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Cement & Concrete Composites 27 (2005) 875–884

Cement & Concrete Composites

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Durability and simulated ageing of new matrix glass fibre reinforced concrete

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Received 7 December 2004; accepted 4 April 2005
Available online 8 June 2005

Abstract

This paper applies a model of glass fibre reinforced concrete (grc) degradation, based on the glass technology principle of static fatigue, to a large body of diverse data, some collected from both industry and open literature and some generated by the authors. Activation energies for the strength loss process in OPC and modified matrix grcs are derived and it is shown that the modified matrix grcs degrade by a different mechanism to OPC grc. In consequence, using traditional acceleration factors to predict the long term behaviour of modified matrix grc can lead to severe over-estimation of durability. It is also concluded that hot water ageing is not suitable for polymer modified grc and that ageing at temperatures over 65 °C may lead to the activation of strength loss processes not encountered during natural weathering in some matrices.

Keywords: Ageing; Durability; grc; Service life

1. Introduction

Early formulations of glass fibre reinforced cement (grc) made from ordinary Portland cement (OPC) and first generation alkali resistant (AR) glass fibres are known to lose some of their strength over time in damp environments [1]. This strength loss may be allowed for during design if it can be characterised. Therefore, it has been necessary to develop some means of accelerating normal ageing and hence the ability to predict the long term strength of grc. An empirically derived durability model [2,3] was developed by Proctor and co-workers from studies of the grc in production at the time, i.e. OPC reinforced by first generation AR fibres, which proposed a correlation between hot water accelerated ageing and natural weathering. This model was presented in terms of acceleration factors, e.g. that 1 day in water at 50 °C is equivalent to ~100 days of weathering in UK climatic conditions.

A growing understanding of the mechanisms of degradation combined with accelerated ageing has enabled the development of fibre/matrix combinations with improved durability. The long term ageing characteristics of these new materials can be different from those of the materials used to formulate the Proctor model owing to changes in matrix chemistry and hydration. Thus, the model should not automatically be assumed to be applicable to these new formulation grcs. Nonetheless, Proctor's acceleration factors are used explicitly (e.g. [4–7]) and implicitly (in that hot water ageing is used) [8,9] by researchers and practitioners to validate the improved durability of new formulations. By applying the old model to new formulation grcs, one might over- (or under) estimate the improvements in strength retention afforded by the new formulations with potentially serious consequences. A new model has been developed [10] which is based on a proposed mechanism responsible for the degradation observed in the material over

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doi:10.1016/j.cemconcomp.2005.04.002

time and can be adapted for use with each matrix/fibre combination. Since the first publication of the new model much more accelerated ageing and natural weathering data has become available for the new matrix formulation grcs. It is the purpose of this paper to fit the new model to this data and compare the results of predicting long term durability for the new matrix formulation grcs using the traditional and new models. Included are the results of testing over 1100 aged grc samples including OPC I and II—i.e. OPC matrices reinforced by first and second generation fibres—and grcs with metakaolin, polymers and sulfo-aluminates. Approximately 44% of the data results from reviewing the literature, 28% has been supplied by industry and the remaining 28% generated by the authors.

1.1. The static fatigue model

Debate continues concerning the exact mechanisms responsible for time-dependent property change in grc (e.g. [11]). The fibre strand used to reinforce grc composites consists of a bundle, normally of about 200 individual filaments, loosely bonded together by a coating or 'size'. Initially, the cement matrix does not penetrate this bundle and some empty space remains between the filaments within the strand and at the interface between strand and matrix. It is known that a microstructural characteristic of grc ageing is densification within the fibre bundle and at the fibre/cement interface, caused by the precipitation and growth of cement hydration products, particularly $Ca(OH)_2$ crystals [1,11–18]. This densification is responsible for the observed increase in the interfacial bond strength between the fibres within the bundle and at the fibre/matrix interface [19,20]. It is argued that densification has two detrimental effects. First, as the interface hardens, cracks in the matrix encountering the fibre will be less likely to divert around it via the weak interface and will thus continue into the fibre [21]. Secondly, a dense, less compliant interface causes the radius of curvature through which a fibre bridging a crack must bend to be reduced, inducing higher stresses and thus an increased chance of failure [12]. It has been observed [1,22] that far fewer $Ca(OH)_2$ crystals precipitate in fibre bundles in non-Portland grc. Sulfo-aluminate modified cements produce little, if any $Ca(OH)_2$ on hydration. Fibre pushout tests and microstructural studies have shown that densification within the fibre bundle does not occur with ageing in metakaolin modified grcs [19,22]. Both these composites have improved durability compared to traditional OPC grcs according to accelerated ageing tests, however strength loss still occurs [19,23,24].

