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Resistance to biogenic sulphuric acid corrosion of polymer-modified mortars

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Abstract

The use of polymer-modified mortar and concrete (PMM and PMC) is investigated to improve the durability of concrete sewer pipes. The aim of the research is to ameliorate the resistance of concrete to biogenic sulphuric acid attack through polymer modification. Prior to the durability tests, experimental research is carried out to reveal the influence of polymer modification on the physical and mechanical properties of mortar and concrete. The results of this research are presented in this paper. Due to the interaction of the cement hydrates and the polymer particles or film, an interpenetrating network originates in which the aggregates are embedded. The density, porosity and location of the polymer film depend on the type of polymer emulsion and on its minimum film-forming temperature (MFT). If air entrainment is restricted, an increased flexural strength is measured. Scanning electron microscope (SEM) analyses reveal the presence of polymer film and cement hydrates in the mortar. The polymer film causes a retardation of the cement hydration as well as a restriction of crystal growth. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer modification; Microscopic structures; Mechanical properties

1. Introduction

The influence of polymer modification on the mechanical and physical properties of mortar and concrete was investigated. Different parameters were taken into account: type of polymer emulsion, curing conditions and polymer–cement ratio. Mechanical testing and scanning electron microscope (SEM) analyses were used to study the structure of polymer modified mortar and concrete.

The influence of polymer modification on the behaviour and structure of cement mortar and concrete has already been described in literature. Different models, which define the interaction and the collaboration between the cement and the polymer emulsion, are proposed and briefly presented in this paper. The results obtained from the tests are discussed in the light of these models.

2. Models of structure formation of polymer-modified concrete and mortar

2.1. Properties of polymer emulsion

Polymer modification generates an interpenetrating network of polymer film and cement hydrates in which the aggregates are embedded [1]. The effect of the polymer modification on the properties of the hardened concrete is in part a result of the formation of this three-dimensional polymer network in the hardened cement paste, and in part a result of a lower water requirement for the mixture [2]. To reveal the influence of the type of polymer emulsion on the properties of concrete, it is necessary to understand the mechanism of polymerisation and polymer film formation.

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Polymer-modified concrete and mortar are most commonly made using a polymer dispersion in water, also called latex. A latex consists of small micelles dispersed in water by means of surfactants, and is produced by emulsion polymerisation.

Emulsion polymerisation takes place in different stages [3]: first, monomers are dispersed in a medium (water) by means of surfactants (surface active agents). The surfactant molecules have one hydrophobic end (one or more hydrocarbon chains), the other one being hydrophilic (anionic, cationic or neutral, depending on the group). They are necessary to keep the monomer particles in dispersion since most monomers are hydrophobic due to the hydrocarbon chain. The monomers migrate to the hydrophobic tail of the surfactant and electrically charged small droplets, called micelles, are formed. Consequently, initiators are added to the continuous phase of the dispersion and activate the monomers in the micelles. The result is an emulsion of polymer particles, called latex. This emulsion is added to the fresh concrete mixture.

Once the water of the latex evaporates or is consumed by the cement hydration, the micelles will come closer. Finally, the attraction force between the polymer particles will overcome the repellant forces of the surfactants, and the polymer particles will coalesce together into a continuous film. This last step greatly depends on the minimum film-forming temperature (MFT) of the polymer emulsion. If this temperature is lower than the working temperature, a continuous film will be formed. In the other case, no continuous film will appear and the polymer will remain in the material as small spheres, closely packed together.

A polymer emulsion is characterised by different properties. The most relevant factors for the use in concrete are the type of monomer, the MFT, the glass transition temperature, the pH, the content of solid parts, the elastic modulus, the elongation at rupture and the stability in a moist alkaline environment of the hardened latex.

The MFT indicates the temperature at which the polymer particles have sufficient mobility and flexibility to flow teogether and form a continuous film [4]. The MFT is also an indication for the strength of the polymer. A high MFT corresponds to a high strength and a "harder" polymer [4]. The glass transition temperature indicates the temperature at which the polymer transforms from an elastic form to a rigid glass-like form [5]. The glass transition temperature is lower than the MFT.

