃, unloaded and loaded.

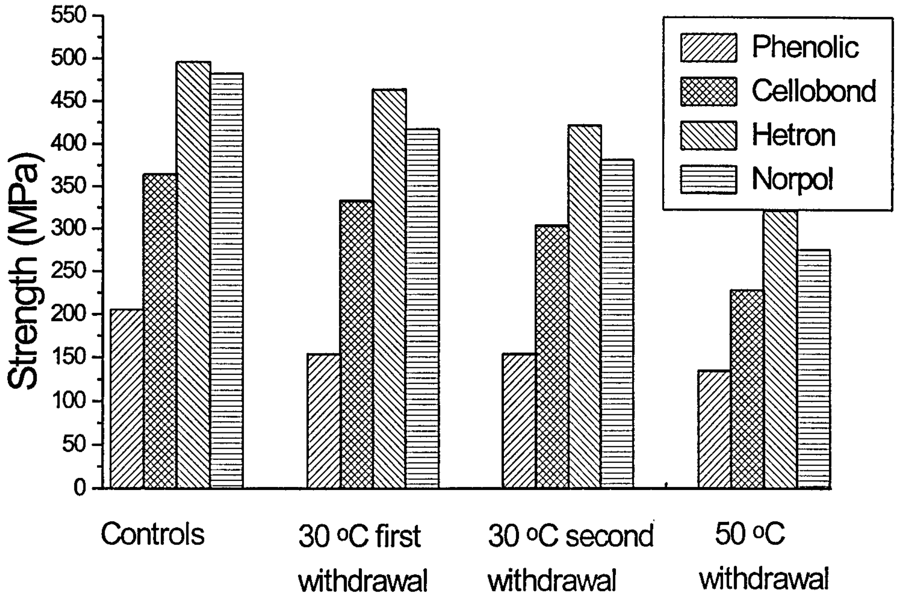


Figure 13: Flexural strength for unimmersed controls, 30 °C immersed specimens at 2 withdrawals and 50 °C immersed specimens.

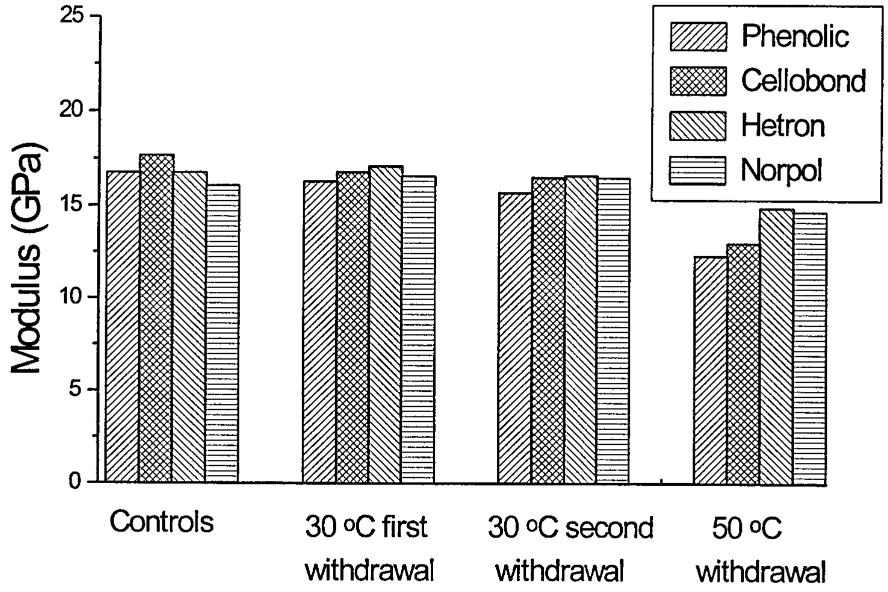


Figure 14: Flexural modulus for unimmersed controls, unloaded 30 °C immersed specimens at 2 withdrawals and 50 °C immersed specimens.

