

## Contribution of materials chemistry to the knowledge of macro-defect-free (MDF) materials\*

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**Abstract:** The latest studies on the reactivity of inorganic-polymeric networks in selected cement-based materials and the focus toward nano- and atomic levels of grafting of polymers on interfaces represent some of the success stories of materials chemistry. Recent developments are reviewed and discussed, with particular emphasis on macro-defect-free (MDF) materials. Experimental evidence of next-nearest-neighbor (NNN) interactions has led to the definition of the scope and model of Al(Fe)–O–P cross-linking under mechanochemical synthesis conditions, in a system combining the most common (Portland) cement and commercially available polyphosphates. Current approaches to synthesis of MDF materials, together with the atomic-level interpretations of both the formed functional interfaces and the adverse influence of moisture, are discussed.

**Keywords:** macro-defect-free; cross-links; cement; polymers; grafting; moisture resistance.

### INTRODUCTION

Materials chemistry has emerged as a distinct discipline during the last 15 years [1]. In the field of cement chemistry and technology, current advances in cement-based chemically bonded ceramics and composites are making major impacts on materials chemistry, materials science, and associated technologies. Macro-defect-free (MDF) materials also belong to this category. Some polymers may be combined with inorganic cements to yield materials with unique properties. A precondition for such application is sufficient stability of the polymer in a high-pH environment, typical for the most cementitious systems. The most frequent candidates comprise polymethyl methacrylate, polystyrene, polyvinyl alcohol/acetate, hydroxypropyl methyl cellulose, sodium polyphosphate, polyacrylamide, and polypropylene glycol. The topical state-of-the-art has been presented by I. Odler in Chapter 13 of *Special Inorganic Cements* (E & FN Spon, 2000) and also J. F. Young and K. Scrivener at the 12<sup>th</sup> International Congress on the Chemistry of Cement (July 2007, Montreal, Canada).

Odler [2] has summarized three fundamentally different ways in which polymers may be combined with cements:

- The polymer may be employed to fill the pore space of the hardened cement paste, giving rise to polymer-impregnated cementitious materials (PoIC). Prehardened cement paste, mortar, or concrete is impregnated with a polymer precursor, which, after having filled the existing pore space, is brought to polymerization. The resultant material is a hardened cementitious body in which the

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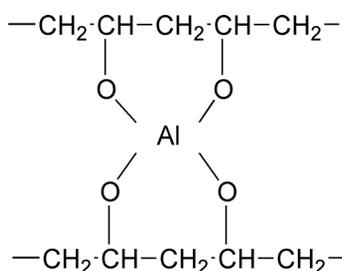
original pores are filled with the polymer. A variety of polymer precursors may be used as impregnating liquids, precursors of polymethyl methacrylate or of polystyrene are those used most commonly.

- A polymeric dispersion may be interblended with the fresh cement paste to yield a combined cementitious-polymeric system, known also as polymer-modified cements and concretes (PoMCs). Upon mixing and subsequent hardening, a three-dimensional polymeric network develops within the material, which is intimately combined with the three-dimensional structure of the hardened cement paste. The initial rate of hydration of the cement may be adversely affected by the presence of polymeric dispersion due to a diffusional barrier around the nonhydrated cement particles [3]. Growth of the cement hydration products restrained by the above mechanism improves a variety of physico-mechanical characteristics of the resulted material, a. o. bonding to old concrete or steel surface, resistance to chemical corrosion and abrasion, high water-tightness [4,5].
- A new material may be created in a chemical interaction between the polymer and the constituents of the inorganic binder if the treatment relies on the high shear twin-roll mixing. This procedure, in addition to eliminating large pores, also helps to induce chemical interactions of polymer and cement [6]. It was also recognized that much of the mechanical strength of these materials is due to the mechanically induced chemical changes [7,8]. Details about the dispute over the correctness of the term “macro-defect-free (MDF)” can be found elsewhere [2,7].