To illustrate these temperature definitions, a styrene–acrylic ester emulsion was poured on a glass plate, and cured at different temperatures during several hours. The result is shown in Fig. 1. The glass transition temperature of this emulsion is −10°C, and its MFT is 32°C. When the emulsion is cured at a temperature lower than the glass transition temperature (Fig. 1(a)), no film is formed, and a rigid structure visibly consists of small polymer droplets. At a temperature between the glass transition temperature and the MFT (Fig. 1(b) and (c)), no continuous film is formed again since the energy and the mobility of the polymer particles are still too small to withstand the shrinkage stresses. Nevertheless, small pieces of film are formed, each of them showing an elastic behaviour. When the ambient temperature during curing is higher than the MFT (Fig. 1(d)), a continuous film is formed with elastic properties.

2.2. Models describing structure formation of polymer-modified mortar and concrete

Different models have been proposed to describe the structure formation of polymer-modified mortar and concrete (PMM and PMC). The most general and commonly used is the model proposed by Ohama [1]. This model can briefly be summarised into three steps.

Immediately after mixing, the polymer particles are uniformly dispersed in the cement paste. During the first step, cement gel is gradually formed by cement hydration and polymer particles partially deposit on the surfaces of the cement gel and the unhydrated cement particles. In the second step, the polymer particles are gradually confined in the capillary pores. As the cement hydration proceeds and consequently the capillary water is reduced, the polymer particles flocculate to form a continuous close-packed layer on the surface of the unhydrated cement particles and cement gel mixture as well as between the aggregate and the cement paste. Ultimately, with water withdrawing due to further hydration, the closely packed polymer particles on the cement hydrates coalesce into a continuous film or

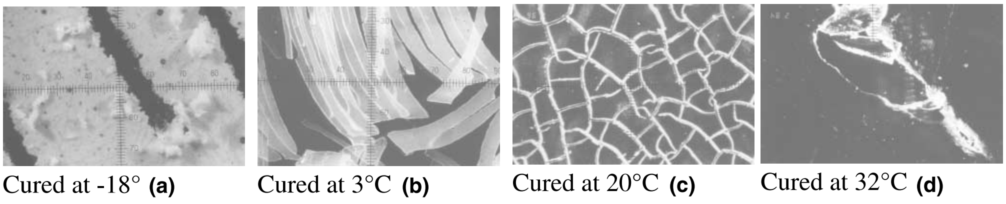
Cured at -18° **(a)** Cured at 3°C **(b)** Cured at 20°C **(c)** Cured at 32°C **(d)**

Fig. 1. Styrene–acrylic ester emulsion cured at different temperatures.

membrane and a monolithic network is formed in which the polymer phase and the cement hydrate phase interpenetrate into each other.

In addition to this model, Puterman and Malorny [6] indicate some slightly different points of view. The main differences are the time at which the polymer film is formed and the influence of the MFT. Puterman and Malorny claim that even when free water is still available in the pores, a polymer film can be formed since the polymers adhere to the surfaces of unhydrated cement particles and form there a closely packed layer which can coalesce into a polymer film. If the MFT is above the curing temperature, the polymer layer is not a continuous film, but it remains as a thick layer of stacked droplets. This layer can thus remain permeable, although it may strengthen and toughen the cement matrix. The consequence of this statement is that cement particles can be partly or completely sealed for hydration at the beginning of the hydration process. In a later stage, hydration can possibly still take place to result in a microstructure in which the polymer film is incorporated and contained within the cementitious phase. This is dissimilar to the model proposed by Ohama in which the polymer film formation takes place after cement hydration and the polymer film is preferably formed in the capillary pores as well as at the transition zone paste-aggregate.

