PROSPECTS OF NOVEL MACRO-DEFECT-FREE CEMENTS FOR THE NEW MILLENNIUM

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INTRODUCTION

High strength cement-based materials developed recently are being used to explore new applications which have not been possible with traditional cement and concrete technology. High flexural strength has not been a property typical of conventional cements, and thus there is no established position for cement technology in many modern industries. The relatively high cost of these materials has limited their uses in civil and architectural applications, which are very common for cements. Searching for new applications in areas currently dominated by metals, plastics and ceramics is a challenging task for cement scientists and engineers.

Macrodefect-free (MDF) cement is a polymer-cement composite at the micrometer and nanometer levels. In these materials the polymer and cement react synergistically to create a unique microstructure with distinct characteristics. MDF cements were first reported [1,2] by the research group of Birchall at Imperial Chemical Industries plc (ICI, United Kingdom). They are characterized by very high flexural strength and high modulus of elasticity. Kendall and co-workers [1] attributed the high strength of these materials to the elimination of large critical flaws, which reduce the strength of cast hydraulic cement pastes. The name Macro-Defect-Free cements was adopted for the new materials, but alternative names such as MDF materials, organo-cement composites, and high flexural strength cement-polymer composites can be also found in the literature.

Recently Young [3] and Odler [5] have given reviews on the chemical and mechano-chemical aspects of MDF cements. These reviews are updated here by our findings on the future potential of blends of sulfoaluminateferrite belite (SAFB) clinker, Portland cement (OPC), and hydroxy-propylmethyl cellulose (HPMC) or polyphospate glass (poly-P). The incorporation of polymer by grafting polymer chains onto the surface of grains and the concomitant modification of the bulk properties are briefly discussed in terms of the theory of functional polymers.

CURRENT STATUS

Following the initial invention and basic findings of Birchall and co-workers, there are an increasing number of reports that the polymer plays a more active role than simply being a rheological aid. These reports include [3-5]: (i) series of flexural vs. compressive strength values, the ratio of these values being much higher than typical of hydraulic cements; (ii) the composition of cement as well as polymer is crucial for material performance; (iii) removal of polymer reduces the strength by 90 % and, if the porosity created by that removal is filled by subsequent hydration, the strength returns to only one third of the original value of MDF cement; (iv) dramatic loss of strength occurs on prolonged exposure to water. It has been concluded [3] that MDF cements have a microstructure with close packed unreacted cement particles (consequent on a low *w/s* ratio) acting as a filler within the binding matrix. The matrix itself consists of two interpenetrating phases, a cross-linked polymer and a nanocomposite interphase region around the cement particles. Several models for the local atomic-level structures are reviewed in [5], a significant aspect of the models essentially corresponds to grafting of functional polymers to solid surfaces as presented in [6].

The monitoring of the synthetic sequence by a Banbury-type rheometer [7] (which mimics a twin roll mill) suggests that the formation of microstructure in MDF materials is a mechanochemical process, and both chemical reactions and mechanical effects are involved to create a highly filled, cross-linked viscoelastic polymer system. The mechanical effects are postulated to be due to fission of polymer chains during high shear mixing, creating fragments which subsequently react to form cross-links. The chemical effects arise from release of ionic species from the hydrating cement, which participate in controlled cross-linking reactions that do not proceed as rapidly as the mechanical mixing. The time dependence of the increase in the cross-link density results in a characteristic plateau in torque vs. mixing time plot, referred to as the window of processability. Crucial aspects of the microstructure are the binding of the matrix with cement particles (formed due to the mechanochemical process) and the grafting of cross-linked polymer chains to the surface of cement grains.

The control and improvement of the moisture resistance is a strategic target for MDF materials. Moisture enters an MDF material by diffusion through the polymer-containing phase, the residual cement particles hydrate destroying the interphase region and ultimately degrading the original binding matrix [3,5]. The extent of moisture absorption of high aluminium MDF cement test pieces at ambient humidity and on immersion in water has been reported [8-10], with the consequent effects on the performance and phase composition [10]. Since the polymer is the conduit for moisture uptake, resistance should be enhanced by increasing the hydrophobicity of the polymer matrix itself. Studies of the control/improvement of moisture resistance (referred to in [3,5,8,11] and discussed further below) rely on up to two of the following methods: (i) removal of unreacted cement (reduction of the concentration of active clinker); (ii) improved cross-linking by increasing the amount of water soluble polymer in cross linked component; (iii) substitution of the water soluble polymer by a hydrophobic polymer.

