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Reinforcement of hydrated portland cement with high molecular mass water-soluble polymers

Richard Morlat · Gilles Orange · Y. Bomal · Pierre Godard

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Abstract A small amount of polymer in water solution form (polyvinylpyrolidone or polyvinylalcohol) was added to a mix high silicate cement + amorphous silica, with reduced water to cement ratio. It was shown that as the molecular mass of the polymer is increased, the fracture stress and the stored energy at fracture of the specimens improved. The polymer induces an increase of the critical stress intensity factor (K_{Ic}) (crack initiation). The fracture behaviour of the polymer modified cement paste beyond the elastic domain is also affected by PVA or PVP additions. The dissipated energy measured using the crack opening displacement CMOD was increased by a factor of two with 4wt% of PVP and by a factor of three with 3wt% of PVA, as a consequence of operative toughening mechanisms. The increase of mechanical properties is explained in case of PVP by crack interactions due to CSH microstructure modifications, and with PVA by crack bridging mechanisms as a consequence of dispersed polymer rich nodules in the hydrates phase.

Introduction

Concretes are heterogeneous materials, made up of aggregates and sand of different grain sizes dispersed in a brittle mineral binder of porous calcium silicate hydrates (CSH). The development of high performance concretes is mainly based on a drastic reduction of the water to cement ratio (w/c) with superplasticizer additions to maintain a good workability, and the improvement of aggregates size and close packing with reactive filler (pozzolanic) [1]. But, whatever is the concrete mix design, the mechanical properties are limited because of the intrinsic brittleness of the hydrated cement phase. The challenge to develop new UHPC concrete is to improve the basic properties of the hydrated cement phase at a micro or nano scale.

Polymer addition in cement-based materials as concrete or mortars is one of the many ways to improve the mechanical properties of these materials: polymer can be used as dispersed soft particles, or as dispersed molecules with CSH hydrates chemical interactions [2–4].

A large class of cement materials which contain polymers is mortars, and in some concrete, the polymer being added as a polymer aqueous dispersions (latex). Compatible styrene butadiene emulsions, acrylate or vinyl acetate emulsions can develop small polymer domains or thin films between sand and cement grains,

R. Morlat (✉) · P. Godard
Université Catholique de Louvain, Unité de Physique et de Chimie des Hauts Polymères, Place Croix du Sud, 1, 1348 Louvain-la-Neuve, Belgium
e-mail: richard.morlat@saint-gobain.com

P. Godard
e-mail: pierre.godard@uclouvain.be

P. Godard
National Fund for Scientific Research (FNRS), Bruxelles, Belgium
e-mail: pierre.godard@uclouvain.be

G. Orange · Y. Bomal
Rhodia Recherche & Développement, 52 rue de la Haie Coq, 93308 Aubervilliers, France

and even at fibre–matrix interfaces [5, 6]. The formation of a polymer network is the proposed mechanism to explain the improvement of properties. The interfacial transition zone is modified and mechanical properties are increased at high polymer content (polymer network) [7, 8].

An other class of cement-based materials modified with water soluble polymer is based mainly on calcium aluminate cement and polyvinyl alcohol, or calcium silicate cement and polyacrylamide (macro-defect free cement MDF) [9, 10]. The polymer content is quite high, with a very low water content, and as a consequence the viscosity is not compatible with the classical processing ways of concrete and mortars: high shear specific processes have to be used to intimately blend the polymer with the cement particles, as calendring. Shaping thin parts is possible by extrusion, injection or pressing. The interactions between polymer, cement grains and hydration products during setting and hardening leads to a specific microstructure, leading to higher mechanical properties. The water sensitivity of these composites limits their application [11].

Polymer can also be used to modify the formation of CSH at a nano-scale during the hydration of cement. Some promising results have been obtained with the intercalation of polyvinyl alcohol (PVA) or polyacrylic acid (PAA) polymer in calcium silicate hydrates to develop new CSH/polymer composites. The intercalation of water-soluble polymers in cement hydrates CSH is an important research topic, as a challenge to the development of tougher and ductile cement based materials. But first results as the work of Matuyama and Young [12] are controversial. In a more recent paper, Merlin et al. [13] showed no clear signs for intercalation of macromolecules in CSH: they suggest that the composite materials formed may be considered as meso-composites in which the individual solid units are not the CSH sheets but crystallites thereof.

This paper considers the effect of limited amount of some high molecular mass water-soluble polymer to control mechanical properties of cement hydrates. The microstructure modifications of the cement paste made of hydrates continuous phase has been analysed in another paper [14]. The modification of the cement paste induced by the polymer is limited and the process still remains compatible with mortar or concrete technologies. Thus, these cement materials are very different from previous high performances MDF. The reinforcement of the polymer modified cement paste will be explained, as a function of polymer reactivity with cement hydrates and molecular mass.

Such polymer modified cement pastes could be considered as a first step in view to develop new UHPC concrete by adding sand, granulates and fibers.

Background on possible reinforcement mechanisms

According to the polymer content, the fracture behaviour is controlled either by the cement hydrates phase or by polymer. So, a small quantity of water soluble polymer with a high molecular mass added in a cement paste could modify the crack initiation and/or crack propagation process. The mechanical behaviour of cement-based materials, as the cracking resistance mechanisms, can be characterised with the Linear Elastic Fracture Mechanics (LEFM) through the critical stress intensity factor (K_{Ic}) and the energy release rate (G_{Ic}).

According to literature, different possibilities of reinforcement can explain the increase of strength and/or toughness observed in polymer modified concrete.

A first mechanism concerns the modification of the residual stresses developed in the hydrated materials. The cement setting is accompanied by a large shrinkage which induces porosity and internal stresses in mortars and concrete [15, 16]. The presence of polymer during the setting step could relax the internal stresses. So as a consequence, polymer additions could modify the crack resistance, i.e. the critical stress intensity factor.

Another mechanism considers possible modification of morphology or chemical nature of the cement hydrates CSH. That is the case of calcium silicate in presence of silane or alkyl carboxylates. The growth of CSH hydrates pack with some macromolecules having functional group compatible with Ca as PVP, PEG or polyacrylamide can be used to control the continuous CSH phase microstructure [17].