2.3. Influence of polymer modification on properties of mortar and concrete

Polymer modification influences the properties of a fresh concrete mixture as well as the properties of the hardened mixture. The fresh mixture is characterised by a reduction in mixing water requirement, a higher air entrainment, improved workability and a retardation effect on the hydration of the cement particles, depending on the type of polymer emulsion. The reduction in mixing water requirement and improved workability can be attributed to the presence of the surfactants in the polymer emulsion [2].

Surfactants used in the polymer emulsion have possibly also an influence on the cement particles, and cause a better cement particle dispersion in the fresh mixture [2]. This improves the workability of the mix, and lowers the water requirement, which on its turn results in a lower water–cement ratio and consequently in reduced porosity and drying shrinkage of the hardened cement paste. The higher workability can also be attributed to the ball-bearing effect of the polymer particles in the emulsion [1]. Due to this ball bearing effect, the relative movements of the cement particles become easier which results in a more dense material.

The retardation effect on the cement hydration can be attributed to different aspects of the polymer modification. First of all, encapsulation of the unhydrated cement particles by the polymer film, as is explained in the model of Puterman and Malorny, may occur. This may shelter the unhydrated cement particle from water which causes a partial or complete incapacity to hydrate. The retardation can also be due to the retention of the water by the surfactants, since the water of the polymer emulsion is taken into account as hydration water. The release of the water could be retarded. A third explanation can be found in the lower water–cement ratio. A smaller amount of water is present for hydration. Furthermore, the migration of the water could be complicated due to the presence of the polymer film.

The polymer modification of hardened concrete, attributed to the polymer film formation causes the improved adhesion, improved flexural and tensile strength, a blocking of the pores that restricts the movement of water and reduces permeability, bridging of microfractures, and toughening of the microstructure. The polymer also improves the bond between cement and aggregate particles [2].

Part of the mechanical improvement can be attributed to the bridging of microcracks by the polymer film. Hence, it is of importance that the polymer film is sufficiently developed and distributed randomly over the structure. However, an increase in tensile strength is also measured on samples modified with a polymer emulsion which has a MFT higher than the curing temperature. In this case, the formation of a continuous film is not guaranteed, and the bridging of microcracks is not a sufficient explanation for the increase in the strength. A reason for the increase could be found in the formation of a more amorphous structure. Indeed, the presence of the polymer particles or polymer film prevents the growth of large crystals [7]. Large crystals possess less adhesion capacity, not only because of the lower surface area and correspondingly weak van der Waals forces of attraction, but also because the surfaces can serve as preferred cleavage sites [8].

One has to take into account that the use of a latex implies not only the presence of polymer particles but also introduces secondary admixtures like surfactants and defoamers to the material which may influence the properties. Therefore, a precise characterisation of the latex is necessary.

3. Materials

A test program was set up to investigate the influence of polymer modification on the properties of cement mortar. Different parameters were taken into account such as the type of polymer, the polymer–cement ratio and the curing conditions. Eight different types of

Table 1
Properties of the polymer emulsions and w/c ratio applied in mortar

Symbol	Type of polymer	MFT (°C)	Solid content (%)	w/c
SAE	Styrene–acrylic ester	32	50	0.40
PA	Polyacrylic	$3 \ll 20$	28	0.35
SB1	Carboxylated styrene–butadiene	5	48	0.35
SB2	Carboxylated styrene–butadiene	$-18 \ll 3$	50	0.35
SB3	Styrene–butadiene	$-18 \ll 3$	45	0.35
SB4	Styrene–butadiene	0	46	0.35
SA	Styrene–acrylic	20	50	0.40
PV	Vinyl copolymer	$3 \ll 20$	40	0.40

polymer emulsions were tested. The properties of the emulsions are given in Table 1.