A few potential applications of MDF materials have been examined, with a view to meeting specific market needs. Thermal and sound insulators for specific applications, reinforcement for ordinary cement pastes or mortars, and formed body shells for specific applications are promising. The technology utilized in making a cement shell for a solar powered car can be easily applied to form armours also. Loudspeaker cabinets were also considered by Alford and Birchall [4]; generally a material higher in damping (tan δ), Young's modulus and density has good acoustic properties. These applications are by no means a comprehensive list, but illustrate the range of potential uses that exist for high flexural strength polymer-cement composites or, at least, provide guidelines for application-oriented experiments. A comprehensive overview of potential market applications for MDF materials (cf. table 1) has been given by the Maeta Techno-Research Inc. in a market survey of Japanese and European manufacturing industries [11].

MDF CEMENT IN THE SYSTEM OF LOW-ENERGY SAFB CLINKER - - OPC - HPMC - poly-P

Both chemical and materials science approaches have contributed to progress in control and improvement of moisture resistance of MDF cements. Our research is focused on the relationship of local atomic structure (cross-links) to the moisture resistance of MDF cements in systems with SAFB clinker (and blends with OPC) with HPMC and/or poly-P. Details of a model for the local atomic structure, as assigned in our magnetic resonance studies [12-14] and cited by Odler [5], are summarised in figure 1 (below). The cross-linking volume and its bonding to the *AFm* skeleton serve as an example of the grafting of polymer chains to the grain surface through specific bonding interactions

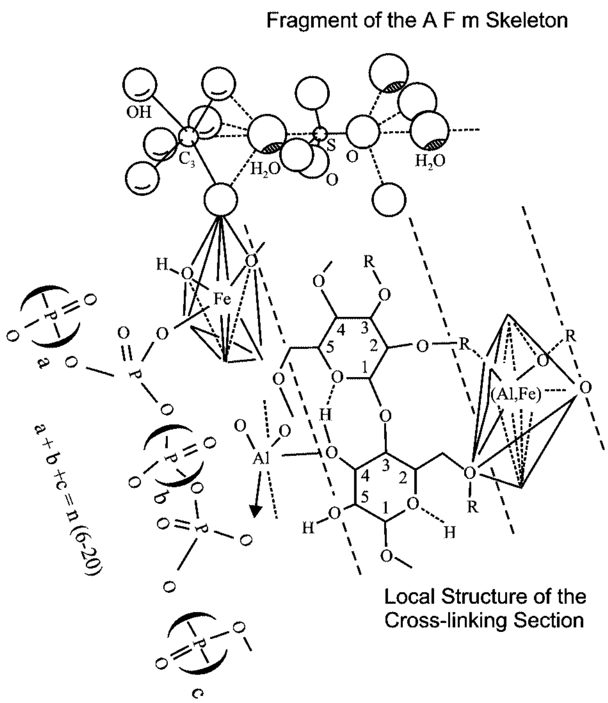

Figure 1. Diagrammatic representation of Al(Fe)-O-C(P) cross-links in the structure of an *AFm*-like skeleton.

Table 1. Information on market needs, adapted from [11].