In damp conditions the environment inside OPC grc is highly alkaline due to the soluble alkalis contained in Portland cement. The Si–O–Si structural network of the glass is attacked by the OH^- ions in the pore solution. Alkali resistant [AR] glasses contain ZrO_2 making it less vulnerable to attack. Studies have shown [25,26] that as the Zr–O bonds are less reactive than the Si–O bonds, a zirconia rich layer builds up on the surface of the glass fibre effectively slowing down the rate of corrosion. The rate of deterioration of the fibres is likely to be dependent on the alkalinity of the matrix [i.e. the availability of OH^- ions]. Investigations into the pore solution chemistry of grc matrices [27] have found that some new matrix formulations are initially less alkaline compared to OPC and these grcs demonstrated enhanced durability compared to OPC grc.

It is generally agreed that strength loss in AR fibres as a result of exposure to alkali environments does not correlate with weight loss or observed loss of section in the fibres; similarly, the surfaces of fibres extracted from degraded grc rarely show sufficient surface damage to account for the loss in composite strength (e.g. [16–18,23,28]). Thus fibre corrosion is frequently dismissed as an important degradation mechanism. In fact it is well known that the strength of glass fibres is critically dependent on the size and population density of surface flaws, introduced by handling and manufacturing processes. In his classical work Griffith [29] developed a relationship between the free energy of body containing flaws under stress and flaw size. He reasoned that there exists a stress level above which there is sufficient energy for crack propagation to occur and the flaw will lengthen until the energy falls back to the equilibrium condition. These flaws are sub-microscopic; for example, the theoretical depth of flaw introduced during strand manufacture, required to reduce the virgin filament strength to the industrial strand strength (3.5 and 1.7 GPa respectively, according to [1] and manufacturers data) is of the order of 100 nm [23]. The resolvable dimension in the microscope (i.e. the flaw width as opposed to depth) might be an order of magnitude smaller given the shape of a crack-like flaw.

These flaws may grow with time, causing a stress corrosion effect referred to as "static fatigue" in the glass technology literature. Static fatigue (so defined as strength loss or failure occurs without any cyclic load being applied see e.g. [30]) is a delayed fracture phenomenon observed in glasses characterised by the following factors:

- 'spontaneous' failure can occur when glass is subjected to stress less than its bulk failure stress;
- at the same stress, samples tested at higher temperatures fail in shorter times;
- the process is dependent on the presence of moisture and pH.

Charles and Hillig [31] postulated that stress corrosion might enhance the effect of stress raisers and cause the time, temperature and atmosphere dependence of strength. The basic assumption is that the energy necessary for the corrosion of a surface is a function of the stress on the surface and the radius of curvature of the surface. When there is no applied stress, the corrosion rate is uniform over the entire 'internal' surface of a flaw, causing it to become blunter i.e. the radius of curvature at the tip of the flaw becomes larger. The growth rate of the flaw thus decreases rapidly to zero. In the case of a significant applied stress, the corrosion rate is enhanced at the tip of the flaw owing to the stress concentration there; the flaw thus grows and becomes sharper, further enhancing the stress concentration and so on. There exists some intermediate stress, known as the static fatigue limit, where the tendency for flaw blunting is exactly matched by that for flaw sharpening. At stresses below the static fatigue limit, fracture is not observed. Above the static fatigue limit, flaw growth progresses continuously with time. The results of Ritter et al. [32], showing decreased strength with decreasing rate of loading, are a direct consequence of this fact. It is thought that in an alkaline environment (i.e. cement pastes where pH $\sim$ 13.0–13.5 [23]) there is no fatigue limit below which flaw sharpening will not occur [33, Gehrke et al. cited in 34]. This suggests that even very small stresses, e.g. those caused by dead loads, shrinkage or mismatch in thermal coefficient of expansion between fibres and matrix, have the potential to activate flaw growth.