MDF materials have been produced from aluminate cements and polyvinyl alcohol/acetate or phenolic resins in limited amounts so far. A serious drawback of MDF materials is their sensitivity to water, associated with a loss of strength. The loss of strength must be attributed to a swelling and softening of the organic polymer phase constituting the MDF material [2]. The efforts to eliminate or at least reduce the adverse effect of moisture on MDF materials comprise: the use of organosilane or titanate coupling agents, or incorporation of an isocyanate compound to cross-link the polyvinyl alcohol chains through urethane bonding [9], in situ reticulation of the polymer [10], and addition of sodium polyphosphate to the original mix [11]. A variety of possible applications is being considered for these materials [2], including armor (personnel, vehicle, fragmentation protection), loadbearing structural elements (floors, ceilings, partitions), nuclear waste containment, transportation of gases and liquids (pipes, containers), plastics fabrication (tools, compressive molds), brake-lining matrixes (replacement for phenolic resins), and electrical engineering applications.

MDF materials are chemically bonded ceramics, free of the macro-defects typically seen in hydraulic cement-based materials. They are formed through a series of specific chemical steps [2,7,12,13] in which appropriate mixes are composed primarily of cement, a water-soluble polymer and water. In addition to the hydraulic reactions of cement with water, the effects of medium pressure load and polymers modify the present interfaces by bonding/grafting of functional groups associated with polymer chains onto the surfaces of unhydrated cement grains [2,7,12,13]. The hardening and strength development of MDF materials is the result of chemical reactions taking place in the material during processing and curing. These include both an interaction between the inorganic cement and polymer, and cross-linking reactions within the polymer itself [14]. Van der Waals forces may also be involved [10]. It is generally believed that the chemically modified polymer interacts with the cations liberated during the cement hydration. It has been suggested [2,9,15,16] that  $\text{Al}(\text{OH})_4^-$  ions released by the calcium aluminate cement cross-link the polyvinyl alcohol/acetate chains (cf. as outlined in Fig. 1).

In addition to the participation of ionic species in cross-linking reactions, it has also been suggested that additional bonds develop between the  $-\text{OH}$  and/or  $-\text{COOH}$  groups of the polymer and ionic species at the cement grain surface [16–18]. Nonhydrated particles of the cement become constituents of the developed structure, held together by a polymeric-inorganic matrix [19]. The bonding forces formed in this way are quite strong, and thus the failure of MDF material tends to occur within the polymer phase or clinker grains rather than at the interface [7–9,13,17]. Both the introduction of a cross-linked atomic-level structure and the modified particle interfaces conform to the model of functional



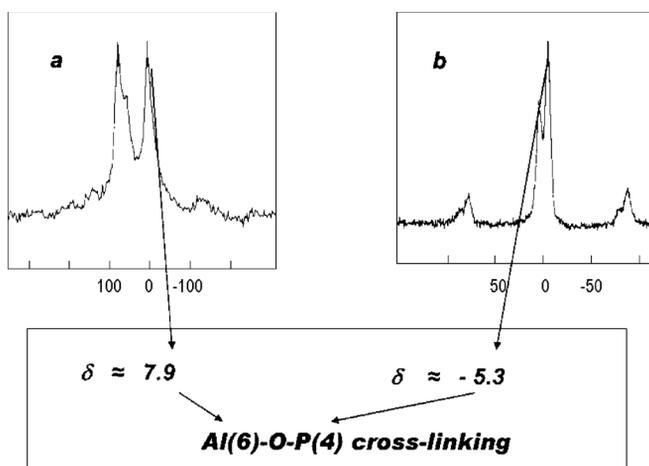
**Fig. 1** Scheme of atomic cross-linking in MDF materials formed from aluminate cement and polyvinyl alcohol/acetate.

polymers [13,20] and comprise a novel atomic-level structure in PoMCs. The cross-linking reactions should involve atoms at the interfaces of a cement-based component with an appropriate polymer [2,13]. MDF formation reactions occur in the presence of water, under medium pressure and with the application of high shear twin-rolling [2,7,12,13]. The goal, and challenge, of chemistry is to describe whether, and how, the above mechanochemistry induces formation of cross-link and affects porosity, microstructure, and moisture resistance (which is generally considered to be the crucial drawback of an MDF material). The more recent knowledge of the atomic-level interactions of the inorganic cement and the specific polymer–sodium polyphosphate, will be discussed in the next chapter.