With these different types of polymer emulsions, mortars were made with a sand–cement ratio of 3:1 and a polymer–cement ratio of 10% (mass of solid phase of polymer emulsion divided by mass of cement). A river sand 0/5 and cement CEM I/42.5/R (a rapid-hardening ordinary Portland cement) were used. The w/c ratio of the different mixtures was varied in order to obtain equal flow of 1.61 ± 0.05 measured according to NBN B14-207. The water of the polymer emulsion was taken into account to calculate the w/c-ratio. The w/c ratio for the mortars modified with the different polymer emulsions is given in Table 1.

4. Testing methods

4.1. Determination of tensile strength of polymer emulsions

Prior to the tests on mortar prisms, the tensile strength of the polymer films was measured. Therefore, the polymer emulsions were poured on a glass plate with a film thickness of approximately 1 mm. After film formation at a temperature higher than the MFT of the polymer emulsion, a 40-mm wide and 150-mm long strip was cut from the film, and subjected to a direct tensile test by an Instron 1026. The tensile test was controlled with a crosshead speed of 0.83 mm/s. The tensile stress was calculated taking into account the changing section of the film, presuming a constant volume during the test. An increase in length corresponds to a decrease in width and thickness.

4.2. Flexural and compressive strength tests

Standard prisms, $40 \times 40 \times 160$ mm^3, were made with the mortar according to NBN-EN 196. Different curing conditions were applied: standard curing conditions (2-day moist curing at 20°C and 95% R.H., 5-day water curing at 20°C and 21-day at 20°C and 60% R.H.); dry curing (2-day moist curing and 26-day curing at 20°C and 60% R.H.) and wet curing (2-day moist curing and 26-day water curing at 20°C). After 28 days, all the specimens were stored at 20°C and 60% R.H.

The flexural and compressive strengths, according to NBN-EN 196 were determined after 7, 28 and 90 days of curing as well as dynamic modulus of elasticity, the dry density and the porosity. The dry density is measured after drying at 40°C. A higher temperature could damage the polymer film. The porosity is measured by water saturation after vacuum suction. All data presented are average values of three mortar prisms.

4.3. Chemical attack test

To investigate the influence of sulphuric acid on the structure of modified cement mortar and concrete, samples were subjected to an accelerated degradation test as described by De Belie et al. [9] and to an immersion test [10]. During the accelerated degradation test, concrete cylinders were mounted on rotating axles. Each cylinder is turning through its own recipient with simulation liquid, a 0.5% H_2SO_4-solution by mass, with only the outer 50 mm submersed, at a speed of 1.04 revolutions per hour. After each attack cycle, which lasts for six days, the concrete is brushed with rotary brushes, and concrete degradation is measured with laser sensors. The experimental results, described more in detail in [10], will be compared with those of the bio-degradation tests with sulphur oxidizing Thiobacillus bacteria, that are actually under development.

4.4. SEM observation of microstructures

Specimens were prepared for SEM investigation of the microstructure of the polymer-modified mortar. After testing of the compressive strength, a small sample of the broken surface was taken, and coated with a gold layer. Some samples were, prior to coating, etched with HCl during 5 h and subsequently washed thoroughly with water and dried at 40°C.

