AGING MECHANISMS AND DURABILITY PERFORMANCE OF INORGANIC BONDED FIBER COMPOSITES

ARNON BENTUR

National Building Research Institute, Faculty of Civil and Environmental Engineering, Technion, Israel Institute of Technology

ABSTRACT

The combination of inorganic matrices and fiber reinforcement is a tool box which can offer numerous degrees of freedom for development of composites having a variety of properties which can be tailored for different applications in the construction industry. However, a bottleneck in these developments is the need to assure adequate long term performance in components where the service life required is several decades. Usually, ad-hoc approach is taken to analyze and predict the performance of specific systems which are being considered, both with respect to assessment of the durability performance and the modifications which may enhance service life. The object of the current paper is to provide an overview of the aging processes, their assessment and the modes to modify and control them. This overview can serve as a guide for making the choices in the development and the assessment of inorganic bonded fiber cement composites, to take into account the matrix, the fibers and the mode of production.

INTRODUCTION

Fiber reinforcement has become a versatile technology used in combination with cementitious matrices to tailor a range of fiber-cement composites to meet special needs in civil engineering. Fibers are used as secondary reinforcement in concrete to enhance its crack resistance and ductility and as primary reinforcement to produce thin sheet components, with end uses such as cladding and permanent formwork. Tailoring of such systems has numerous degrees of freedom with respect to the composition of the matrix, the composition of the fibers and the overall geometry of the fiber, ranging from discrete short fibers to textile fabrics [1,2].

The numerous degrees of freedom can enable the development of composites with desired mechanical performances. However, in the design of such composites there is a need to assure adequate long term performance. Long term effects include changes in mechanical properties (strengthening, weakening, embrittlement) and volume changes leading to cracking. The changes in properties and behavior are induced by various chemical and physical interactions, between the reinforcement and the matrix, and these are sensitive to the external environmental conditions. These interactions can be quite complex and in order to be identified by accelerated tests there is a need to choose a test which can trigger these special aging processes. In spite of the complexity of these interactions and the need to assess each system on its own, with regards to the specific fibers and the matrix used, there are several underlying principles which are relevant to all the systems. These common aspects will be highlighted and reviewed in this paper, which can provide a preliminary guideline to assess what kind of long term performance problems may be invoked in a specific system and suggest for it an adequate accelerated test. Some of the concepts were first identified in [1,3].

THE NATURE OF LONG TERM EFFECTS

Long term behavior issues arising from volume changes can be easily predicted and identified when considering the nature of the matrix and the fibers. Matrices rich in cement and fibers which are less volume stable, such as wood chips and cellulose, are more prone to volume stability issues. The magnitude of the volume instability can be easily quantified by short term wetting/drying tests which are quite familiar to engineers and materials technologists. Therefore they will not be further discussed in this paper.

Long term problems can also arise from changes in mechanical properties over time. In terms of performance of a component, the properties of significance are the tensile strength which affects the overall stability, and the toughness (quantified in a variety of ways, such as the area under stress-strain curve in tension or flexure). Toughness can serve as an estimate for the ability of the composite to withstand cracking. The range of behaviors of these properties over time, reflecting different aging mechanisms can be classified into three types, as shown in Figure 1 [1].