Effects of temperature can also be accounted for as stress corrosion involves a thermally activated chemical reaction taking place preferentially at the crack tip. The Arrhenius equation (e.g. [2]) relates the reaction rate of corrosion to temperature [35].

$$k = k_0 \exp\left(\frac{\Delta G}{RT}\right) \tag{1}$$

where k is the reaction rate, ΔG is the activation energy required for the reaction to take place, k_0 is the "frequency factor" of collisions between the reactants (which is related mainly to the concentration of the reactants but also to the probability of molecules reacting when they meet), T is temperature in Kelvin and R is the universal gas constant. Deriving the activation energy for the corrosion process allows the reaction rate of corrosion at high, accelerated ageing temperatures to be correlated with the corrosion rate at lower natural weathering temperatures. It has been argued that this is a dangerous assumption [36] because at high temperatures there may be enough free energy to overcome the activation energy of reactions that do not occur at lower temperatures because of their high activation energy barrier. Therefore, ideally the reaction that alters the strength of the glass should be isolated and the activation energy of this reaction used to correlate high temperature reaction rates with natural weathering rates. Unfortunately, due to the complex nature of glass corrosion in cement matrices, the exact form of this reaction is not fully understood. Glass fibre strength changes studied by means of the SIC test [3,37] in which a short length of glass fibre reinforcement strand is embedded in a block of cement have shown that one activation energy was applicable over the whole temperature range. This indicates that one reaction mechanism is responsible for the strength loss and supports the validity of extrapolating long term behaviour at low temperatures from data obtained from short hot water tests. Analysis of the rate of strength loss in grc composites [2] indicated that the activation energy of glass strand strength changes also applied to composite strength changes over the temperature range of interest.

It has been shown [10] that the strength loss with time observed in ageing of grc may be modelled using the relationship:

$$S = \frac{1}{\sqrt{1 + kt}} \tag{2}$$

where S is the normalised strength, defined as the strength at time t divided by the original unaged strength, t is the time and k is the reaction rate of the corrosion responsible for strength loss. This allows data sets from different composites and test methods to be compared. Values of k are assumed to be unique to each combination of matrix and ageing temperature; k is assumed to vary with temperature as Eq. (1).

2. Materials and methods

The author's own data results from testing three main matrix formulations—ordinary Portland cement (OPC

Table 1
Mix designs of grc hand spray mixes

	Cement, kg[a]	Sand, kg	Polymer, kg	Water, kg	Plasticizer, g	Fibre, %
O II	25	25		8	125	4.5–5
P II	25	25	2.5	6.75	125	4.5–5
N II	30.3[b]	25		9.25	125	4.5–5
M II	25[c]	25				

[a] Total cementitious materials.

[b] Nashrin formulation: Blue circle Mastercrete 12 kgs, blast furnace slag 12 kg (w/w SiO_2 32.4%, Al_2O_3 12.9%, CaO 42.3%, MgO 6.5%, SO_3 2.0%), NSR sulfo-aluminate additive 6 kg (w/w Al_2O_3 19.6%, CaO 39.0%, SO_3 34.7%, R_2O 0.15%) (manufacturer's data), set controlling agent Sette D-400 0.6 kg.

[c] M matrix: 20 kg OPC, 5 kg Cemstar meta-kaolin (w/w SiO_2 55.3, Al_2O_3 41.3, Na_2O 0.1%, K_2O 2.5%) (authors' data).

Table 2
Sources of data sets used in modelling

Matrix	Fibre	Ageing condition	Reference
OPC	I	UK weather	[1]
			[44]
		Arizona weather	[44]
		Toronto weather	[44]
		Cloncurry weather	[44]
		Inisfail weather	[44]
		20 °C	[1]
		35 °C	[1]
		50 °C	[1]
		60 °C	[1]
		80 °C	[1]
OPC	II	UK weather	[1]
			[45]
		Arizona weather	[46]
		Toronto weather	[45]
		Cloncurry weather	[45]
		Inisfail weather	[45]
		Saitama weather	NEG
		20 °C	FTI IP
		38 °C	own
			own
		50 °C	[1]
			own
			[3]
		60 °C	FTI IP
			[47]
		65 °C	[23]
		70 °C	own
		80 °C	own
MK	II	UK weather	GG
		Florida weather	[48]
		38 °C	own
		50 °C	[24]
			[49]
			own
		65 °C	[23]
		70 °C	own
		80 °C	own
Polymer	II	38 °C	own
		50 °C	own
			[24]
			[49]
		60 °C	FTI IP
		80 °C	own
Nashrin	II	38 °C	own
		50 °C	own
		60 °C	FTI IP
		65 °C	[23]
		80 °C	own

Key: own: Data generated by the authors not previously published. NEG: Data supplied by Nippon Electric Glass Co. Ltd. Export Sales Office, 1-14 Miyahara 4-Chome, Yodogawa-Ku, Osaka, 532-0003, Japan. Commercial in confidence. FTI IP: Data supplied by I. Peter at Fibre Technologies International, Avonmouth Way, Avonmouth, Bristol, BS11 9YA, UK. Commercial in confidence. GG: Data supplied by G. Gilbert at CEMCOTEC Ltd., 13 Yewdale, Shevington, Wigan WN6 8DE Commercial in confidence.