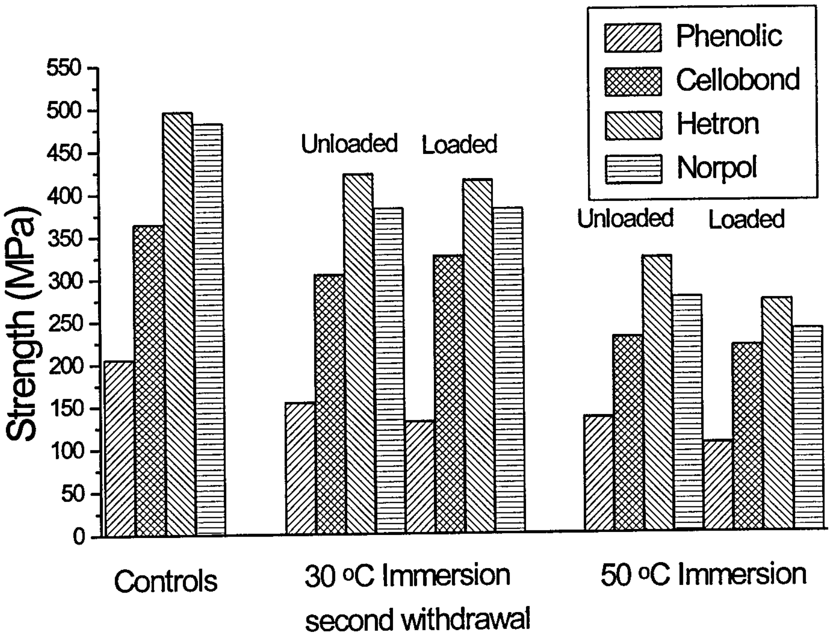


Figure 15: Flexural strength for control specimens, 30 °C specimens immersed for 800 days and 50 °C specimens immersed for 400/490 days.

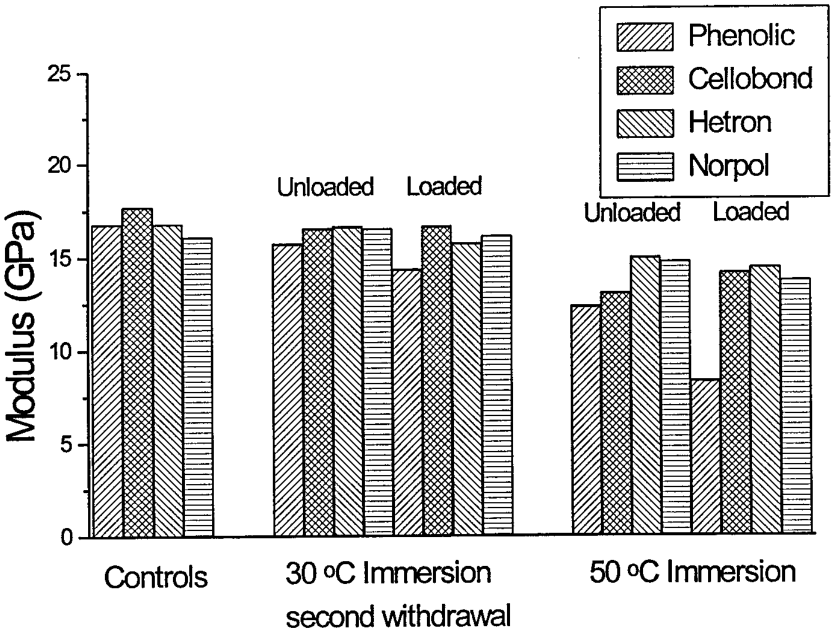


Figure 16: Flexural modulus for control specimens, 30 °C specimens immersed for 800 days and 50 °C specimens immersed for 400/490 days.