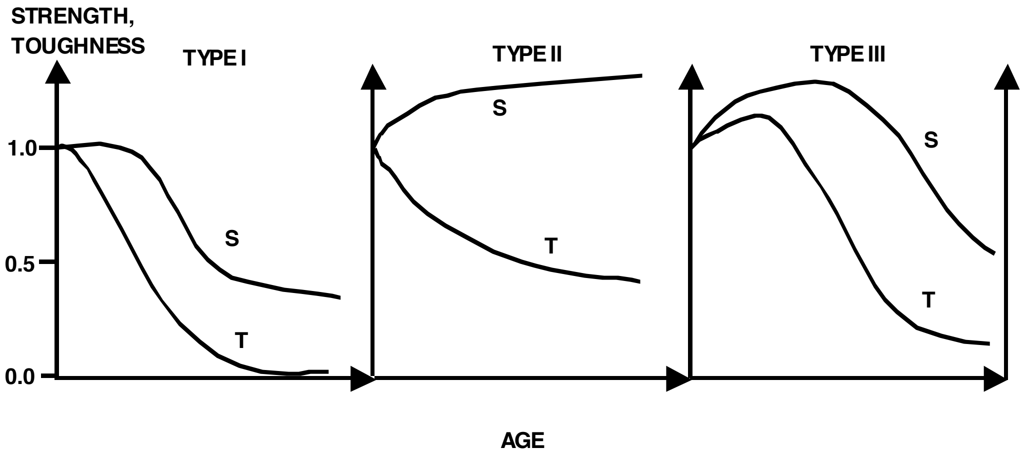


Figure 1: Classification of aging effects in terms of strength (S) and toughness (T) curves over time, after Bentur and Mindess [1].

The processes which can lead to such outcomes can be one of the following, or their combinations:

- Fiber weakening due to chemical attack
- Fiber-matrix physical/mechanical interactions induced by microstructural changes over time
- Fiber microstructural changes induced by interactions with the matrix

These interactions will be discussed in the following sections.

FIBER DEGRADATION AND WEAKENING

The two main mechanisms which may lead to fiber degradation and weakening are associated either with the alkaline nature of the matrix which can lead to breakage of bonds and promote damage in reinforcements as may happen in fibers such as glass and cellulose, or corrosion of steel fibers in systems where the alkalinity is lost and the cover over the fibers is extremely small. When this is the only mechanism to affect the long term properties of the composite, the aging curves will be of type I (Figure 1), showing reduction in both strength and toughness. Extensive studies have been reported on such systems and various strategies have been developed to overcome them [4-14].

Research and practice have indicated that although the cover thickness over steel fibers dispersed in concrete is much smaller than in conventional reinforcing bars, the corrosions of the fibers is significantly smaller than might be predicted based on the concept of corrosion in conventional rebar reinforcement in concrete. Several mechanisms were proposed to account for this phenomenon [6,7,9,10,11]:

- Lower tendency for cracking in fiber reinforced concrete
- The small diameter of the fibers which does not allow for significant amount of rust to form and thus matrix spalling is largely eliminated
- Lack of electrical conductivity in a system with short discrete fibers compared to the continuous and long rebars
- Denser interfacial matrix microstructure around the steel fibers compared to conventional reinforcement.

These of course do not imply that the risk of corrosion is completely eliminated, but in normal exposure it is limited largely to the portions of the fibers protruding from the concrete surface which corrode and fall apart, but the portions left behind are largely undamaged [6,10]; the critical crack width below which corrosion of regular steel fibers does not occur is estimated to be in the range of 0.10 to 0.25mm [6,10]; the critical chloride content threshold is higher in steel fiber reinforced concrete compared to the accepted values in conventionally reinforced concrete [11].

In the case of glass fibers there is considerable evidence for alkaline corrosion due to the breakage of Si-O-Si bonds in the glass triggered by the high pH level. Formation of pits and defects due to this mechanism have been registered clearly in E-glass fibers. Earlier studies have indicated that such effects are largely eliminated when Alkali Resistant (AR) glass fibers are being used [4,12]. Recent studies in conjunction with durability of Textile Reinforced Concrete (TRC) have however indicated that chemical corrosion may take place also in AR glass fibers, showing strength loss of over 50% when such fibers are stored in simulated concrete pore solution [8]. The studies in the references cited above [4,12] were carried out by testing single filaments or bundled ones in simulated pore solution, to eliminate other effects induced by physical interaction with the matrix. The apparent contradictory findings require special attention. It may have to do with the nature of the size. However it should be noted that the study in [8] was carried out with fibers with and without size, and the trends in strength loss were similar. From a practical point of view one should note that even in the studies showing strength decline, the strength loss levelled off, and residual strength of about 40% was retained for very long time periods (throughout the whole testing period). This residual value might be sufficient to maintain considerable portion of the composite properties.

Alkaline attack has also been shown to be an issue in natural untreated fiber reinforcement whereby strength loss has been registered in highly alkaline matrices [5]. This loss is much greater in natural fibers compared to cellulose fibers which are obtained by pulping processes. This superior behavior may be due to the fact that in the latter much of the hemicelluloses and lignin, which are more sensitive to alkaline attack, have been removed in the pulping process.