II), cement with the addition of 5% polymer (Poly II), and a proprietary cement with sulfo-aluminate based additives [trade name Nashrin] (Nash II). A limited test program was carried out using a matrix with cement plus 20% w/w/ metakaolin (MK II). All three matrices were reinforced by short, randomly orientated AR glass fibres second generation AR glass fibres were used, some supplied by NEG and some by CemFIL; preliminary research indicated that in the context of this research there is no significant difference whichever fibre is used. Details are given in Table 1 and are typical of GRC hand spray mixes used in the UK and France with a 1:1 sand/cement ratio and a low w/c (water/cement) ratio of 0.32. The Nashrin formulation had a w/c ratio of 0.31. The boards were manufactured by the spray-up method where by the chopped fibre and cement slurry were sprayed from separate nozzles onto a mould where they mix as they impinge on the surface. The fibre volume fraction was 4.5–5%. Specimens measuring 5 × 55 × 250 mm were cut from the boards. Six control specimens were tested to provide baseline data for normalisation and the remainder were aged in water at 38, 50, 70 and 80 °C and tested in quadruplicate at appropriate intervals until strength had dropped to approximately 40% of the original strength. The modulus of rupture [MOR] was assessed using 4-point bend testing on a Testometric rig specially designed for grc testing according to BS-EN 1170, with a minor span of 90 mm and a loading rate of 2 mm/min.

A large proportion of the data included in this study has been sourced from the literature and from industry. Data sources for each sample are referenced in Table 2. Much of this data has been supplied by industry sources and is confidential. Where published reports exist, these have been detailed in the reference list. Where data has been supplied directly by industrial researchers in confidence for limited use, this has been acknowledged. The temperatures used to model the natural weathering data are annual mean temperatures adjusted for seasonal variance with respect to thermodynamic equivalence according to the rationale previously described [38]. The model uses normalised strength defined as the strength after ageing divided by the original strength allowing comparisons to be made of strength data from bend testing and tensile testing.

3. Results

Degradation of the composites is reflected in the change in bending stress/strain curves with ageing as shown in Fig. 1. OPC II and Poly II composites become badly degraded after 28 days at 50 °C but Nashrin retains much of its pseudo-ductility [i.e. the area under the load–deflection curve], albeit with reduced strength, after 316 days at the same ageing temperature.

Strength vs. time data for each grc at each ageing temperature were plotted and a least squares approach

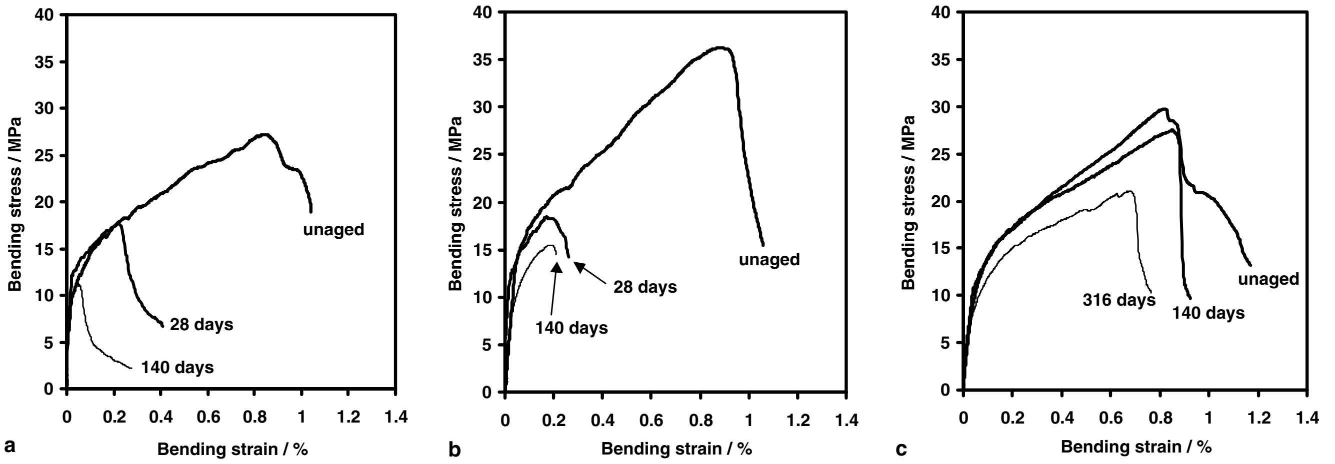

Fig. 1. Evolution of stress–strain curves for OPC II (a), Poly II (b) and Nash II (c) composites aged at 50 °C.