field	intended applications	required performance
construction	roofing (tiles), permanent formwork, fire resistant doors cover for underfloor cable pits, OA floor, Sewage pipe, airport bridge, monument, electric poles in coastal area, partition panel, door or window shutters	lightweight, durability, fire-proofing, impact resistance, smaller deflection, productivity, possible size, cost, workability, maximum angle sheet folded without damage, nailing
steel, machinery	replacement for angle steel, replacement for steel towers moulds for plastics or leather industry, printing rollers for newspapers, repairing material for moulds, thermal insulators for injection molds, tube, exhaust, handgrips for iron pots	thermal resistance, acoustic damping, incombustibility, insulating properties, high strength, hardness, cost, machineability, ability to apply colours, dimensional accuracy, ability to process by injection moulding
chemical engineering	corrosion - resistant tanks, oil tank	corrosion resistance, setting shrinkage, cost
electrical engineering	cover for cable ducts, globe insulators, propellers in electrical generators, pipe, housing for rotators, electrical parts	lightweight, thermal resistance, dimensional stability, shaping, machineability, ability to apply colours, surface roughness, adhesion
transportation	tyre wheel, yacht, airplane, frame for motorcycle, boat deck, interior panel for train, thermal insulation, stiffening plate for outer shell of cars, brake lining, pallets	thermal and chemical resistance, outdoor stability, acoustic damping, stiffness, dimensional accuracy, shaping, mixing with powders from waste FRP products
miscellaneous	toy, swing, playground slide, model plane, model house, signboard, pipe, fireproof safety box, cooler box, artificial teeth, handicraft material for children	low thermal conductivity, outdoor stability, non-toxicity, cost, smaller in deflection, productivity, strength equal to steel

(functional groups of the polymer participate in the formation of Al and Fe oxycation polyhedra).

The sensitivity of MDF samples to relative humidity (RH) limits the moisture resistance and use of these materials. Thus, a very important task, not only for scientists but also for technologists, is to minimize the negative influence of high RH on MDF materials. The origins of moisture sensitivity are principally discussed by Young, Lewis, Igarashi and Pushpalal [3,8,9,11]. Our studies are aimed at (i) reduction of the concentration of the active clinker component, (ii) increase of the content of water soluble polymer in cross-linked section of the product matrix. To decrease the concentration of reactive clinker, SAFB clinkers are used in which C_2S phase is passive under MDF synthesis conditions. To increase the concentration of polymer, water soluble polymers which do not decompose during MDF processing are tested. We have demonstrated [12-16] the potential of these low-energy clinkers and cements for the MDF process, in particular (a) the involvement of Al, Fe, P, C and O atoms in Al(Fe)-O-C(P) cross-links within amorphous *AFm*-like reaction product/intergranular gel, (b) thermoanalytical characteristics of cross-links, giving the temperature of cross-link decomposition and partial degradation of polymeric phase at 250-450°C and (c) the influence of cross-link chemistry on porosity, electrical impedance and microstructure, as well as on bulk moisture resistance. We have proposed an impregnation effect incorporating Al(Fe)-O-C(P) cross-links [14,15].

The raw materials for MDF cement processing and subsequent moisture treatment were: SAFB clinker blended with OPC (CEM I 42.5) in the mass ratio 85:15, HPMC {corresponding to the viscosity of a 2 % aqueous solution 80-120 cP}, poly-P of formula $(NaPO_3)_n$ (used in solution) and $Na_5P_3O_{10}$ (used as powder). Processing was as follows: (i) initial dry premixing of the cement blends was followed by either (a) addition of HPMC or poly-P powders (5 % of total mass) and water to give w/s = 0.2 or (b) addition of an aqueous solution of poly-P to incorporate 5 % (by mass) of poly-P and to give w/s = 0.2; (ii) twin-rolling until the mixture reached the consistency of dense dough (up to 5 min); (iii) static 5 MPa pressure in a pellet die (10 mm diameter) applied for 30 min ≤ t ≤ 5 h; (iv) chemical reactions were kinetically frozen by air drying. Moisture resistance was tested for cylindrical tablets and for ground powders; both these series were stored in desiccators at controlled relative humidity (RH) values of 52 % and 100 %, and subsequently at ambient laboratory conditions. Mass changes were recorded periodically until constant mass defined equilibrium at the given RH. Data obtained are summarised in figure 2 (*vide infra*); figure 2a shows equilibrium data after storage at RH = 100 %, and figure 2b shows equilibrium data for the same samples subsequently stored under ambient laboratory conditions (and defines the irreversible mass change). TG/DTA studies (TA Instruments SDT 2960) on materials after the moisture resistance tests are compared with data for virgin MDF cements (table 2) in order to highlight the chemical/phase changes occurring during moisture attack. Further methodological details are given in [11-16].