FIBER-MATRIX PHYSICAL AND MECHANICAL INTERACTIONS

Experience and research has indicated that there are systems which will exhibit changes in properties over time, and these cannot be correlated with degradation of the fibers. In such cases behavior over time of type II and type III curves can be noted. These types of behavior have been shown to occur in systems with a variety of fibers, such as glass, carbon and cellulose [1].

The main cause for this type of behavior is the growth and deposition of hydration products around the fibers leading to densening of the interfacial microstructure. Various mechanisms have been proposed to explain how changes at the interface may affect the overall mechanical performance of the composite:

- Enhancement of fiber-matrix bond
- Development of local flexural stresses in inclined fibers bridging across cracks
- Flaw enlargement and notching leading to weakening of the fibers

Enhancement in bond strength should lead to strengthening of the composite but may be detrimental to its toughness in the case of short fiber reinforced composite: if the bond exceeds a critical value the mode of failure would be fiber fracture rather than fiber pull-out. Relatively high bond values have been reported after aging of bundled glass filaments [15]. This state of affairs is beneficial from the strength point of view, utilizing efficiently the fiber, but is detrimental from the toughness point of view, where the pull-out failure mechanism is able to consume considerable energy and is responsible for the toughness induced in fiber-cement composites. Changes of this type can account for the Type II mode of behavior.

Local flexural stresses are induced in a brittle matrix composite when an inclined fiber is bridging over a crack, and the crack opening upon continued loading is accompanied by geometrical constraints which induce local bending at the point of entry of the bridging fiber into the crack [1,16]. If the fiber is brittle, e.g. glass and carbon, this local bending cannot be relaxed and it results in build-up of local flexural stresses. Several models have been developed to account for this phenomenon and serve as a basis for calculation of the total stresses in the fiber: (i) the tensile stress induced by the load required to bridge the external load on the composite, across the crack, and (ii) the tensile stress induced locally by bending. If the local flexure is sufficiently high, pre-mature failure of the fiber will take place, leading to both strength and toughness decline. This type of effects is larger in systems in which the fiber is brittle and of high modulus of elasticity and the matrix, to start with, is dense.

Flaw enlargement and notching was proposed in recent years as an important mechanism which could account for the aging behavior of glass fiber systems with a variety of matrices, where the differences between their long term performance could not be explained by simple type Arrhenius relations [17-20]. The concept of flaw enlargement is essentially a static fatigue type mechanism of a stress corrosion nature, whereby the corrosion process is accelerated in stressed zones. Several processes can be related with this concept:

- Thermal stresses developed due to mismatch between the thermal coefficients of the fiber and matrix
- Precipitation of CH and its nucleation at pre-existing flaws
- Preferential leaching of components from the glass surface

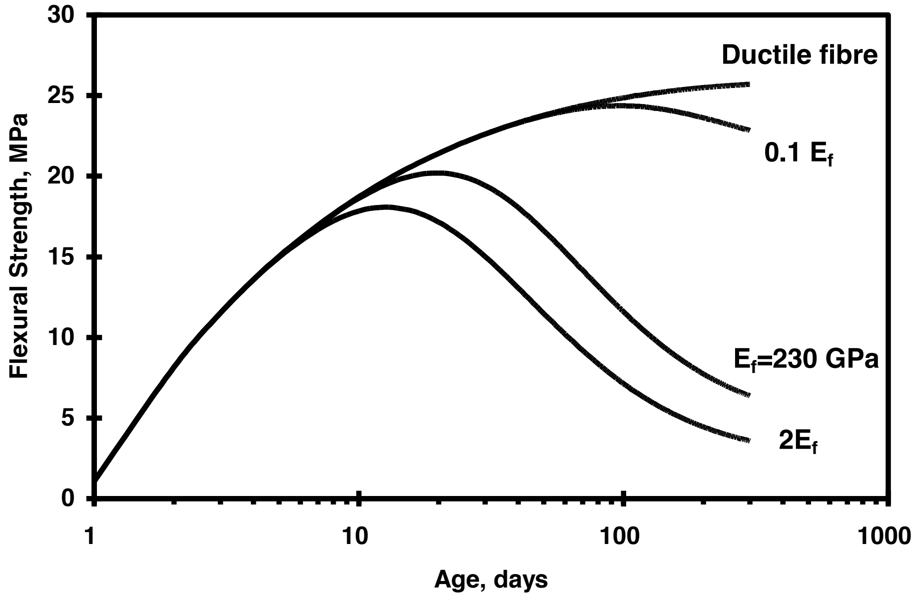
Combined mechanisms: The mechanisms outlined above may act simultaneously or in sequence and therefore it is not easy to resolve between them, especially since the driving forces for all of them bear general similarity: deposition of hydration products, the nature of these products and the pore solution in contact with the fibers. One can envision microstructural changes which at first evoke the bond strengthening effect leading to greater resistance to pullout, resulting in strength and toughness enhancement, while later on resulting in flexural effects or flaw growth, leading to premature fiber failure, resulting in type III behavior. This was for example suggested to be the case in carbon fiber reinforced cement composite, using high modulus PAN type carbon fibers and a dense cementitous matrix [21]. Model calculations based on such combined influences could be used to evaluate the influence of bulk parameters of the fiber and matrix on the long term performance, as shown in Figure 2. Reduction in the modulus of elasticity of the fiber and its diameter are favourable for enhancing durability performance due to their influence on reduction of the bending stresses.