A general mechanism considers the possible interaction between cement hydrates phase microstructure and crack (*crack interaction*). This interaction effect can be observed when aggregates (particles, or dispersed phase) are incorporated in a brittle matrix. Modifications of fracture toughness of such composites are induced by a direct interaction between the crack front and the dispersed phase. So, the energy release rate (G_{Ic}) can be divided in different terms which the first one is the contribution of the reference matrix, and the others can be due to various mechanisms:

(i) a generalised micro-cracking due to local stress around dispersed particles [18];
(ii) the crack trapping or crack pinning: the presence of nodules with a higher mechanical resistance than

hydrates can block the crack propagation [19]. This mechanism is often found in concrete reinforced with fibres. Moreover, the geometry and the dispersion of particles determine the main parameters of the increase of toughness;

(iii) the crack deflection: when crossing a particle, a crack can be deviated from a linear propagation plane or separated in multiple microcracks (branching) [20]. In concrete, the use of sand [21, 22] or fibres [23] can generate such fracture mechanisms by an increase of the fracture surface. The interface between fibres or aggregates and hydrates must not be too strong to allow some decohesion [24];

(iv) the crack bridging: with a cohesive interface between aggregates (particles) and hydrates [25, 26], or particles with an important aspect ratio such as short fibres, a bridging strength can appear which control the crack opening by the presence of a ligament in the crack wake. This mechanism appears in concrete modified by polymer dispersions like styrene–butadiene latex or as in MDF cements [27].

A model proposed by Becher [28] leads to an estimation of the gain in toughness ΔK due to bridging mechanisms:

$$\Delta K = \sigma_f^p \left(\frac{V_f.r}{6(1-\upsilon^2)}\frac{E_c}{E_p}\frac{G^m}{G^i}\right)^{1/2} \qquad (1)$$

where, σ_f^p is the fracture stress of particles; V_f is volume fraction of particles, r is particles radius; v is Poisson ratio of composite; E_c is composite modulus, E_p is particles modulus; G_m is matrix surface energy, G_i is interface surface energy.

Another general mechanism is possible, with a process zone development at the crack front *(crack shielding)*: the material microstructure is modified under stress leading to a local shielding of the propagating crack tip. This mechanical behaviour could be compared to the plastic zone which appears in metals, even if mechanisms which produce this process zone are different. The zone localised at the crack front of the main propagating macrocrack is modified, and the process zone propagates with the crack during loading [25]. In both cases, the mechanical behaviour is no more linear nor elastic, because of mechanisms which dissipate large quantity of energy. In structural ceramic, this phenomenon—called crack shielding- has been well identified: it is induced by a phase transformation or a microcrack formation under local stress. Concrete can also present crack shielding because of a multicracking of CSH matrix along the main crack [29, 30], but without modification of the hydrates. An analytical method proposed by Evans and Faber [31] in the case of the microcrack in brittle materials permits to calculate a toughness increase according to next equation:

$$\frac{K_{mes}}{K_0} = 1 + 0.4 f_s \qquad (2)$$

where, K_{mes} is the measured toughness; K_0 is toughness of ref material (no cracked); f_s is microcracks volume fraction at saturation.

The fracture toughness (K_{Ic}) of the cement hydrate phase is very low: typical values are about 0.2 MPa.m$^{1/2}$. Toughening mechanisms have to be developed through polymer additions to increase the fracture toughness at values superior to 1 MPa.m$^{1/2}$.

Experimental methods

A cement paste with no aggregates or sand was developed, to determine the effect of water soluble polymer.

Materials

A commercial high silicate content Portland cement HTS 52,5 PMES CP2 (Lafarge, France) was mixed with 15 wt% of silica fume MST (Société Européenne Produits Réfractaires, Le Pontet-France): silica fume is reactive enough to control the production of Portlandite $Ca(OH)_2$ through pozzolanic reaction.

To keep the water to cement ratio down to 0.2 with good paste rheology, a superplasticizer Mapfluid X404 (Mapei, Italy) is added at 2.0 wt% with respect to cement.

The water-soluble polymers used are polyvinylalcohol (PVA) and polyvinylpyrolidone (PVP) with different molecular masses; their characteristics are given in Table 1. DPw is the weight-average polymerization degree of the polymer. The degree of hydrolysis of the PVA is higher than 98% to avoid that acetate monomer of partially hydrolysed PVA

Table 1 Polymers molecular masses

	Commercial name	Mw (g/mol)	DPw
PVA4-20	Rhodoviol (Rhodia)	20000	450
PVA30-5	Rhodoviol (Rhodia)	79000	1800
PVP10k	K15 (Aldrich)	10000	90
PVP40k	K30 (Aldrich)	40000	360
PVP160k	K60 (Fluka)	160000	1440
PVP1.3m	-(Aldrich)	1300000	11700

induces porosity, leading in this case to an important decrease of hydrated cement mechanical properties.

Mixing procedure, and specimens preparation

After mixing of the cement and the silica fume powders for 10 min in a mixer, the superplasticizer and the solution of polymer are added and mixed during 4 min. Different aqueous polymer solutions were prepared to obtain cement pastes with different polymer/cement ratios between 0.007 and 0.04, as listed in Table 2. The paste rheology is not constant, but the water/cement ratio is equal to 0.2 in all formulations.

The fluid paste is poured into metallic moulds treated with a release agent. Because of the low content in aluminate of the HTS cement (less than 3% aluminate) hydration and setting rates were very slow. Therefore, the test-bars were demoulded after 3 days and then cured, at first in water at 90 °C for 1 day and then out of water at 90 °C during another day.

Cement pastes made of cement hydrates and reactive amorphous silica were produced with two types of specimens:

- small beams: $100 \times 10 \times 10\ \text{mm}^3$
- large beams: $200 \times 20 \times 17\ \text{mm}^3$

The specimens were then stocked and stabilised in a dessicator for at least two weeks before testing.

Mechanical properties Bending test measurements

The mechanical behaviour of the small beams was determined using a three points bending test (span of 70 mm), at a constant crosshead rate of 500 microns/min (Instron 4301). All cement pastes were tested using at least five beams.