used to fit Eq. (2) to the data to establish values of k (see Eq. (2)). Fig. 2 shows examples of the fit of the curve to some examples from the largest data set, namely that for OPC II grc. Data is included from both from accelerated ageing and natural weathering. Fig. 3 shows some of the data for modified matrix grcs. A range of examples is shown, to illustrate the relative sparseness of some of the data sets. However, these sparse data sets are still valuable as they are the only data available and have thus been included in the study; suitable statistical treatment has been applied such that the impact of each data set on the eventual analysis is appropriate to its nature. The same method was repeated to determine k values for each composite over a range of accelerated ageing and natural weathering temperatures.

Plotting the natural logarithm of experimentally derived k values against the inverse of the ageing temperatures in Kelvin produces an Arrhenius plot (Figs. 4–7) from which an activation energy ΔG for the strength loss process can be determined from the slope of the least-squares fit line (see Eq. (1)). The pre-exponential term k_0 was obtained from the intersect of the trend line with the y-axis. Both factors are shown on the graphs along with the correlation coefficients of the best-fit lines. Fig. 4 (OPC II) also shows, for comparison, the best-fit line calculated for composites made with obsolete first generation fibres, showing that the activation energy is very similar for both grcs and increases in durability are evidenced in changes to the pre-exponential term. Note that in Fig. 6 (MK II composites) the data is statistically best represented by two lines, indicating that above about 60–65 °C a strength loss process is activated which is not significant at lower temperatures, placing a limit on the degree to which ageing can be accelerated for this formulation. The activation energy and pre-exponential term returned are for the lower temperature relationship.

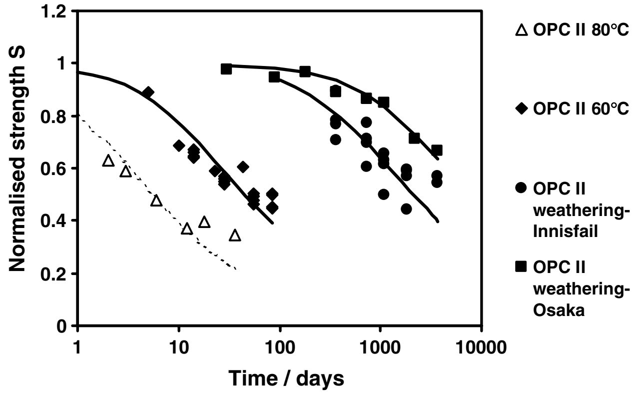

Fig. 2. Typical normalised strength S vs. time data and fitted curves for OPC II composites. Solid symbols/solid lines are data from industry or literature, open symbols/dashed lines are data generated during this study.

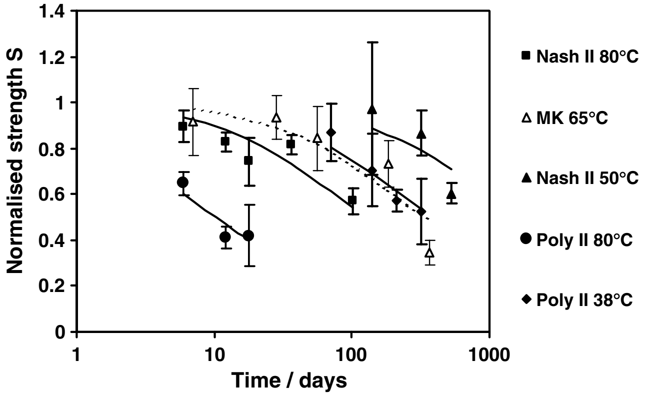

Fig. 3. Typical normalised strength S vs. time data and fitted curves for modified matrix grcs. Closed symbols/solid lines are data generated during this study, open symbols/dashed lines are data generated during previous studies.

The activation energy can be used to express the results in terms of acceleration factors in a similar way to that of Proctor and co-workers [2,3] by using Eq. (3)

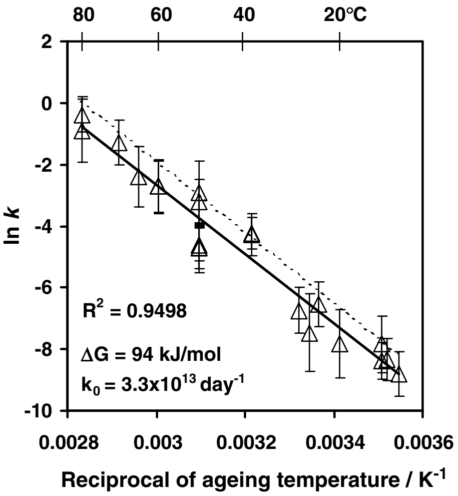

Fig. 4. Arrhenius plot for ageing of OPC grc. Solid line and data points: OPC II composites. Dashed line is best fit for first generation obsolete OPC I composites (data points omitted for clarity, $\Delta G = 97$ kJ/mol, $k_0 = 2.0 \times 10^{14}$ day^{-1}). Error bars = 90% confidence intervals (1.64 SD) in ability of k to predict S.