## CHEMISTRY-DRIVEN RESEARCH AND KNOWLEDGE OF MDF MATERIALS

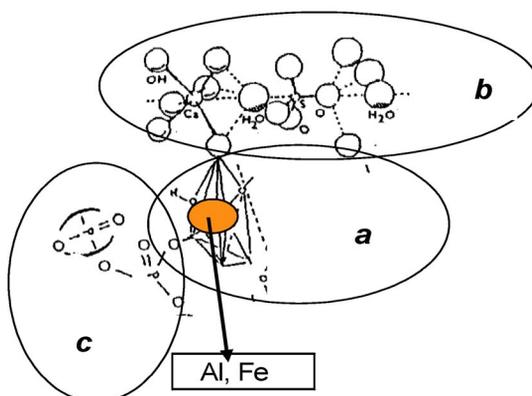
Portland cement, calcium aluminate cement, and sulfoaluminate-ferrite-belite cement have been employed as constituents of an MDF material. In addition to polyvinyl alcohol/acetate and polyacrylamide, some other polymers have also been employed as the organic constituents of MDF materials, including polypropylene glycol [21] and hydroxypropyl-methyl cellulose [11,18]. Efforts have also been made to produce MDF material in which the role of organic polymer is taken over by an inorganic polymer, specifically sodium polyphosphate [11,22,23]. The latest data on both particular cross-linking reactions of inorganic polymer and consequences of the formation of such cross-links are exemplified and underpinned below. The raw materials for the case studies of MDF process and subsequent moisture tests were: Portland cement (CEM I and CEM III types), polyphosphates of formula  $(\text{NaPO}_3)_n$ , and  $\text{Na}_5\text{P}_3\text{O}_{10}$ . The synthesis procedure complied with that presented in Odler's review [2,13,23]. Both the standard methods of materials chemistry for the characterization of test samples [magic-angle spinning (MAS)-NMR and thermal analyses] and a purpose-developed methodology for testing the moisture resistance demonstrate both the progress in mechanochemically induced cross-linking and the extent of moisture attack.

Peak positions in  $^{27}\text{Al}$  and  $^{31}\text{P}$  MAS-NMR ( $\delta \approx 7.9$  and  $-5.3$ , respectively) are characteristic of Al(6) (octahedrally coordinated aluminum) and P(4) (tetrahedrally coordinated phosphorus atoms), both with rather complex second coordination spheres [24–26]. The data confirm Al(6)–O–P(4) cross-linking [2,13,24] as the typical next-nearest-neighbor (NNN) interactions in successfully synthesized MDF specimens in the system Portland cement + polyphosphate. The appearance of a peak at  $\delta \approx 60$ , characteristic of Al(4) tetrahedrally coordinated aluminum atoms [27,28], in the  $^{27}\text{Al}$  spectra indicates the presence of residues of unhydrated clinker phases [2,7,13] after the MDF synthesis. Due to the content of polyphosphate it can be assumed that cross-linking fully protects the polyphosphate chains. The assumption is experimentally verifiable as phosphorus atoms tetrahedrally coordinated alternatively by H and Al atoms as NNN (cf. the  $^{31}\text{P}$  spectrum in Fig. 2).