Table 2 Influence of polymers on density and elastic modulus of cement pastes

	Polymer volume (%)	Density (d)	Modulus E_g (GPa)
Reference	0	2.26 ± 0.01	37.0 ± 1.0
0.7% PVA4-20	1.1	2.23 ± 0.01	36.5 ± 0.6
1% PVA4-20	1.6	2.18 ± 0.01	34.6 ± 1.1
1.5% PVA4-20	2.4	2.06 ± 0.02	32.6 ± 0.9
3% PVA4-20	4.7	1.95 ± 0.03	28.0 ± 1.1
0.7% PVA30-5	1.1	2.17 ± 0.02	35.3 ± 0.3
1% PVA30-5	1.6	2.16 ± 0.02	33.9 ± 1.0
3% PVA30-5	4.7	2.07 ± 0.02	31.0 ± 1.5
1% PVP10k	1.6	2.25 ± 0.01	36.5 ± 0.6
3% PVP10k	4.7	2.20 ± 0.02	32.5 ± 0.8
1% PVP40k	1.6	2.21 ± 0.01	35.1 ± 0.2
3% PVP40k	4.7	2.13 ± 0.01	31.8 ± 0.7
1% PVP160k	1.6	2.22 ± 0.03	36.9 ± 1.0
3% PVP160k	4.7	2.11 ± 0.02	32.0 ± 1.5
1% PVP1,3m	1.6	2.15 ± 0.03	34.2 ± 0.8
3% PVP1,3m	4.7	2.01 ± 0.07	29.4 ± 1.5
4% PVP1,3m	6.2	2.03 ± 0.03	28.3 ± 0.6

The mechanical behaviour of the tested beams is linear elastic, with brittle fracture (Fig. 1): maximum strength and fracture energy are determined from the following relationships:

Maximum stress:

$$\sigma_{\max} = \frac{3 \,.\, P_{\max} \,.\, S}{2 \,.\, b \,.\, D^2} \tag{3}$$

Maximum strain:

$$\varepsilon_{\max} = \frac{6 \,.\, y_{\max} \,.\, D}{S^2} \tag{4}$$

Energy:

$$W = \int P \,.\, dy \quad = 0.5 P_{\max} \cdot y_{\max} \tag{5}$$

where, P_{max} is the fracture strength; y_{max} is fracture displacement; S = span, b is specimen thickness, D = specimen depth.

To have a better control of the crack propagation, a closed loop controlled test machine (Shenck RMC100) was used with a strain transducer (0.1 µm resolution) fixed on the specimen: larger specimen sizes were used in these experiments. The crack mouth opening displacement CMOD measurement was used as a feedback control, with a controlled opening rate of 6–60 µm/min. The damage localisation during loading (microcracks) was detected by acoustic emission sensors (Mistras2001, Euro Physical Acoustic, France), together with the measurement of the total dissipated energy (Eq. 5). Strain was calculated from CMOD instead of crosshead displacement:

$$\varepsilon = \frac{CMOD}{s} * \frac{D}{D + z} \tag{6}$$

where, s is the distance between the fixation points of the transducer (Fig. 2); z is distance between the transducer and the specimen

Flexural modulus (E_f) was also measured by the slope of the σ–ε curve, at small strain.

The critical stress intensity factor K_{Ic} is measured on single edge notched beam specimen (SENB) with CMOD control (Fig. 2): a notch was made on large size specimens with a thin diamond saw. Notched beams were tested in accordance with the ISO13586 procedure, with a relative notch length of 0.4 (a/D). The

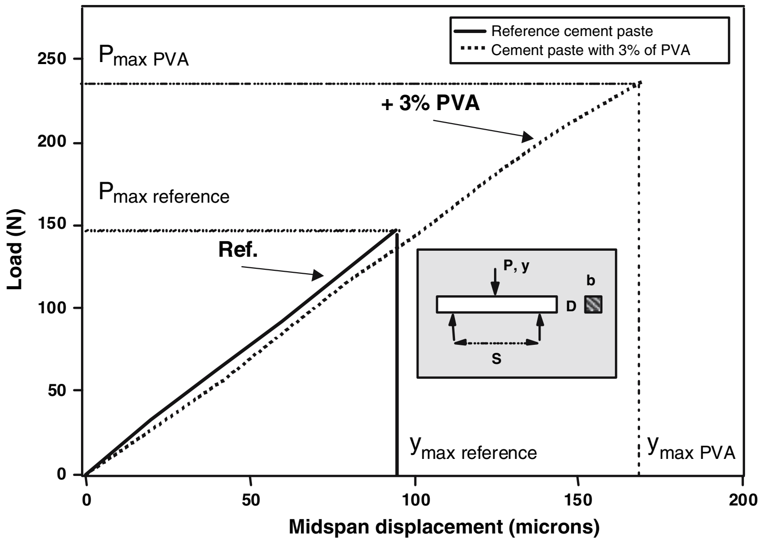

Fig. 1 Load–displacement curves for unnotched small specimens

critical release rate energy G_{Ic} and the critical stress intensity factor K_{Ic} are calculated using the linear elastic fracture mechanic (LEFM), with respect to the different criteria required by the procedure.

$$KIc = f(a/D) * \frac{P_Q S}{D^2 * b} \tag{7}$$

where, P_Q is the strength at the beginning of the cracking; *f*(*a*/*D*) is corrective factor due to specimen geometry (see ISO13586); a is notch length, *b* is specimen thickness, *D* is specimen depth.

$$GIc = \frac{W_B}{b * D * \phi(a/D)} \tag{8}$$

where, W_B is the fracture energy; $\varphi(a/D)$ is corrective factor due to specimen geometry (see ISO13586); a is notch length, *b* is specimen thickness, *D* is specimen depth.

We have also calculated others parameters such as elastic w_e and inelastic energies w_{ne} (Fig. 2):

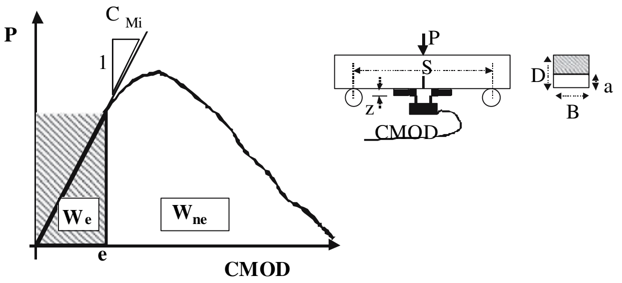

Fig. 2 Testing configuration and experimental Load–CMOD curve for notched specimens (SENB)

$$\mathrm{Wtot} = \int_0^\infty P.de = \mathrm{w_e} + \mathrm{w_{ne}} \tag{9}$$

Fracture behaviour of heterogeneous materials as concrete cannot be explained from Linear Elastic Fracture Mechanic (LEFM), because validity conditions are not respected: the process zone is too large. So, only the cohesive crack model developed by Hillerborg [32], and recently improved by Elices and Planas [33, 34], can be used to explain the mechanical behaviour of such brittle materials. But, in our polymer modified pastes, as in ultra high performance concrete (UHPC) or mortars with fine microstructure [35], the K_{Ic} and G_{Ic} parameters can be measured from bending test on notched beams.