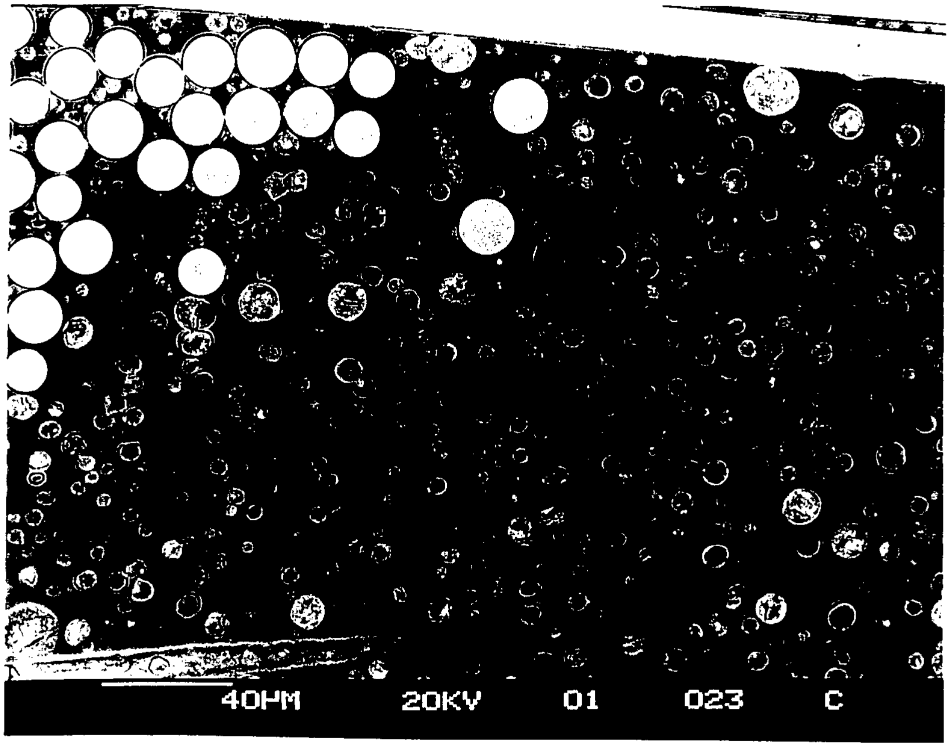
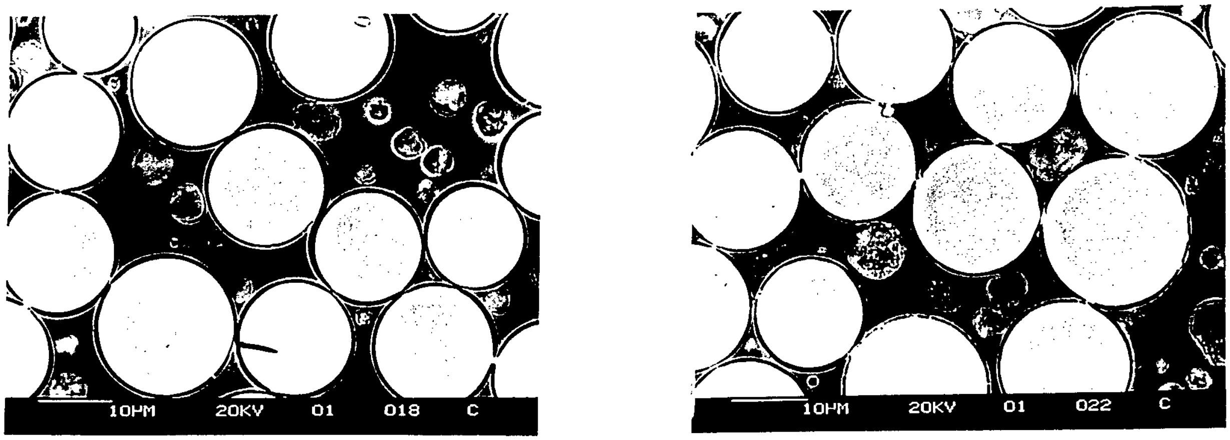
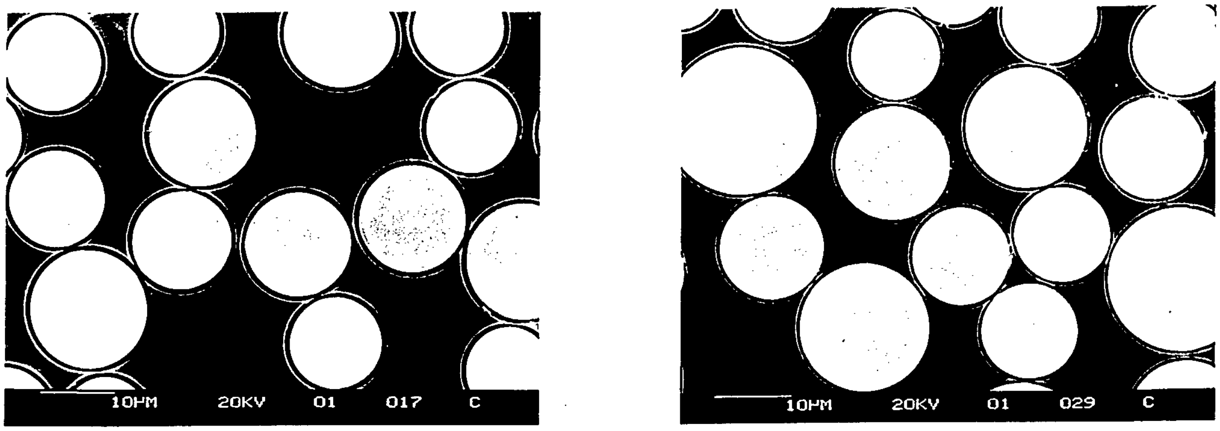