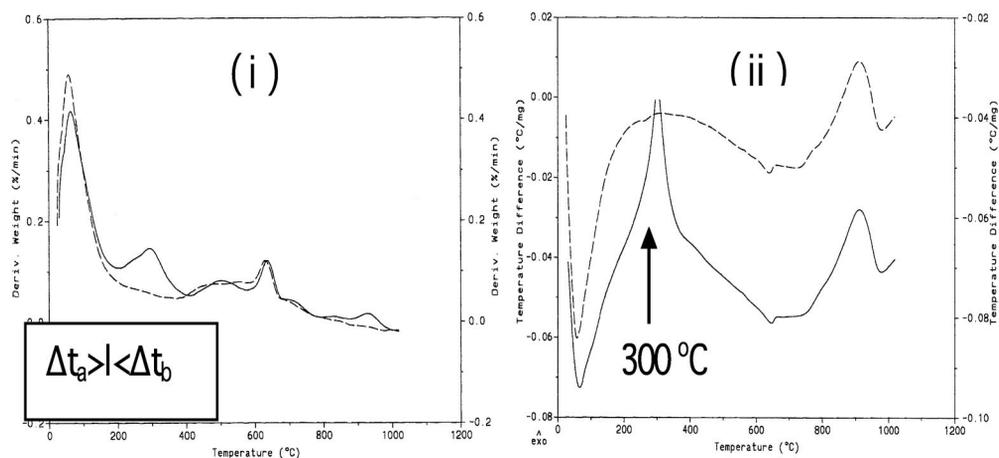
**Fig. 2** Typical  $^{27}\text{Al}$  (a) and  $^{31}\text{P}$  (b) MAS-NMR spectra of MDF probes synthesized in the system Portland cement + polyphosphate. The chemical shifts for Al and P atoms, respectively, illustrate the presence of Al(6)–O–P(4) cross-links.

It is evident from parameters of both  $^{27}\text{Al}$  and  $^{31}\text{P}$  MAS-NMR spectra (cf. Fig. 2, and the above discussion) that the NNN interactions are relevant between Al and P atoms through oxygen atoms. Polyphosphate chains participate in the cross-linking of hydrated phases/components (cf. the “schematic view” in Fig. 3). The knowledge represents a topical piece of evidence that MDF materials in addition to hydraulic reactions exert also nano- (and micro-) scaled modifications of interface due to the mechanochemical treatment of the reagent mixture. Defined cross-links arise from a pressure-induced chemical interactions of available polymeric species and cement grains. Both the cross-linked atomic structure and the modified interface coincide well with the model of functional polymers [20], cf. also Fig. 7, and suggest that nano-aspects crucially contribute to the design of MDF materials representing a new type of atomic-level structure in modified cementitious materials.



**Fig. 3** Schematic view of the cross-links, as proposed from MAS-NMR data and Mössbauer spectroscopy [29,30]; (a) Al, Fe coordination polyhedra, (b) hydrated phase/component, (c) polyphosphate chain.

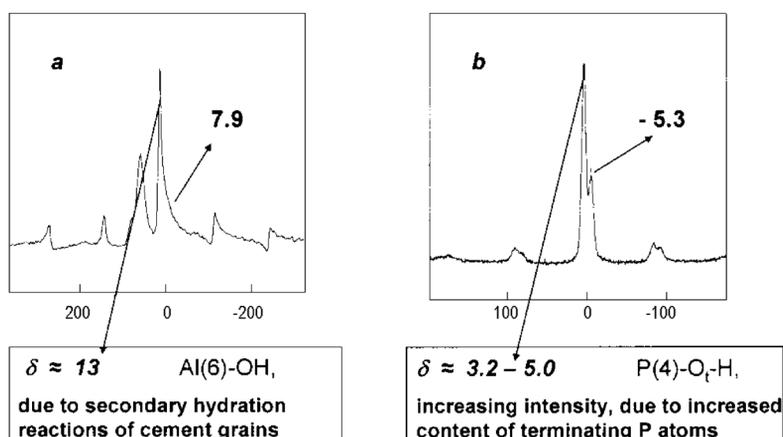
Cross-linked functional interfaces, as well as the *AFm* and *C-A-S-H* phases, and portlandite- $\text{Ca}(\text{OH})_2$ , are present to an extent within MDF specimens. (*AFm* and *C-A-S-H* denote, in the short-hand cement chemistry notation, two crucial “classical” cementitious hydrated compositions—calcium aluminatoferrite monosulfate hydrate and calcium aluminosilicate hydrates, respectively). The relationship  $t_b > t_a$  (cf. Fig. 4, where  $t_b$  stands for the temperature interval of decomposition of the cross-linked functional interface and  $t_a$  stands for the temperature interval of decomposition of *AFm* and *C-A-S-H*) is further evidence for the cross-linking nanostructure playing a key role in stabilizing the MDF product. These data demonstrate the validity and role of the postulated design for local atomic structure in MDF materials [2,7,13], which has now been extended to include the MDF-relevant compositions in the system Portland cement + polyphosphate.