Elastic Modulus

The Young's modulus was determined by vibration method (Grindosonic). This non destructive test allows to measure the natural frequency of materials with a known geometry and weight, by using an Impulse Excitation technique.

For a rectangular beam, elastic modulus E_g for the flexion vibration can be obtained using the theory of Pickett [36].

$$E_g = 0.94642 * (\rho * L^4 * f^2/D^2) * T \tag{10}$$

where, ρ is the density; *f* is measured frequency; *D* is beam height; *L* is beam length; *T* is correction factor depending on geometry and Poisson ratio.

Elastic properties of the material such as Young's modulus, shear modulus or Poisson ratio can be calculated easily.

Results

The polymer additions to cement paste have two effects:

(i) a slight decrease of the cement paste density, with a higher compliance;
(ii) an increase of the mechanical properties, with higher fracture strength.

Density and elastic modulus

The main results concerning the density and elastic modulus are shown in Table 2.

The presence of polymer induces a decrease of the density and elastic modulus of the cement paste specimen, in particular when the polymer rate is higher than 2wt%. The reasons are the low density of polymer itself (rule of mixtures), the porosity increased and the air void content resulting from the mixing and moulding process. The density and modulus can be corrected as follows, if the porosity increase is not too high [37]:

$$d_c = d_{ref} * (1 - p) \tag{11}$$

$$E_{g_c} = E_{ref} * (1 - p) \tag{12}$$

where, p is the porosity.

The use of specific parameters, i.e. parameters normalised to the density, allowed to minimize the influence of macroporosity. The specific elastic modulus E_{gc}/d_c of the reference cement paste is equal to 16±1 GPa, whereas we obtain 15±1 GPa for the elastic modulus of the cement pastes reinforced with a polymer rate inferior to 4% in weight. The small difference can result from the difference of modulus between polymers and cement paste.

The normalisation of modulus by density has already been used in cement pastes modified by styrene butadiene emulsions [38], where a macro-porosity was induced by the polymer. In PVP and PVA modified cement pastes, the porosity modifications induced by the presence of polymers will be developed in another paper [14]. We have shown that the addition of less than 4wt% of polymer modifies slightly the viscosity of the paste during the mixing procedure, which generates a macro-porosity with large pore size superior to several microns. So, the use of normalised elastic modulus by taking into account the density shows clearly the influence of the polymer on the cement paste modulus: the specific modulus is not significantly modified by the presence of polymers, at the used content (i.e. < 4wt%).

Influence of polymers on cement paste mechanical behaviour

Fracture strength (unnotched specimen)

The linear elastic behaviour of polymer modified cement pastes has been studied on unnotched specimens with two different sizes, as a function of polymer rate and polymer molecular mass.

In a first step, the influence of polymer content and molecular mass on maximum stress and maximum energy is measured on small size specimen. The maximum stress at fracture as fracture energy is reported through specific values (σ/d, and W/d) to show the real effects of PVA and PVP polymer additions. Figure 3 reports the influence of the PVA content with two molecular masses on specific fracture strength gain and energy gain: $\Delta\sigma/\sigma_{\text{ref}}$, and $\Delta W/W_{\text{ref}}$. Both properties increase significantly, and quite linearly, with the volume polymer content. With the more important polymer fraction, the fracture strength is increased by a factor around two (+80%) whereas the fracture energy is increased by a factor three (+200%). The molecular mass of PVA seems to have no noticeable influence on these properties.

The influence of PVP on mechanical properties is dependent on polymer content but also on polymer molecular mass (Fig. 4: 1wt% PVP). With PVP, higher is the molecular mass higher are the fracture strength and energy. But, with a more pronounced way than with PVA, the mechanical properties resulting from addition of PVP are largely related to the polymer content and the PVP molecular mass, through the porosity which is induced during the mixing procedure. The most noticeable increases are obtained with 4 wt% of high molecular mass of PVP (+35% for specific fracture stress, and +110% for specific fracture energy).

If the amount of high molecular mass PVP is higher than 4wt%, mechanical properties decrease because porosity significantly increases with polymer content, whereas this behaviour already appears with 2 or 3wt% of lower molecular mass PVP.

The highest polymer fraction is equal to 3wt% with PVA30-5 (4.7 v%), whereas 4wt% of PVP with a high molecular mass (6.2 v%) can be easily added to

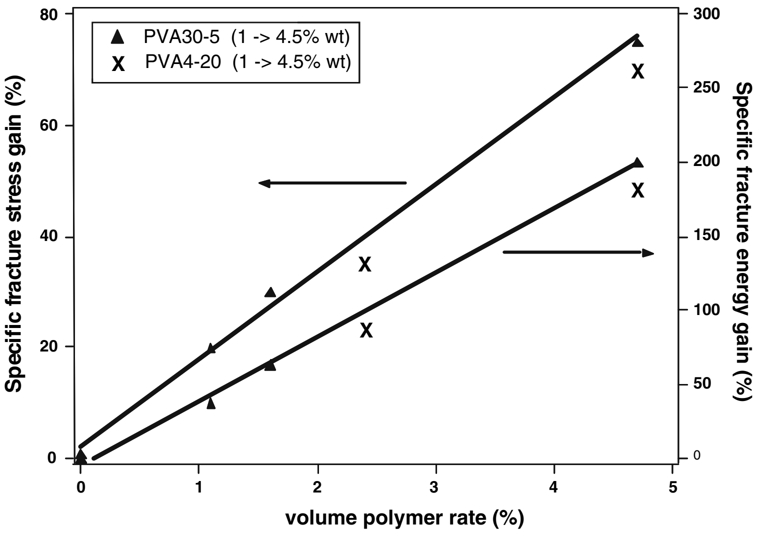

Fig. 3 Influence of PVA content (v%) on specific fracture stress and specific fracture energy of cement paste

cement pastes with a good workability. The influence of these polymers on the main mechanical properties measured in bending on small specimens are summarised in Table 3. We can notice that the stress and energy gains are less important with PVP than with PVA, even if there is an important increase compared to the reference cement paste without polymer.

Figure 5 shows typical bending curves obtained with large specimens. As with the small beams, the use of less than 4wt% of polymers (PVP, and PVA) increases the different cement paste mechanical properties. The mechanical behaviour is brittle (unstable fracture), but the presence of polymer delays the fracture of specimen after the appearance of first crack as it is detected by acoustic emission: without polymers, the cracks appear just before the maximal strength. The fracture behaviour is very different with 3wt% of PVA, where the cracking process is well controlled up to the maximum stress, with large deformation (CMOD opening). This is confirmed by acoustic emission analysis. The main characteristics deduced from these curves are listed in Table 4.