Another type of mixed mode is simultaneous changes in the interfacial microstructure around the fiber and microstructural changes in the fiber itself. This has been reported to occur in cellulose fiber-cement composites under conditions which promote carbonation [22,23]. In such instances the matrix is becoming denser and the fiber is petrified with its inner cavity being filled with hydration products. The final outcome upon aging is increase in strength and embrittlement, type II behavior (Figure 1).

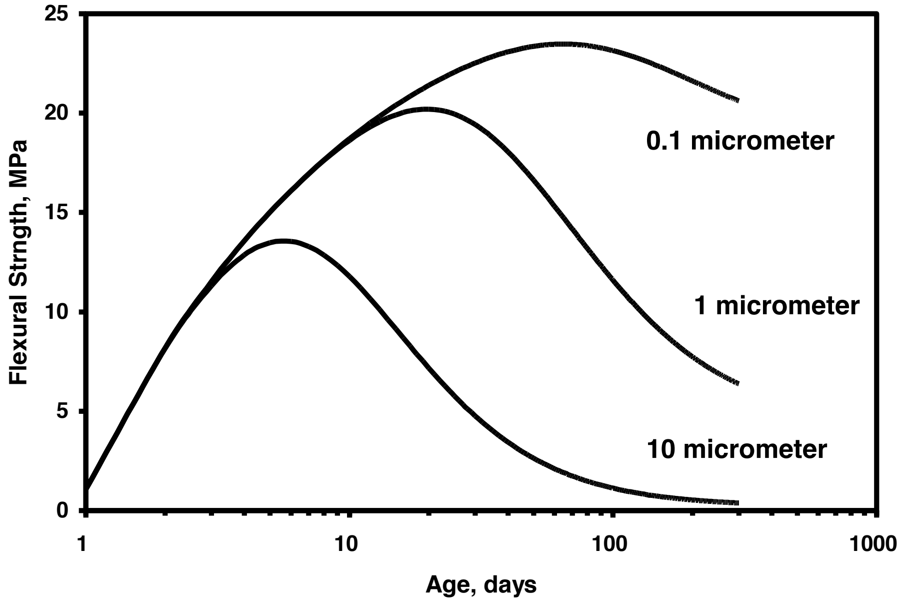
DURABILITY CONTROL BY MEANS OF MICROSTRUCTURAL MODIFICATIONS

Numerous attempts have been made to resolve durability issues by modification of the cementitious matrix, either reducing its pH for fiber systems in which alkali attack is the cause for problems, or microstructural modifications of the matrix where interfacial interactions between the matrix and fibers are leading to durability problems. Partial modifications of Portland cement matrix by use of additives such as fly ash and slag were only partially successful [24-28]. Drastic modifications and improvement in durability performance have been reported when using composite cements rich in additives (> 70% slag and metakaolin), or non-Portland cement matrices [29-32]. However, the use of non-Portland cement matrix has considerable disadvantages because of the limited availability of such matrices which can not be produced economically for special applications where the volume consumption is low.