**Fig. 4** Typical DTG (i) and DTA (ii) curves of MDF test probes; full lines—successful synthesis; dashed lines—synthesis not successful.

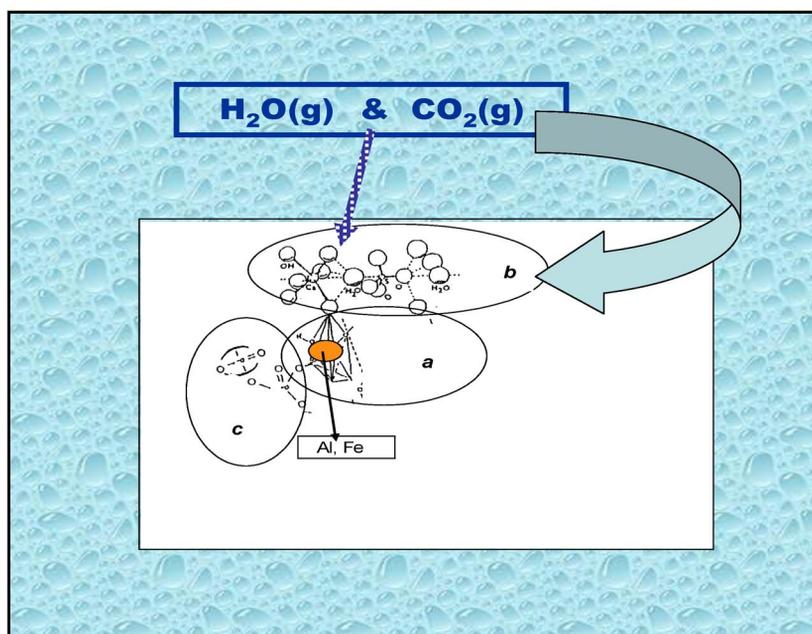
Control and improvement of moisture resistance is a strategic target in MDF materials technology [2,7]. It is generally accepted that moisture enters the MDF material through the system of pores in a polymer-containing interface and approaches the residual unhydrated cement particles [7–9,11,13,17]. In this diffusion process, the only consequence is that the secondary hydrates destroy part of the interphase region, thereby degrading this part of the original interface and the binding matrix. MDF test specimens that have been successfully synthesized in the case studies of the system of Portland cement + polyphosphate have been studied after their exposure to a moist environment. The MAS-NMR and thermal analysis data help to reveal the local atomic-level changes resulting from the moisture attack (Fig. 5).

The appearance of a peak at  $\delta \approx 13$  in  $^{27}\text{Al}$  MAS-NMR spectra {corresponding to  $\text{Al}(6)\text{-OH}$  [27,28]}, as well as the increased intensity of the peak at  $\delta \approx 3\text{--}5$  {corresponding to  $\text{P}(4)\text{-O}_\text{t}\text{H}$  [25,26]} in  $^{31}\text{P}$  spectra, are the common characteristics of spectra for MDF specimens after exposure to moisture (Fig. 5). Both are clear evidence of secondary hydrolysis, which entails the formation of calcium aluminate hydrates and the shortening of the poly-P chains because of the MDF–moisture interaction. The MAS-NMR spectra indicate also the persistence of cross-links after moisture attack and prove that the observed secondary hydrolysis occurs in the domains that are free of cross-links. Indications of mass and phase changes rely on four basic decomposition steps [11,30,31] evident in TGA-DTA curves (cf. also Fig. 4). The thermogravimetric determination of the relative contents of hydrated and cross-linked phases in initial and moisture-affected MDF specimens [30–32] demonstrates that moisture uptake is accompanied only by increasing contents of cementitious calcium aluminosilicate hydrates and  $\text{CaCO}_3$ .