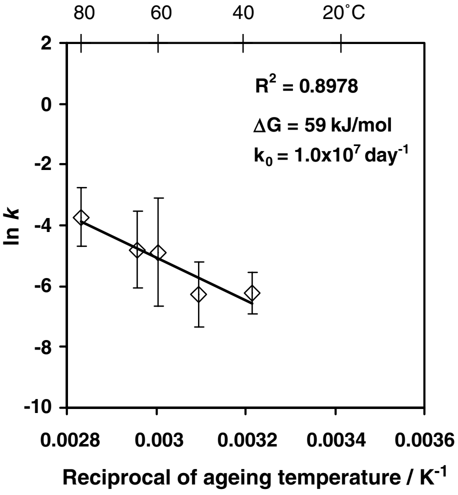

Fig. 5. Arrhenius plot for ageing of Nash II grc. Error bars = 90% confidence intervals (1.64 SD) in ability of k to predict S.

$$A_{(a,b)} = \exp\left(\frac{\Delta G}{R} \cdot \left(\frac{1}{T_a} - \frac{1}{T_b}\right)\right) \tag{3}$$

where $A_{(a,b)}$ is the acceleration factor of high ageing temperature T_b with respect to the lower weathering temperature T_a. Table 3 compares acceleration factors calculated relative to UK weathering (thermodynamic equivalent 11 °C) for various temperature/formulation combinations with those advanced by Proctor and co-workers. According to them, for example, 1 day at 50 °C is equivalent to 101 days of exposure in a UK climatic environment; according to the findings of this study, the actual degree of acceleration varies depending on the matrix type, from 120 for OPC II grc to 18 for MK II type grcs. The potential for overestimation of durability of new matrix formulations if Proctor and co-workers' acceleration factors are applied thereto (e.g. [4–6]) is obvious. This can be further illustrating by directly comparing the durability of the matrices using 'half-lives' i.e. predicting the time $t_{0.5}$ taken for the strength of a given composite to become half its original value (Table 4) by substituting $S = 0.5$ into Eq. (2):

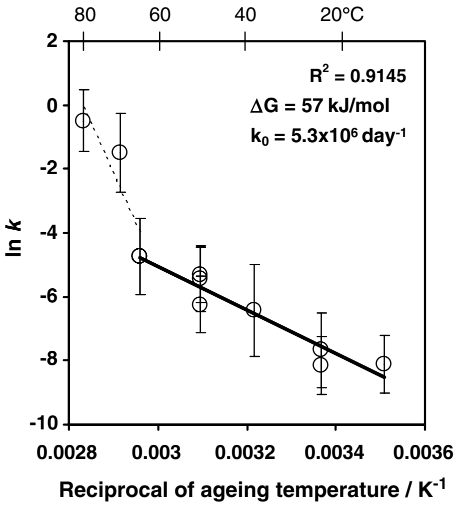

Fig. 6. Arrhenius plot for ageing of MK II grc. Error bars = 90% confidence intervals (1.64 SD) in ability of k to predict S. Numbers quoted are for solid line.

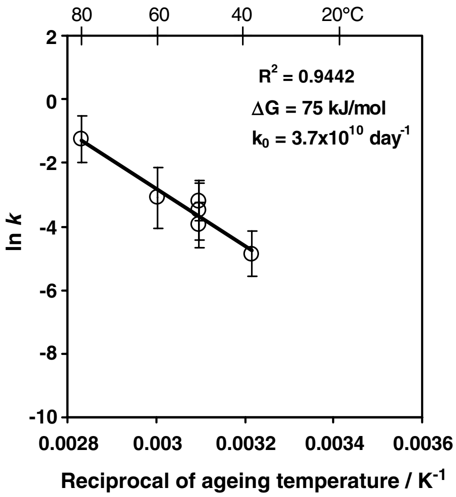

Fig. 7. Arrhenius plot for ageing of Poly II grc. Error bars = 90% confidence intervals (1.64 SD) in ability of k to predict S.