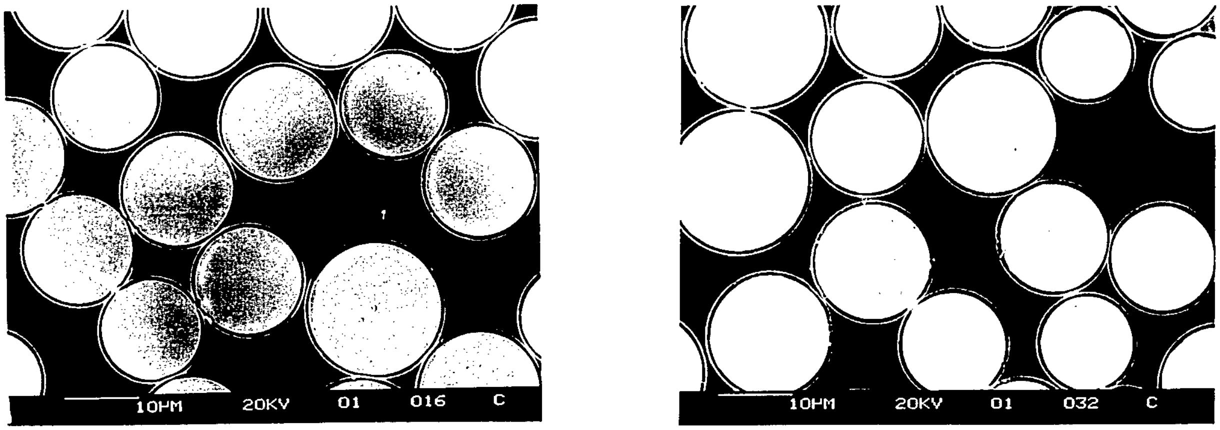
Figure 17: Scanning electron micrograph of a polished section of phenolic GRP showing the microporosity in the resin matrix. The micropores generally have a smaller section than the ~15 µm glass fibres seen above.



phenolic



Cellobond



30 °C *Norpol* *50 °C*

Figure 18: Scanning electron micrographs of polished sections of GRP withdrawn after immersion at 30 °C or 50 °C for phenolic, Cellobond polyester and Norpol vinylester.