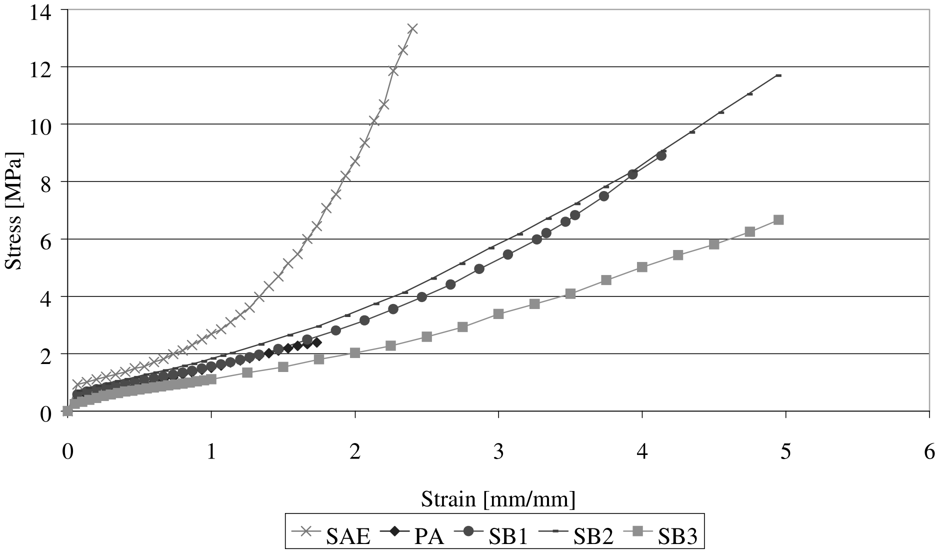

Fig. 2. Stress–strain curves for the different types of polymer emulsions.

5. Test results and discussion

5.1. *Effect of MFT*

The results of the tests on the polymer films (Fig. 2) indicate that in particular the film of the SAE-polymer emulsion shows a high strength at small elongation, which indeed corresponds to a high MFT [4]. The stiffening of the SAE-polymer film with increasing stress/strain can indicate that stronger chemical bonds occur between the polymer particles than for the other polymer films. The polymer film made of PA-emulsion showed a small maximum extension and a low tensile strength. This is due to a large amount of air voids present in the film. Addition of a defoamer to the polymer emulsion could improve the properties of this film.

5.2. *Strength properties of polymer-modified mortars*

Fig. 3 shows the results of the flexural strength measurements. The results indicate an increase in the flexural strength after 28 days up to 30% for the polymer-modified mortar. Only the mortars modified with PA and SA showed much lower results, due to the large porosity. Table 2 gives the results of the porosity measurements as well as of the dry density. The results indicate a decrease in the porosity due to polymer modification, except for PA- and SA-modified mortars. This trend might be a consequence of the measuring procedure. Possibly, the very small pores are not filled by the water, and therefore the decrease in the porosity could also point at a decrease in the size of the pores, as is mentioned in [1] and not in total porosity. In the future experiments, mercury porosimetry will be done to verify this statement.

In all cases, the compressive strength after 28-day standard curing is lower than the compressive strength

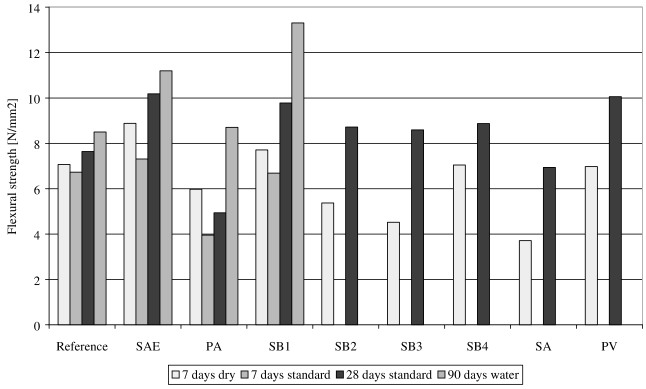

Fig. 3. Flexural strength of mortars after different times of curing.

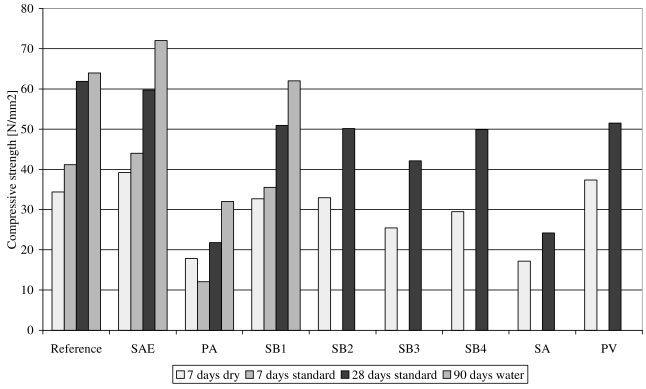

Fig. 4. Compressive strength of mortars after different times of curing.