The measured mechanical properties of cement paste, in bending tests, are affected by the specimen size. For the reference cement paste, fracture stress (6.2 MPa) and fracture energy with larger specimens are lower than fracture stress (15 MPa) and fracture energy with smaller specimens. Moreover, the influence of molecular mass of PVA on mechanical behaviour is different following the specimens size. So, mechanical properties are more sensitive to PVA molecular mass when beams size is higher. The mechanical properties improvement of cement paste is more important with PVP on large beams.

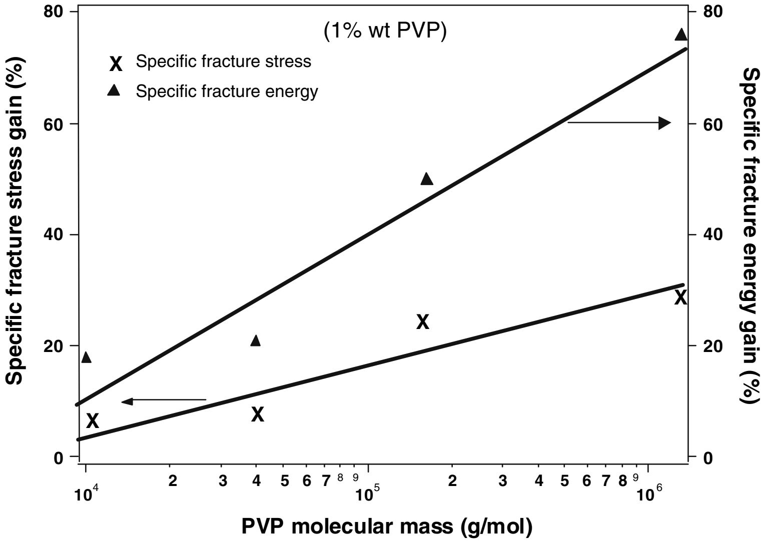

Fig. 4 Influence of PVP molecular mass (1 wt% of polymer) on cement paste mechanical properties

Table 3 Main mechanical properties obtained with bending tests, with 3 wt% PVA or 4wt% PVP (small size specimen)

	Density	Modulus (GPa)	$\sigma_{\max}$ (MPa)	Energy (kJ/m^3)
Reference	2.26 ± 0.01	37.0 ± 1.0	15.0 ± 1.0	3.0 ± 0.4
4% PVP1.3m	2.03 ± 0.03	28.3 ± 0.6	18.5 ± 1.5	6.1 ± 0.8
3%PVA4-20	1.95 ± 0.03	28.0 ± 1.1	22.5 ± 1.5	9.0 ± 1.2
3%PVA30-5	2.07 ± 0.02	31.0 ± 1.5	24.0 ± 1.5	9.3 ± 1.3

Fracture toughness (notched specimen)

In cement-based materials with fine microstructure as in the tested polymer modified cement pastes, LEFM validity conditions are respected, and the K_{Ic}–G_{Ic} parameters can be measured from bending test on notched beams. The elastic behaviour of the specimen and its non linear behaviour after the first crack initiation with the crack mouth opening displacement (CMOD) can be observed. Figure 6 shows the fracture behaviour of different polymers reinforced cement pastes, as determined with notched specimen: one can see several differences in case of PVA and PVP additions, during loading to the maximum stress (peak stress) and after the peak stress.

The fracture mechanics parameters of the reference cement paste and the parameters of the polymer modified cement paste specimen are reported in Table 5: crack initiation parameters K_{Ic}, G_{Ic}. Other parameters such as elastic energy w_e and inelastic energy w_{ne} of different cement pastes have also been determined. It can be observed that polymers and specially PVA improve the critical stress intensity factor (K_{Ic}) and the energy release rate (G_{Ic}). The behaviour of cement pastes with polymers is also less brittle, with a controlled fracture process after the maximal strength, with large dissipated energy (w_{ne}).

The Load–CMOD curves are linear at low stress level, with a measured CMOD of 3 microns in case of the reference cement paste, and up to 6 microns with polymer modifications. With reference cement paste, a small non linear zone is present before the maximum stress, and a rapid decrease of strength appears after the maximum, with limited dissipated energy.

For PVP, the linear zone is more important, but a rapid decrease always exists after the maximum stress, when the first cracks appear. Then, the main crack is stopped and stress increases again on several microns before decreasing rapidly which traduces a control of the cracking damage by the microstructure. For PVA, the fracture behaviour is different, specially after the maximum strength. A large linear zone is observed before the peak stress, and the decrease of the strength after the maximum is well controlled. This is the consequence of the improvement of the fracture toughness, in polymer modified cement pastes. The post-peak fracture process is controlled, with a large energy dissipation.

The controlled fracture after peak stress corresponds to the development of a damage process zone at the notch tip. The characterisation of the process zone is not easy: energy criteria have to be used to determine the crack growth resistance curve G-Δa (R-curve) [39].

The different energy values presented in Table 5 confirm that both PVA and PVP additions, even at low content (< 4wt%) improve the energy dissipation during the fracture process of the cement hydrates phase. Fracture behaviour with the two polymers are quite different. The crack initiation is controlled with

Fig. 5 Influence of polymer additions on strain–stress curves

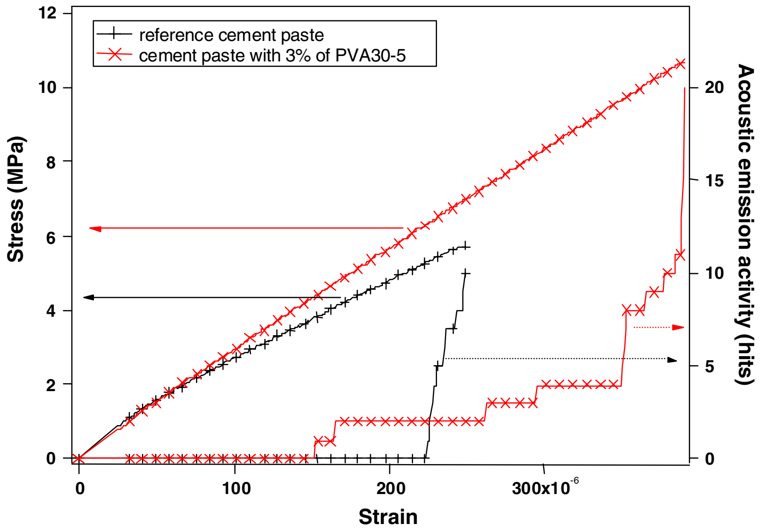

Table 4 Main mechanical properties from bending test, with 3wt% PVA or 4wt% PVP (large size specimen)

name	density	Flexural Modulus (GPa)	σ_{max} (MPa)	Energy (kJ/m^3)
Reference	2.25 ± 0.02	30 ± 1	6.2 ± 0.6	1.0 ± 0.2
3% PVA30-5	2.08 ± 0.02	30 ± 3	11.2 ± 1.6	3.1 ± 0.9
3% PVA4-20	2.10 ± 0.02	24 ± 1	7.3 ± 1.0	1.8 ± 0.2
4% PVP1.3m	2.07 ± 0.02	29 ± 4	8.8 ± 1.2	2.3 ± 0.6

both polymers; but a major difference is observed with the post-peak dissipated energy, which is more important with PVA additions.