Table 2. Summary of TG mass change intervals (°C) and DTA peak temperatures (°C) for MDF cement samples derived from blends of SAFB clinker and Portland cement.

MDF cement samples				
polymer additive	as synthesized (virgin)		after attack at RH = 100% and storage under ambient conditions	
	TG	DTA	TG	DTA
HPMC	20-250 250-500 * 500-600 (CH)	190 282 *	20-250 250-500 * 500-700 (CH) (Cc)	92, 180 295* 680 (Cc)
poly-P	20-250 250-500 * 500-600 * *(CH)*	181 308 *	20-250 250-500 * 500-720 * *(CH) (Cc)*	76, 180 315 * 667 (Cc)

Thermal events are assigned as follows: * - decomposition of the cross-linked volume of MDF cement; *CH* - decomposition of portlandite, $Ca(OH)_2$; *Cc* - decomposition of $CaCO_3$. Values in the presence of poly-P appear independent of whether $(NaPO_3)_n$ or $Na_5P_3O_{10}$ is used in the synthesis.

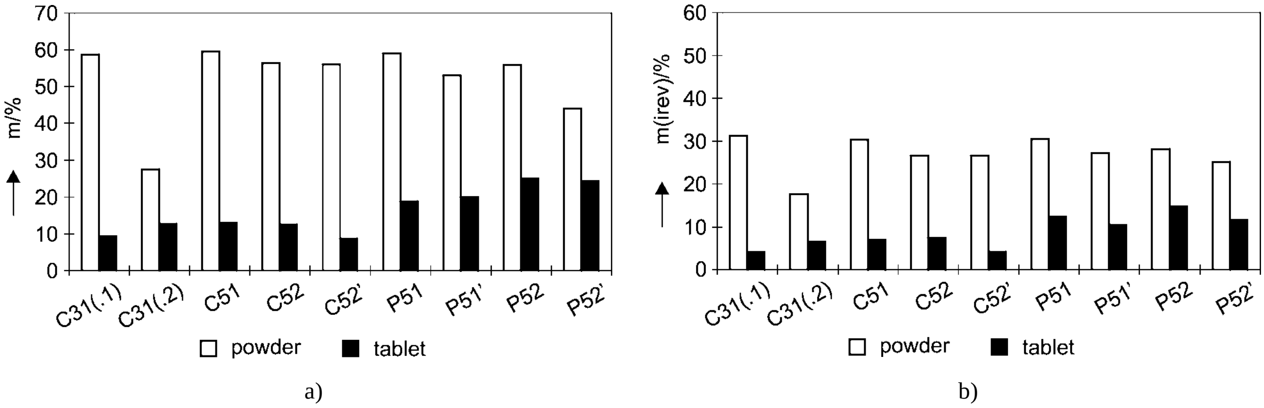

Figure 2. Moisture sensitivity expressed as a) Δm (%) (total mass increase at RH = 100%) and b) Δm_{ir} (irreversible mass change) of individual MDF compositions. Left-hand columns give the values for powders, right-hand columns for tablets of the same composition. Compositions C are specified in the text. Compositions P (pressed without twin-rolling) illustrate the adverse effects of an incomplete synthesis procedure.

TESTS OF MOISTURE RESISTANCE AND THERMAL STABILITY IN THE SYSTEM SAFB CLINKER - - OPC - HPMC - poly-P

The moisture and thermal stabilities of MDF cements were investigated in this system. A considerable volume of information arose from (i) mass changes (totals Δm at a given RH and irreversible components Δm_{ir}, the latter as a measure of moisture resistance, c.f. figure 2) and (ii) thermoanalytical traces of powdered MDF cements showing cross-links and phase changes during moisture attack in air.