Table 2
Porosity and dry density of the samples cured for 28 days at standard conditions

Type of mortar	Ref.	SAE	PA	SB1	SB2	SB3	SB4	SA	PV
Porosity (%)	8.1	4.5	18.8	3.9	5.2	5.9	3.8	20.7	6.3
Density (kg/m^3)	2565	2220	1173	2108	2065	2030	2122	1682	2140

of the reference mortar (Fig. 4). This is due to the retardation effect caused by the polymer modification. The compressive strength of the samples modified with SB1 and SAE, water cured during 90 days, is comparable with the compressive strength of the reference mortar.

The question remains if the SAE emulsion is capable to form an adequate continuous film since the MFT (32°C) is higher than the curing temperature (20°C). SEM investigation revealed a polymer film as can be seen in Fig. 5, but this film could be formed during preparation of the sample for the microscopic analysis, since the etched samples were dried at 40°C before coating. However, a test on the pure polymer emulsion indicated that no reemulsification nor a retarded film formation is possible once the polymer emulsion is cured at a certain temperature. The use of the freeze-drying method in further research will clarify this point.

The curing of the polymer-modified mortar and concrete involves two steps: cement hydration and polymer modification. The sequence in which both mechanisms take place is not yet fully understood. Cement hydration is promoted in wet conditions. Polymer film formation takes place when water evaporates and is thereby favored in dry conditions. This phenomenon is visible in Figs. 3 and 4. The flexural strength of the samples cured during seven days at dry curing conditions is higher than that of the samples cured at standard curing conditions (2-day moist and 5-day water curing). However, since the compressive strength is mainly determined by the strength of the cement matrix, it is higher under standard curing conditions, and therefore standard curing is preferred to dry curing in order to reach a higher compressive strength.

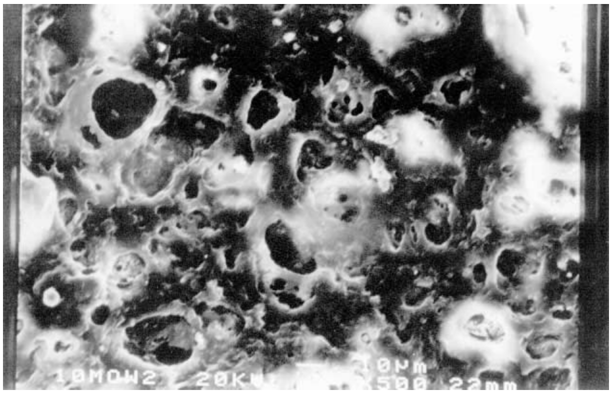

Fig. 5. Polymer film in sample with 10% SAE-etched sample.

5.3. Structure of polymer-modified cement mortar – SEM investigation

The influence of polymer modification on the structure of mortar and concrete is multiple. First of all, there are the bridging of the microcracks, the improved adherence of the cement paste to the aggregate and furthermore the reduction of the pore size and of the degree of crystallinity.

Research done by Afridi et al. [7] indicates a change in morphology of the $Ca(OH)_2$ crystals due to polymer modification. In the absence of polymers, the crystals of $Ca(OH)_2$ are unable to withstand the stresses generated during early hydration, and are therefore distorted to accomodate the spaces formed by the structure of the unhydrated particles and the primary hydration product.

However, the structure of $Ca(OH)_2$ produced in the presence of polymer particles is modified to the extent that the crystals become capable of withstanding such stresses, and hence are found without or with little deformation. This points out the action of the polymer as a kind of bonding agent between the different layers, even in an early stage of hydration.

In this research, a comparable morphology of $Ca(OH)_2$ crystals was found as can be seen in Fig. 6 for a sample modified with 10% SB1. More developed $Ca(OH)_2$ crystals are visible, and at a larger magnification, some small bridges between the different layers can be noticed.