A different approach can be taken, based on treatment of the fibers themselves to eliminate interfacial detrimental effects, when microstructural changes at the interface are the cause for poor durability performance. In such instances Portland cement matrix can be used combined with small a content of material which is introduced at the interface. Such an approach was used for cellulose fibers, trying to cover the fiber with silanes to avoid degradation of the fiber-cement by water absorption or to increase the interaction among fiber and matrix [33-35], as well as for glass fibers by modifications of the sizing applied on them during the production process [1]. Another approach was demonstrated recently for glass fiber reinforced cement, in which the glass fiber strands were treated with microsilica slurry, and immediately afterwards the impregnated reinforcement was incorporated in a Portland cement matrix. Such a process can be implemented readily in TRC systems. The microsilica particles which are 50 to 200nm size can penetrate readily in between the glass filaments in the strand and prevent thereafter growth of hydration products in between the filaments in the strand, thus preserving the toughness of the system after prolonged aging [36]. The effectiveness of this approach is demonstrated in Figure 3, showing the decline in pull-out energy of a system without such treatment (curve R in Figure 3), compared to preservation of the pull-out energy in systems treated with 50 nm and 200nm microsilica particles (curves SFS and SFL respectively, in Figure 3). The concept of such treatments was developed based on the understanding of the degradation mechanisms as discussed in section 4.



(a)



(b)

Figure 2: Modelling the influences of the modulus of elasticity of the fiber (a) and its diameter (b) on the changes of fiber-cement composites over time at a constant fiber content, due to continued hydration which leads to the densening of the interfacial microstructure (after Katz and Bentur [21]).

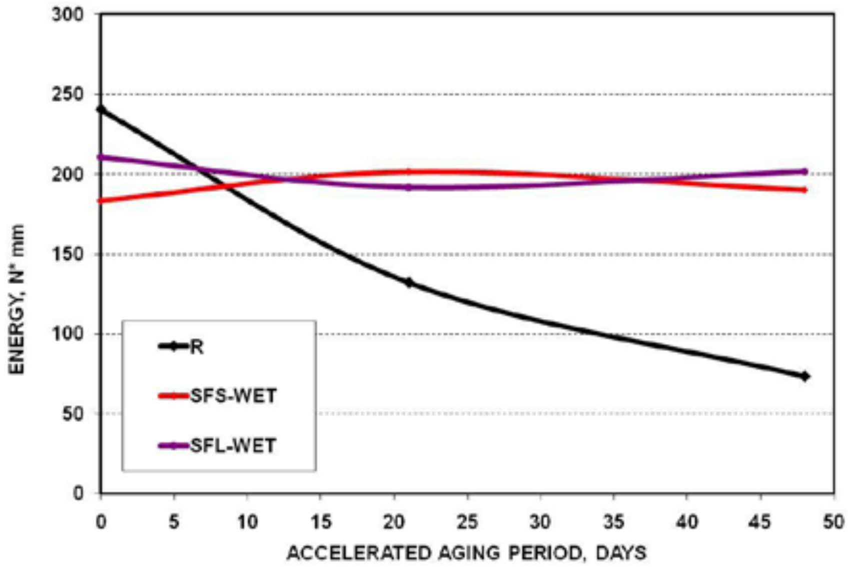


Figure 3: The pull-out energy after prolonged accelerated aging in AR glass composite systems with Portland cement matrix, with untreated strands (curve R) and strands treated with 50 and 200nm microsilica particles (curves SFS and SFL, respectively). Adapted from [36].

CONCLUSIONS

(i) Fiber-cement composites may undergo long term processes which can lead to marked changes in mechanical properties, strength as well as toughness. These changes may be favorable, leading to enhancement in properties, or detrimental, resulting in decrease in strength and embrittlement.

(ii) The mechanisms for the changes are highly dependent on the composition of the fiber and its geometry, as well as the nature of the matrix and its composition. Thus, the long term performance is highly sensitive to the combination of fiber and matrix and it is also influenced by the production method of the composite. As a result the prediction of the long term performance should be evaluated for each system separately.

(iii) There are several underlying mechanisms controlling long term performance. Based on the composition of the composite one may predict which of them may occur upon aging, and on that ground provide an assessment of the nature of long term performance with respect to changes in strength and toughness. When these mechanisms are identified one may specify an accelerated aging treatment relevant to assess the long term performance as well as suggest measures to eliminate or reduce long term detrimental effects.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the Israel Science Foundation Grant No. 898/06 for supporting this research. Thanks are expressed to Elkem Materials in Norway and Eka Chemicals AB in Sweden for supplying the microsilica and amorphous silica slurry.