$$t_{0.5} = \frac{3}{k} \tag{4}$$

It can be seen that the non-OPC matrix grcs are between about 1.2 and 2 times as durable as OPC matrix grc depending on the service temperature. Yet industrial

Table 3
Acceleration factors relative to UK weathering for hot water ageing of various grcs

Matrix/ageing temperature	38 °C	50 °C	60 °C	70 °C	80 °C
OPC II	31	120	340	920	2300
Nash II	9	20	39	72	130
MK II	8	18	35	n/a[a]	n/a[a]
Poly II[b]	*16*	*47*	*108*	*240*	*500*
Proctor et al. (OPC)	n/a[c]	101	272	693	506

[a] Ageing at >~65 °C inappropriate owing to break in Arrhenius curve for MK grc.

[b] But see Section 3 last paragraph.

[c] Not given by Proctor et al.

Table 4
Predicted $t_{0.5}$ values (years) for various grc formulations in service at 10–20 °C

Thermodynamic equivalent service temperature, °C[a]	OPC II	MK II	Nash II
10	48	49	55
12	37	42	46
15	24	33	36
20	12	22	23

[a] Typically 1–4° higher than average climatic temperature for North European type environments. See Ref. [38] for details.

researchers validating new matrices for grc have implied e.g. half-lives of well over 100 years [6] or negligible strength loss after 30 years [4]—i.e. order of magnitude improvements in durability—by assuming that the factors derived for OPC matrices can be applied to other formulations. Calculated values of k for each matrix at various service/ageing temperatures are given in Table 4. These can be used in Eq. (2) to predict the strength vs. time curves for these grcs. Note how at low temperatures, k is similar for all matrices, while at higher temperatures there is a large difference between the values for OPC II and the others, emphasising how durability for these newer matrices can be overestimated.

It should be noted that grc will not lose strength indefinitely. Once the composite strength has been reduced to the strength level of the concrete matrix, no further strength loss will occur, since the matrix does not, under normal circumstances, degrade. After this point, the fibres only provide 'post-peak' toughness enhancement (i.e. after the peak stress in a displacement controlled tensile or bending test has been achieved), which is unpredictable and critically dependent on the strain rate applied during testing. If the matrix strength is expressed as a fraction of the unaged composites strength, this can be used as a critical strength S_{crit} in Eq. (2), which can then be solved for t;

$$t = \frac{1}{k}\left(\frac{1}{S_{\text{crit}}^2} - 1\right) \tag{5}$$

Table 5
k values for OPC II, Nash II and MK II grc at various ageing/service temperatures

Temperature, °C	k (OPC II), 10^{-3} day^{-1}	k (Nash II), 10^{-3} day^{-1}	k (MK II), 10^{-3} day^{-1}
10	0.170	0.150	0.166
15	0.340	0.231	0.253
20	0.662	0.351	0.379
25	1.26	0.526	0.561
30	2.35	0.778	0.819
35	4.30	1.14	1.18
40	7.72	1.64	1.69
50	23.5	3.29	3.32
60	67.0	6.35	6.26
70	180	11.8	11.4
80	456	21.1	20.1

to give the mean 'ductile life' of the composite i.e. the time period during which the fibres will have a significant effect on the post-cracking, pre-peak behaviour (i.e. multiple cracking behaviour [39] will be observed). For example, if S_{crit} is assumed to be 0.35, a typical value for good quality grc, then at an equivalent service temperature of 15 °C (see Table 5 for k), the mean ductile life of OPC II, Nash II and MK II composites would be calculated as 58, 85 and 78 years respectively.

Note that $t_{0.5}$ values etc. have not been advanced for Poly II grc. The values for ΔG^* and k_0 given in Fig. 7 would suggest $t_{0.5} \approx 14$ years at 12 °C. Data from the industrial partners involved in this study combined with that published in the open literature (in particular the recent detailed long term study by Ball [40]) suggests that in fact no such severe degradation takes place during natural weathering. This would appear to confirm that hot water ageing is inappropriate for polymer-modified matrix grc, presumably owing to the over-rapid dissolution of the polymer at elevated temperatures, and the acceleration factors given for Poly II in Table 3 are thus of limited use.

4. Discussion

The activation energy of OPC composites made with first generation AR glass fibre (OPC I) and OPC II composites is very similar, 97 cf. 94 kJ/mol respectively (Fig. 4). This suggests that the same basic strength loss mechanism is at work in both composites and that the increased durability of the second generation composite can be attributed to the difference in the pre-exponential term k_0 (2.0×10^{14} cf. 3.3×10^{13} day^{-1} respectively). The pre-exponential term is related to the availability of reactants for the reaction in question. Microstructural evidence [22] shows that the enhanced coating or 'size' on second generation AR glass fibres inhibits the precipitation of $Ca(OH)_2$ at the fibre–matrix interface and within the strand that is prevalent in OPC I [16,18,41].