Discussion

The observed increase of critical stress intensity factor (K_{Ic}) and energy release rate (G_{Ic}) of cement paste with PVA and PVP additions cannot be explained by a modification of the chemical nature of hydrates [40], even if a decrease of the hydration rate is observed (specially with PVA). The hydration rate modification could probably modify the fracture behaviour of the CSH phase itself, but is not sufficient to multiply by a factor 3 the energy release rate as it is the case with PVA additions. Other mechanisms should be considered to explain the observed toughening effect, as a consequence of the organisation and the repartition of the polymers and the CSH hydrates.

In the case of brittle material, the fracture process is mainly controlled by the critical defect (Griffith): the defect size is correlated to the microstructure (in the absence of external flaws or cracks). The determination of the fracture strength and the critical stress intensity factor permits to calculate the effective critical defect size (a_{eq}), through the Griffith formula:

$$a_{eq} = \frac{K_{Ic}^2}{\pi * (1.12 * \sigma_{fract})^2}, \text{ or } : \sigma_{fract} = \frac{K1c}{1.12\sqrt{\pi}\sqrt{a_{eq}}} \tag{13}$$

Without polymer, the effective critical crack length is equal to 90±10 microns, whereas the addition of PVA and PVP slightly increases the value of inherent flaw size to 110±10 microns and 150±10 microns respectively (small size specimen). As a consequence, the increase of the fracture strength is due to the increase of the critical stress intensity factor K_{Ic} (Fig. 7).

The fracture strength values are lower for large size specimen compare to small ones: this size effect can be explained by the internal stresses from shrinkage. The previous relation has to be re-written as follows:

$$\sigma_{mes} + \sigma_{res} = \frac{K_{Ic}}{1.12 * \sqrt{\pi}\sqrt{a_{eq}}} \tag{14}$$

where, σ_{mes} is the measured stress; σ_{res} is residual stress; K_{Ic} is fracture toughness; a_{eq} is effective critical crack length.

For instance, the residual stresses would be equal to about 8.8 MPa in case of the reference cement paste.

Possible toughening mechanism in case of PVP

The use of only 4wt% of PVP with a high molecular mass induces a significant improvement of the cement paste fracture toughness, with an increase of the critical stress intensity factor (K_{Ic}) by 60% whereas the energy

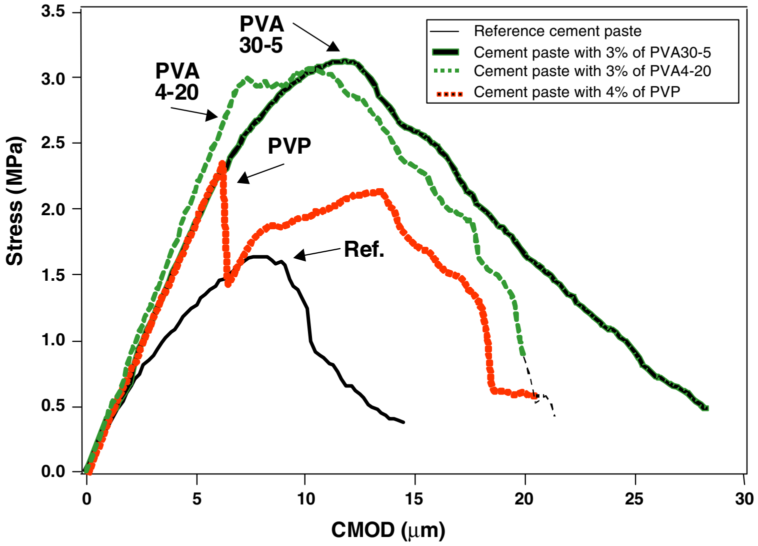

Fig. 6 Stress–CMOD curves on notched beams (SENB). Effect of PVP or PVA additions

Table 5 Main fracture properties from bending test (SENB)

	$E_{J\text{-}S}$ (GPa)	K_{Ic} (MPa√m)	G_{Ic}(J/m^2)	w_e (J/m^2)	w_{ne}(J/m^2)	w_{tot}(J/m^2)
reference	35±4	0.28±0.05	2.5±0.5	1.2±0.2	4.2±2.5	5.5±2.5
4% PVP1.3m	34±5	0.45±0.05	5.2±1	2.6±0.4	8.2±1	10.8±1
3% PVA4-20	34±2	0.47±0.05	5.6±1	2.6±0.6	9.8±3.0	12.5±3
3% PVA30-5	34±4	0.55±0.05	8.0±2	4.0±1	12.0±0.5	16.1±0.6

release rate (G_{Ic}) is doubled. Recent studies by scanning electron microscopy [14] have demonstrated that the organisation of hydrates is modified by PVP polymer with an increase of the hydrates porosity. Chemical interactions appear between hydrates and the well dispersed polymer in the hydrates phase (Fig. 8).

A more disordered microstructure makes easier the multiplication of cracks in the cement paste. The model proposed with Eq. 2 permits to explain an increase of fracture toughness of only 3wt% instead of 60%, supposing that the supplementary nanoporosity produces microcracks.

The crack propagation process is influenced by the cement paste microstructure (crack interaction), which induces an increase of the mechanical properties. The good dispersion of polymer in cement hydrates phase and the development of chemical interactions between the organic and mineral phases lead to a reinforcement by crack deviation, even crack bridging.

PVP reinforcement seems to be more important as the specimen size is increased, compare to reference cement paste (+30% on $\sigma_{\max}$ with smaller specimens compare to +55% with larger specimens, respect to reference cement paste). This can be due to stresses relaxation phenomena during the setting step of cement, in presence of the organic phase: the magnitude of residual stresses increases with the size of the structure.