REFERENCES

1. A.Bentur and S.Mindess, Fibre Reinforced Cementitious Composites, 2nd edition, Taylor and Francis, London and New York, 2007.
2. W. Brameshuber, W., editor, Textile reinforced concrete: State of the art report, RILEM TC 201-TRC, Rilem Publications, 2006.
3. A. Bentur, 'The Role of Interfaces in Controlling the Durability of Fiber Reinforced Cements', *ASCE J. of Materials in Civil Eng.* 12, 2000, 2-7.
4. L. Franke and E. Overback, 'Loss in Strength and Damage to Glass Fibers in Alkaline Solutions and cement Extracts', *Durability Build. Mater.* 5, 1987, 73-79.
5. H.E. Gram, 'Durability Studies of Natural Organic Fibers in Concrete, Mortar or Cement' Paper 7.1 in *Development in Fibre Reinforced cement and Concrete,* RILEM symposium (Sheffield, 1986), R.N. Swamy, R.L. Wagstaffe, and D.R. Oakley editors, RILEM, Cachan Cedex, France, 1986.
6. G.C. Hoff, 'Durability of Fiber Reinforced Concrete in a severe marine Environment', in *Concrete Durability*, ACI SP-100, American Concrete Institute, Detroit, MI, 1987, pp. 997-1026.
7. P.S. Mangat and K. Gurusamy, 'Corrosion resistance of steel fibers in concrete under marine exposure', *Cem. Con. Res.* 18, 1988, 44-54.
8. J. Orlowsky, M. Raupach, H. Cuypers and J. Wastiels, 'Durability modelling of glass fibre reinforcement in cementitious environment', *Materials and Structures* 38, 2005, 155-162.
9. L. Ferrara, R. Fratesi, S. Signorini and F. Sonzogni, 'Durability of steel fibre-reinforced concrete precast elements : experiments and proposal of design recommendations', in M. di Prisco, R. Felicetti and G. A. Plizzari (eds.) *Fibre-Reinforced Concretes, BEFIB 2004*, RILEM Proceedings PRO 39, Bagneux: RILEM Publications, 2004, Vol. 1, pp.565-74.
10. J.-L. Granju and S. U. Baluch, 'Corrosion of steel fibre reinforced concrete from the cracks', *Cement and Concrete Research* 35, 2005, 572-77.
11. P.S. Mangat and K. Gurusamy, 'Corrosion resistance of steel fibers in concrete under marine exposure', *Cem. Con. Res.* 18, 1988, 44-54.
12. L.J. Larner, K. Speakman and A.J. Majumdar, 'Chemical interactions between glass fibres and cement', *J. Non Cryst. Solids* 20, 1976, 43-74.
13. L. Franke and E. Overbeck, 'Loss in strength and damage to glass fibres in alkaline solutions and cement extracts', *Durab. Bldg. Mat.*, 1987, 73-79.
14. V.T. Yilmaz and F.P. Glasser, 'Reaction of alkali-resistant glass fibres with cement: Part 1, Review, assessment and microscopy', *Glass Technology* 32, 1991, 91-98
15. W. Zhu and P.J.M. Bartos, 'Assessment of interfacial microstructure and bond properties in aged GRC using a novel microindentation method', *Cement and Concrete Research* 27, 1997, 1701-1711.
16. M.S. Stucke and A.J. Majumdar, 'Microstructure of glass fibre reinforced cement composites', *J. Mat. Sci.* 11, 1976, 1019-1030.
17. P. Purnell, N.R. Short, C.L. Page and A.J. Majumdar, 'Microstructural observations in new matrix glass fibre reinforced cement', *Cement and Concrete Research* 30, 2000, 1747-1753.
18. P. Purnell, A.J. Buchanan, N.R. Short, C.L. Page and A.R. Majumdra, 'Determination of bond strength in glass fibre reinforced cement using petrography and image analysis', *J. Material Science* 35, 2000, 4653-4659.
19. P. Purnell, N.R. Short and C.L. Page, 'A static fatigue model for the durability of glass fibre reinforced cement', *Journal of Materials Science* 36, 2001, 5385-5390.
20. P. Purnell, N.R. Short, C.L. Page, A.J. Majumdar and P.L. Walton, 'Accelerated ageing characteristics of glass-fibre reinforced cement made with new cementitious matrices, *Composites Part A: Applied science and manufacturing* 30, 1999, 1073-1080.