Thus the durability is directly related to the availability of $Ca(OH)_2$ to the fibres; the reduced (but not eliminated) availability reduces the pre-exponential term k_0 but does not change the basic degradation process (and hence ΔG). Whether the degrading action of $Ca(OH)_2$ is physical, relating to densification of the fibre–matrix/fibre–fibre interface (e.g. [12,22]) or chemical, relating to some physico-chemical reaction between the $Ca(OH)_2$ and the glass, e.g. the aggravation of flaw growth or nucleation of flaws at the fibre surface by $Ca(OH)_2$, is not entirely clear. Evidence that complete interface densification can take place in other composites without loss of properties, and that OPC II grc aged at either 20 °C or 65 °C for 1 year shows a similar level of interfacial/interfilamental $Ca(OH)_2$ deposition (in neither of which is the interfilamental space anywhere near completely filled) but diametrically opposed levels of degradation [22], suggests that the effect is chemical.

The activation energy for MK II and Nash II composites are themselves very similar (57 and 59 kJ/mol respectively), but together different from that of OPC composites. The initial alkalinity of Nash and MK type matrices is somewhat lower than that of OPC ($\sim$200 mmol/l OH^- cf $\sim$ 500 mmol/l OH^- in pore solution [27] – or pH 13.7 cf pH 13.3) but we might expect such a relatively small change to only have an effect on the pre-exponential term (i.e. availability of reactants) rather than change the reaction mechanism. The change in ΔG is also too large to be explained by a change in the stress applied to the fibres by internal mechanisms (shrinkage, mismatch in coefficient of thermal expansion etc.) since considerable proportions of the failure stress need to be applied in order to obtain significant changes in the apparent activation energy of crack growth in silica fibres [42]. In Nash-type sulfo-aluminate modified matrices, $Ca(OH)_2$ is absent from the hydrated phase assemblage [27]. In MK-type matrices, bulk $Ca(OH)_2$ content is decreased [27] and $Ca(OH)_2$ tends to precipitate away from the fibre [22]. Thus it seems that in these grcs, the absence of $Ca(OH)_2$ changes the degradation mechanism.

Activation energies for relevant reactions that might shed light on the nature of the degradation process are not common in the literature. The activation energy for the aqueous stress corrosion of silica glass is variously quoted as between 44 and 89 kJ/mol, with most estimates centred on about 60 kJ/mol (see e.g. sources reviewed in [42]). No literature seems to report the activation energy for stress corrosion of Zr-modified AR glass, but since the corrosion in such glasses almost exclusively concerns the Si network [26], we might assume that a similar activation energy applies. The pozzolanic reaction (i.e. the reaction between $Ca(OH)_2$ and active silica) is believed to have an activation energy of around 80 kJ/mol [43]. Thus the silica breakdown reaction directly involving $Ca(OH)_2$ has a higher activation energy than that involving only aqueous solution. This is consistent with our results and the hypothesis that the degradation of OPC II grc involves chemical reaction between $Ca(OH)_2$ and the glass fibres (rather than simply physical effects caused by densification), while the degradation of the other matrices is controlled by simple aqueous stress corrosion.

5. Conclusions

The mechanism of degradation of grc depends on the matrix formulation. The presence or absence of $Ca(OH)_2$ at the fibre–matrix interface is a key factor. The action of $Ca(OH)_2$ is chemical rather than physical. Matrices modified with e.g. sulfo-aluminates and/or metakaolin, which produce little or no $Ca(OH)_2$ on hydration, have an activation energy for the strength loss process of 57–59 kJ/mol; traditional OPC matrix grc has an activation energy of 94–97 kJ/mol. This difference in activation energy means that using hot water accelerated ageing regimes based on the work of Proctor et al. for OPC grc to predict the durability of new matrix formulations can lead to severe overestimation of durability. New acceleration factors and ageing regimes have been proposed and Proctor's original factors updated. Hot water ageing is not suitable for predicting the long term behaviour of polymer-modified grc. In metakaolin modified grc, ageing at over 65 °C is not appropriate as it appears to activate a strength loss mechanism not significant at service temperatures.

Acknowledgments

This work was made possible by EPSRC Grant GR/R18291. Thanks go to the GRCA, Graham T. Gilbert, Vetrotex Cem-FIL, NEG and Iain Peter.

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