Possible toughening mechanism in case of PVA

Microstructure analysis of PVA reinforced cement pastes has shown that stacking and densification of hydrates was not significantly modified by this polymer, contrary to PVP. PVA polymer was essentially dispersed as polymer rich nodules in CSH hydrates with a size depending on the polymer molecular mass (Fig. 8). With high molecular mass PVA (PVA30-5), the polymer rich nodules have a diameter superior to 10 microns visible with an optical microscope, whereas the nodules diameter becomes submicronic with lower molecular mass PVA (PVA4-20).

Beside the development of an interface between nodules and hydrates phase, a large interphase is consolidated during the hydration process, where hydrates and PVA are closely embedded: this is due to important chemical interactions between PVA and cement hydrates [40, 41]. The stress transfer from cement hydrates to nodules is high, and as a consequence crack propagates through the nodules instead of getting around them [14]. Polyvinyl alcohol (PVA) is known to develop strong cohesive interface with cement hydrates CSH, by a physico-chemical local modification of hydrate products as CSH, CH and ettringite. That is the case of PVA fibers which develop high bonding to cement matrix through interface chemical reactivity [42]. The aggregate-paste transition zone is

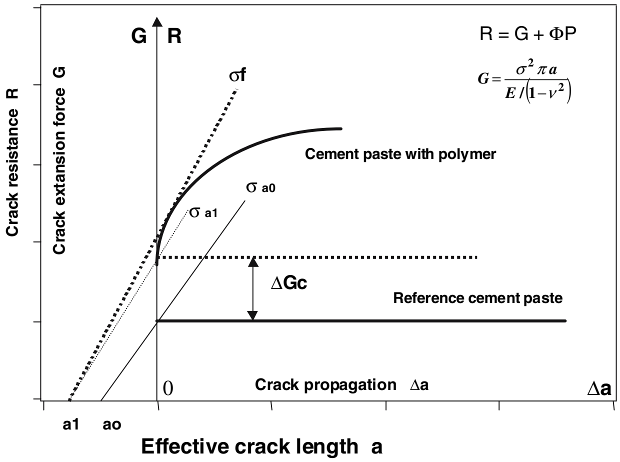

Fig. 7 Schematic toughening process of brittle cement paste with polymer additions

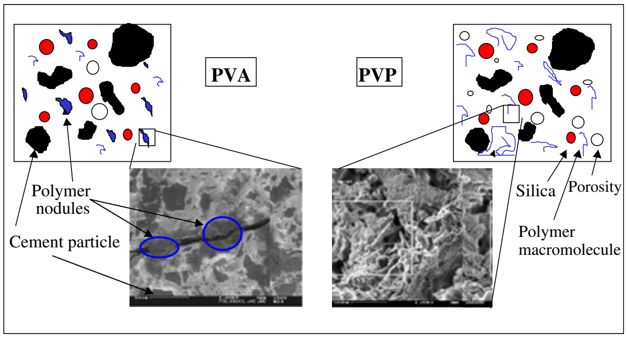

Fig. 8 Microscopic analysis (SEM) and hand-drawn versions of SEM micrographs of polymer modified cement pastes (< 4wt% polymer) PVA, dense hydrates microstructure, with polymer nodules PVP, porous hydrates microstructure, with polymer macromolecules

modified by water-soluble PVA, leading to an increase of the bond strength.

The PVA modified cement paste appears as a brittle mineral matrix reinforced with soft organic particles with a cohesive interphase. Therefore, the increase of the stress intensity factor (K_{Ic}) and the energy release rate (G_{Ic}) can be explained by mechanisms like crack bridging. The model presented previously (Eq. 1) permits to calculate an increase of fracture toughness of 0.20 MPa√m for PVA30-5 (compare to 0.25 MPa√m) and 0.1 MPa√m for PVA4-20 (compare to 0.2 MPa√m). This model can explain the increase of fracture toughness generated by the presence of PVA particles in the cement paste.

If nodules size is smaller (with PVA4-20), the model is less efficient because most of polymer macromolecules are dispersed in hydrates instead of taking the shape of dense particles. So, PVA4-20 reinforced cement paste has a mechanical behaviour intermediate between PVP and PVA30-5. The fracture mechanisms discussed for PVP modified cement pastes, such as microcracks or cracks deviations, can also explain the toughness increases with this low molecular mass PVA polymer.

The influence of the polymer nodule size (with PVA) is observed with unnotched specimen, where the polymer molecular mass has also some influence on the initiation and the unstable propagation of the crack. On notched beams, the energy release rate (G_{Ic}) is doubled with low molecular mass PVA (PVA4-20) and multiplied by three with high molecular mass PVA (PVA30-5). So, with low molecular mass PVA (PVA4-20), some nodules have a too low size to stop the crack propagation.

The presence of these nodules further explains the fracture behaviour of PVA modified cement pastes in the non linear elastic zone. If the crack propagation control is difficult with PVP after the maximum fracture stress, the decrease of the stress is delayed and controlled with PVA. A large quantity of energy is dissipated during the non linear zone compare to the linear elastic zone. By the way, the fracture behaviour of these composites is similar to classical reinforced composite such as rubber reinforced polymer or cement–latex composites. The behaviour of such composites could also be compared with MDF [9, 10], even if mixing procedures, PVA amounts and cements are different: in all the case, PVA increases composite mechanical properties, in particular by crack bridging mechanism.

The use of particles with a lower elastic modulus in a brittle matrix has to be considered in the case of cement paste modified with water-soluble polymers.

Conclusions

The use of water-soluble polymers with a high molecular mass can significantly improve some mechanical properties of a cement paste (hydrated high silicate Portland cement + amorphous silica), as it is observed in bending tests. The use of less than 4 wt% with respect to cement of PVA and PVP increases the total fracture energy by a factor of three with a good workability of the slurry. This increase is mainly associated with modification of crack growth as characterised by improvement of the critical release rate energy G_{Ic} and the critical stress intensity factor K_{Ic}. The non-elastic energy (w_{ne}) dissipated after the fracture stress (peak stress) is also significantly increased, in particular with the high molecular mass PVA.

Whereas PVP influences the fracture behaviour by a modification of the CSH hydrates, the presence of nodules of PVA induces a better control of the fracture process, particularly during damage propagation.

As a consequence, it would be interesting to develop high performance concrete with such polymers modified cement paste as binder phase, by adding sand, quartz flour and fibers in optimised formulations. In addition to reinforcement of the cement paste, polymers used in this study could also improve the interphase zone between aggregates and hydrates, contributing to the performances of concrete.