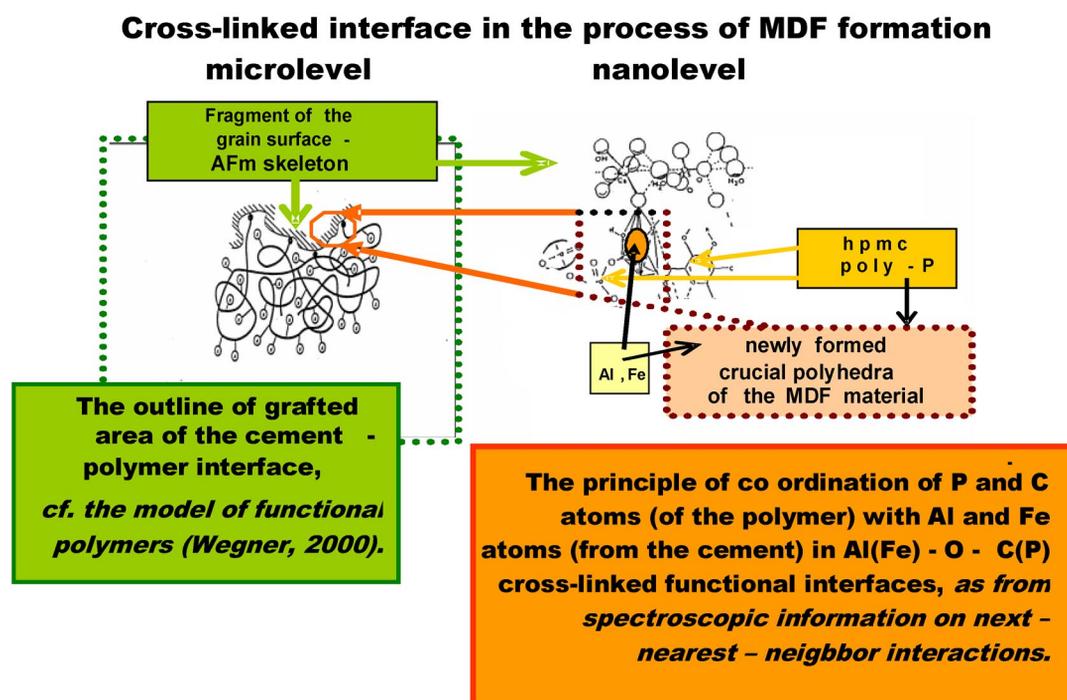
**Fig. 5** Typical  $^{27}\text{Al}$  (a) and  $^{31}\text{P}$  (b) MAS-NMR spectra of MDF probes after the moisture uptake. Chemical shifts  $\delta \approx 13$  and (3.2–5) of Al and P atoms, respectively, arise from secondary interactions of test pieces with the moist environment.

The data of MAS-NMR spectroscopy and thermal analysis are in mutual agreement also with earlier reports [7–9,13,17] regarding both the persistence of cross-links in the moist environment and the availability of the residual cementitious hydrates and cement particles toward secondary reactions with  $\text{H}_2\text{O}$  (g) and  $\text{CO}_2$  (g) from the moist environment (cf. Fig. 6).



**Fig. 6** Attack of atmospheric gases upon the MDF probe, the localization of secondary interactions as from the data of MAS-NMR spectroscopy and thermal analysis.