21. A. Katz, A. Bentur, 'Mechanisms and processes leading to changes in time in properties of GFRC', *Advances in Cement Based Materials* 3, 1996, 1-13
22. A. Bentur and S.A.S. Akers, 'The Microstructure and Ageing of Cellulose Fibre Reinforced Autoclaved Cement Composites', *International Journal of Cement Composites and Lightweight Concretes* 11, 1989, 111-115.
23. B.J. Pirie, F.P. Glasser, C. Schmitt-Henco and S.A.S. Akers, 'Durability studies and characterization of the matrix and fibre-cement interface of asbestos-free fibre-cement products', *Cement and Concrete Composites* 12, 1990, 233-244.
24. S. Leonard and A. Bentur, 'Improvement of the durability of glass fiber reinforced cement using blended cement matrix', *Cem. Concr. Res.* 14, 1984, 717-728.
25. J. Bijen, 'Glass fibre reinforced cement: improvements by polymer addition', in *Advances in Cement-Matrix Composites*, D.M. Roy, A.J. Majumdar, S.P. Shah and J.A. Manson editors, Proc. Materials Research Society Meeting, Materials Research Society, 1980, pp. 239-249.
26. B. Singh and A.J. Majumdar, 'The effect of PFA addition on the properties of GRC', *Int. J. Cem. Comp. & Ltwt. Concr.* 7, 1985, 3-10.
27. S.G. Bergstrom and H.E. Gram, 'Durability of alkali-sensitive fibres in concrete', *Int. J. Cem. Comp. & Ltwt. Concr.* 6, 1984, 75-80.
28. A. Peled, J. Jones and S.P. Shah, 'Effect of matrix modification on durability of glass fiber reinforced cement composite', Materials and Structures 38, 2005, 163-171.
29. M. Tanaka and L. Uchida, 'Durability of GFRC with calcium silicate -$C_4A_3\overline{S} - C\overline{S}$ -Slag type low alkaline cement', in Proceedings - Durability of Glass Fiber Reinforced Concrete Symposium, S. Diamond (editor), Prestressed Concrete Institute, Chicago, 1985, pp. 305-314.
30. A. Bentur, K. Kovler and I. Odler, 'Durability of some glass fiber reinforced cementitious composites', in *5th International Conference on Structural Failure, Durability and Retrofitting*, K.C.G.Ong, J.M.Lau and P.Paramasivam editors, Singapore, 1997, pp. 190-199
31. B. Singh and A.J. Majumdar, 'GRC made from supersulphated cement: 10 year results', *Composites* 18, 1987, 329-333.
32. J. Pera and J. Ambroise, 'New applications of calcium sulfoaluminate cement', *Cement and Concrete Research* 34, 2004, 671-676.
33. X. Lin, M.R. Silsbee and D.M. Roy, 'Improvements in the durability of cellulose reinforced cementitious composites', in: K.L. Scrivener, J.F. Young (Eds.), 'Mechanisms of Chemical Degradation of Cement-Based Systems', E & FN Spon, London, 1997, pp. 106– 113.
34. K. Bilba, M.-A. Arsene, M.-A., 2008. 'Silane treatment of bagasse fiber for reinforcement of cementitious composites', *Composites, Part A: Applied Science and Manufacturing* 39A(9), 2008, 1488-1495.
35. G. Telysheva, T. Dizhbite, A. Arshanitsa, J. Hrols and J. Kjaviav, 'Modification of the properties of pulp fibers for their application in the production of composite materials', *Cell. Chem. Technol*. 33 (5–6), 1999, 423–435.
36. A. Bentur, Z. Cohen, A. Peled, P. Larianovsky, R. Tirosh, R., M. Puterman, and M. Yardimci, Controlled telescopic reinforced system for high performance fiber-cement composites, Fibre Reinforced Concrete: Design and Applications, Proc. the 7th RILEM International Symposium (BEFIB 2008), R. Gettu (editor), RILEM PRO 60, France, pp. 243-252, 2008.