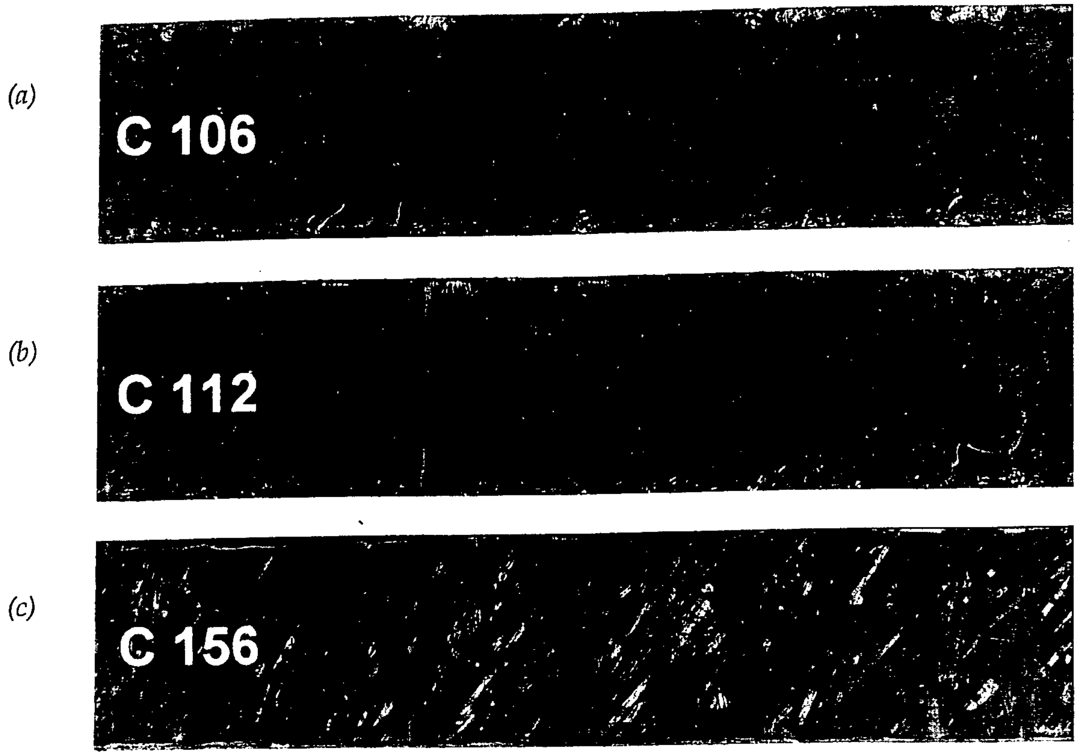


Figure 19: GRP beams of Cellobond polyester GRP after immersion at (a) 30 °C for 140 days, (b) 30 °C for 810 days (near saturation) and (c) 50 °C for 400 days (near saturation), illustrating the visual prominence of glass fibres from the higher temperature ageing.

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Immersed in Seawater

E.P. Gellert and D.M. Turley

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19. ABSTRACT

Glass fibre reinforced plastic (GRP) materials for marine applications undergo losses to mechanical properties during ageing. This study examined a polyester, a phenolic and two vinylester GRP materials. Specimens were immersed in seawater, unloaded or loaded at a high service temperature of 30°C, or at 50°C as an accelerated ageing condition. Water uptake was monitored. After ageing to near saturation the losses in flexural strength ranged from 15 to 25% for the unloaded specimens. Loading in flexure at 20% of the strain to fail while ageing did not significantly affect the water uptake or losses to mechanical properties. Greater losses in mechanical properties from the 50°C immersion were accompanied by indications of abnormal degradation. The accelerated ageing condition therefore appears unsuitable for the assessment of these materials.

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