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References

1. High performance fiber reinforced cement composite (1995) 2nd International Workshop. Ann Arbor, Michigan, Vol. 2, Naaman AE, Reinhardt HW (ed)
2. Roy DM (1987) New strong cement materials: chemically bonded ceramics. Science 235:651
3. Kardon JB (1997) Polymer-modified concrete: review. J Mater Civil Eng 9:85
4. Hasegawa M, Kobayashi T, Dinilprem Pushpalal GK (1995) A new class of high strength, water and heat resistant, polymer-cement composite. Cem Concr Res 25:1191
5. Sumathy CT, Dharakumar M, Soraja Devi M, Saccubai S (1997) Modification of cement mortars by polymer latex. J Appl Polym Sci 63:1251
6. Ohama Y (1995) Handbook of polymer-modified concrete and mortars. Noyes Publications, USA
7. Jiang W, Roy DM (1995) Microstructural aspects of high-performance cement-based materials. Mat Res Soc Symp Proc 370:115
8. Aquino MJ, Li Z, Shah SP (1995) Mechanical properties of the aggregate and cement interface. Adv Cem Based Mater 2(6):211
9. Chu T-J, Roberson RE (1994) Viscoelastic behaviour of macro-defect-free cement. J Mater Sci 29:2683

10. Bortzmeyer D, Frouin L, Montardi Y, Orange G (1995) Microstructure and mechanical properties of macro-defect-free cements. J Mater Sci 30:4138
11. Lewis JA, Boyer M, Bentz D-P (1994) Binder distribution in macro-defect-free cements: relation between percolative properties and moisture adsorption kinetics. J Am Ceram Soc 77(3):711
12. Matsuyama H, Young JF (1999) Intercalation of polymers in calcium silicate hydrate. Chem Mater 11:16
13. Merlin F, Lombois H, Joly S, Lequeux N, Halary JL, VanDamme H (2002) Cement-polymer and clay-polymer nano and meso composites: spotting the difference. J Mater Chem 12(11):3308
14. Morlat R, Biebuyck J-J, Godard P, Microstructural analysis of high molecular mass polymer modified cement pastes, to be published
15. Igarashi S-I, Bentur A, Kovler K (2000) Autogenous shrinkage and induced restraining stresses in high-strength concretes. Cem Concr Res 30(11):1701
16. Bissonnette B, Pierre P, Pigeon M (1999) Influence of key parameters on drying shrinkage of cementitious materials. Cem Concr Res 29(10):1655
17. Orange G, Chane-Ching JY, Klur Y (1999) Rhodia Internal Research Report 'Bétons ductiles'
18. Garashi S, Kubo HR, Kawamura M (2000) Long-term volume changes and microcracks formation in high strength mortars. Cem Concr Res 30(6):943
19. Beaudoin J-J, Gu P, Myers RE (1997) Flexural strength of cement paste composites containing micron and sub-micron nickel particulates. Cem Concr Res 27(1):23
20. Struble LJ, Stutzman PE, Fuller ER (1989) Microstructural aspects of the fracture of hardened cement paste. J Am Ceram Soc 72(12):2295
21. Abell AB, Lange DA (1997) The role of crack deflection in toughening of cement-based material. Brittle Matrix Composites, 5 Proc. Int. Symp. pp 241–250
22. Zampini D, Jennings HM, Shah SP (1995) Characterisation of the paste-aggregate interfacial transition zone surface-roughness and its relationship to the fracture-toughness of concrete. J Mater Sci 30:3149
23. Lange DA, Ouyang C, Shah SP (1996) Behaviour of cement based matrices reinforced by randomly dispersed microfibers. Adv Cem Based Mater 3(1):20
24. Easley TC, Faber KT, Shah SP (1999) Use of a crack-bridging single-fibre pullout test to study steel fiber/cement matrix composites. J Am Ceram Soc 82(12):3513
25. Li VC, Maalej M (1996) Toughening in cement based composites.1. Cement, mortar, and concrete. Cem Concr Compos 18(4):223
26. Thouless MD (1988) Bridging and damage zones in crack growth. J Am Ceram Soc 71(6):408
27. Poon CS, Groves GW (1987) The effect of latex on macro-defect-free cement. J Mater Sci 22:2148
28. Becher PF, Hsueh C-H, Angelini P, Tiegs TN (1988) Toughening behavior in whiskers-reinforced ceramic matrix composites. J Am Ceram Soc 71(12):1050
29. Zhang D, Wu K (1999) Fracture process zone of notched three-point-bending concrete beams. Cem Concr Res 29(12):1887
30. Otsuka K, Date H (2000) Fracture process zone in concrete tension specimen. Eng Fract Mech 65:111
31. Evans AG, Faber KT (1984) Crack-growth resistance of microcracking brittle materials. J Am Ceram Soc 67(4):255
32. Hilleborg A, Modeer M, Peterson PE (1973) Analysis of crack formation and growth in concrete by fracture mechanisms and finite elements. Cem Concr Res 6:773
33. Planas J, Elices M, Guinea GV (1995) The extended cohesive crack. In: Baker G, Karihaloo BL (ed) Fracture of brittle disordered materials. London
34. Elices M, Planas J (1996) Fracture mechanics parameters of concrete: an overview. Adv Cem Based Mater 4(4):116
35. Orange G, Acker P, Vernet C (1999) A new generation of UHP concrete: Ductal. In: Reinhardt HW, Naaman AE (ed) Damage resistance and micromechanical analysis, Proceedings of third International RILEM Workshop, Mainz May 99, pp 101–112
36. Spinner S, Tefft WE (1961) A method for determining mechanical resonance frequencies and for calculating elastic moduli from these frequencies, Proceedings ASTM 61
37. Boccaccini AR, Fan Z (1997) A new approach for the Young's Modulus-porosity correlation of ceramic materials. Ceram Int 23:239
38. Morlat R, Godard P, Bomal Y, Orange G (1999) Dynamic mechanical thermoanalysis of latexes in cement paste. Cem Concr Res 29(6):847
39. Cotterell B, Mai YW (1996) Fracture mechanics of cementitious materials, Ed. Blackie Academic & Professional, Chapman & Hall
40. Morlat R, Jonas A, I Klur, Godard P Characterization of hydrates nature and polymer-hydrates interactions in high molecular mass PVA and PVP modified cement pastes, to be published
41. Morlat R, Nonat A, Godard P Hydration kinetic of cement pastes modified by high molecular mass polymers, to be published
42. Kanda T, Li VC (1998) Interface property and apparent strength of high-strength hydrophilic fiber in cement matrix. J Mater Civil Eng 10(1):5