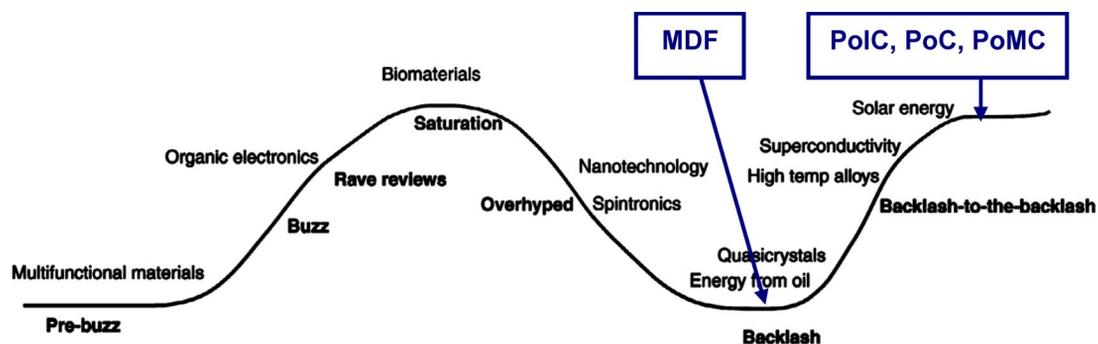
Formation reactions, induced under processing conditions, promote the desired Al(6)–O–P(4) cross-linking interactions. On exposure to moisture, the evidence for Al(6)–OH and P(4)–OH species in secondary hydrates arises although the previously formed cross-linked species do not appear to be degraded. MDF materials are examples of cement-based composites where chemical knowledge is crucial both to (i) the design (pressure-induced Al–O–P cross-linking is the key nanoscale aspect of the formation process), and to (ii) the exploitation (the interface is compacted and stabilized by regions of Al–O–P cross-links, which also enhance the moisture resistance of the material). Specific functionalization of interface and surface occurs due to the mechanochemical treatment. Both the micro- and nanoscopic levels are graphically shown in Figs. 3 and 7 and represent the key features of the processes necessary to form MDF materials [2,13,30–32]. The processes of synthesis, formation of cross-links, and the bulk parameters of MDF pieces are governed by the principles and mechanisms of the theory of functional polymers [20], cf. micro level of the model in Fig. 7. The nanoscopic details of schemes in Figs. 3, 6, and 7 have been constructed in light of the case study; the data on NNN interactions, thermal stabilities of Al(6)–O–P(4) cross-links, and structure of interface zone [24,30–32] represent an original background for those schemes.



**Fig. 7** Cross-linked functional interface in the MDF materials; (right) the nanolevel presentation of interactions [present case study and 30–32]; (left) the microlevel model of grafting derived in [13,30,31] from general Wegner’s model [20].

## A FUTURE OUTLOOK

One of the inspiring assessments of the progress of mankind (in the most general sense) has presented Pearton [33] in “a tide” model and its FLOP (Florida Law of Original Prognostication) curve to indicate positions and forecasts of selected materials research and technology fields. The current advances in polymer-modified concretes and cement-based chemically bonded ceramics and composites indicate the positions of PoIC, PoC, PoMC, and MDF materials in the FLOP curve, cf. Fig. 8.



**Fig. 8** FLOP curve (from Pearton's essay [33], reproduced with kind permission of the author, doi:10.1016/S1369-7021(07)70221-3) and the positions indicated for a selection of polymer-modified concretes and cement-based materials (this paper).

Materials chemistry approaches toward MDF materials, reviewed in this paper, have shown that the performance of these materials is governed, in addition to hydration reactions, by nano-level modifications of the interface due to the pressure-induced cross-linking interactions of unhydrated cement grains with the polymeric species. MDF materials are early examples of a future harness of the cementitious reactions to produce high-performance materials using near-ambient temperatures [34,35]. This strategy has the potential of capturing the attention of not only future generations of cement chemists but also the materials science community [35].

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