MDF materials synthesized with *w/s* = 0.2 and HPMC showed at RH = 100 % a total equilibrium mass increase $\Delta m \approx 13$ %, with the irreversible component $\Delta m_{ir} \approx 6$ % (C51, C52, C52` in figure 2). The samples made with poly-P as the only polymer (C31(.1) and C31(.2) in figure 2) gave equilibrium $\Delta m \approx 5$ % and $\Delta m_{ir} \approx 3$ %. Poly-P appears a better polymer than HPMC for processing in this system, and this result is very important from the point of view of the prospects for MDF technology. Partial reversibility of moisture uptake is similarly reported in [10] for MDF cements based on high aluminium cement sequentially placed in the environments of high/low humidity.

The mass increases for powdered samples at RH = 100 % are very high, achieving the range $\Delta m \approx 39$-75 %. Δm_{ir} values are *ca.* 50 % of the total mass change in every case. Both partial conversion of clinkers during the original MDF syntheses and disruption of cross-links are indirectly responsible for the observed mass increase when powdered samples are compared to tablets. Due to the formation of cross-linked volumes, the unreacted clinker grains are partially prevented from the secondary interactions [14-15] in tablets. This type of surface impregnation is removed by grinding, which consequently enables the completion of conversion due to the secondary hydration and carbonation reactions in moist atmospheres. The materials studied showed significant differences also in equilibration times on exposure to high relative humidity; tablets required treatment in a moist atmosphere for up to 25 days, whereas powders needed ca. 35 days for equilibration.

Comparison of data for tablets and powdered MDF cements show that the level of moisture resistance is determined by the atomic structure of cross-links. Further improvement is achieved by delayed drying of the samples after the original syntheses [20]. When comparing the effects of HPMC and poly-P, our studies show the advantage and potential of poly-P for the MDF cements; the compactness of Al(Fe)-O-P cross-links increases the intrinsic density and impregnates the system against moisture sensitivity. In terms of a functional polymers approach [6], the intensity of grafting of polymer chains to the surface and the impregnation of MDF cement itself increase if poly-P alone is used and with prolonged processing (delayed drying of samples). The phenomenological link between functional polymers and MDF cements is further technologically relevant evidence of the grafting effect of functional polymers bonding to the surface of particles.

The chemical changes after moisture attack are a further important topic [19]. These can be deduced from thermoanalytical traces for "fresh" and moisture-attacked samples (summarised in table 2) by analysis of characteristic decomposition temperatures [12, 16, 17]. After moisture attack phases with $T_{decomp} < 250$°C are present at higher mass percentage, the decomposition of the constant amount of cross-linked material occurs at $250 < T_{decomp} < 500$°C, and a new $CaCO_3$ phase with $500 < T_{decomp} < 750$°C is detected. Considering the details of the local structure of MDF cements based on SAFB clinker [12-15], and the diagram in figure 1, there are two inequivalent volumes with respect to moisture resistance; the more resistant volume has a cross-linked Al(Fe)-O-C(P) skeleton and the second, less resistant, volume is composed of cementitious hydraulic phases (cf. chapters by Odler and Lawrence in Lea's Chemistry of Cement and Concrete, 4th Edn, 1998). Moisture attack also results in the formation of some $CaCO_3$ [16-18].

CONCLUSIONS

Cements and cement-based advanced materials, including MDF cements, have potential for a healthy long-term future with research and development providing better quality products. New niche market products could serve mankind, if industry grasps the benefits available. Universities and research institutes have an important function here in playing an increasing role in fundamental understanding related to technical problems encountered in the field.

Our studies have displayed the advantages and potential of polyphosphate (poly-P) polymers for the MDF cements synthesized from SAFB clinker, and for blends of these with OPC; compact Al(Fe)-O-P cross-links increase the intrinsic density and impregnate the system against the uptake of moisture. A preliminary model of functional polymers is directly relevant, functional groups from the polymer participating in the formation of Al/Fe oxycation polyhedra. The density of this mode of grafting the polymer to the surface of cement grains increases when poly-P is used and with a prolonged processing time.

Fundamental chemical and materials science research is necessary in tackling the long-desired strategic goal for the application of MDF cements i.e control and improvement of moisture resistance. The phenomenological link between functional polymers and MDF cements, especially in the bonding/grafting of polymer chains to grain surfaces and the concomitant modification/improvement in mechanical properties, will ultimately provide control of fabrication and use for MDF cements.

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