One of the influences of polymer modification is the strengthening of the transition zone between the aggregate and the paste. The transition zone is considered the strength-limiting phase in concrete [8]. It is characterized by a larger porosity and a higher amount of oriented crystals. Due to polymer modification, the porosity of the transition zone decreases, and additional bridging between the matrix and the aggregate appears. When the transition zone of an etched sample is studied, polymer film bridges are clearly visible. Figs. 7 and 8 present the transition zones of the mortars modified with 10% SA and with 10% SB1. The difference in porosity is clearly visible. This is reflected in the results of the strength measurements as discussed before.

Fig. 6. Ca(OH)$_2$-crystal in sample modified with 10% SB1.

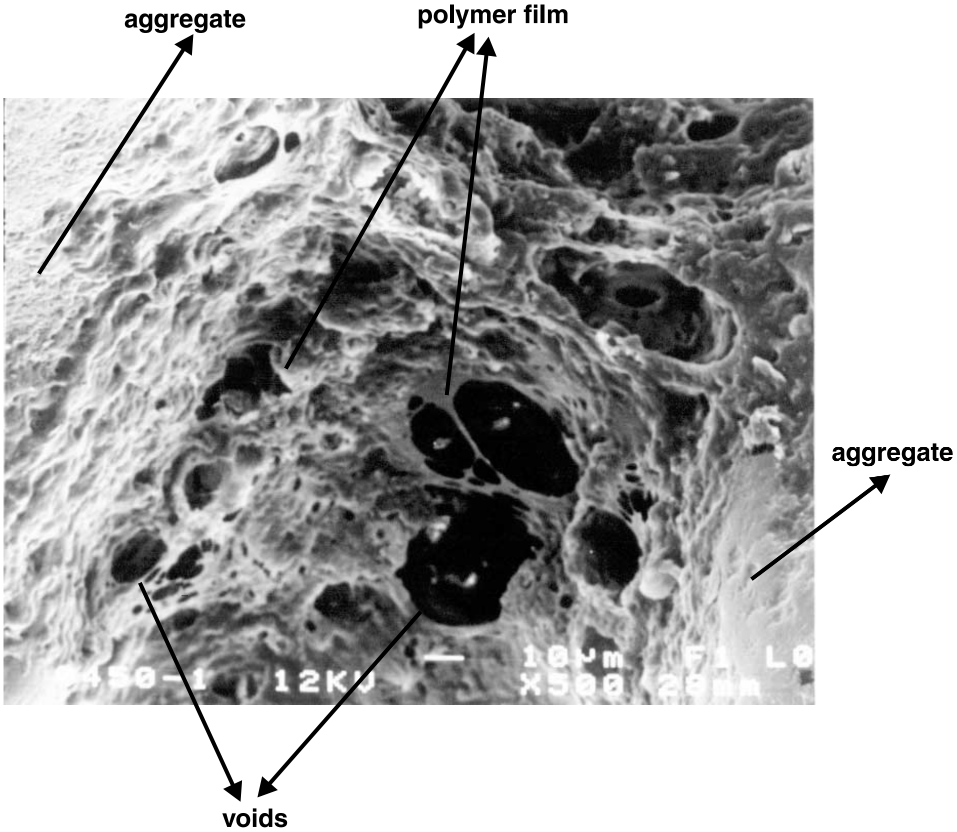

Fig. 7. Transition zone of sample modified with 10% PA-etched sample.

The structure of different samples, attacked during six cycles of the accelerated degradation test, was inspected by means of SEM. As a first conclusion, it can be said that polymer emulsion does not prevent corrosion of concrete by acid attack, but it influences the growth of crystals at the interfaces. This can be seen in Figs. 9 and 10.

Fig. 9 presents a transition zone aggregate-paste in an unmodified sample, prepared with CEM III/A/42.5/LA, a blast furnace slag cement. Large $CaSO_4 \cdot H_2O$ crystals

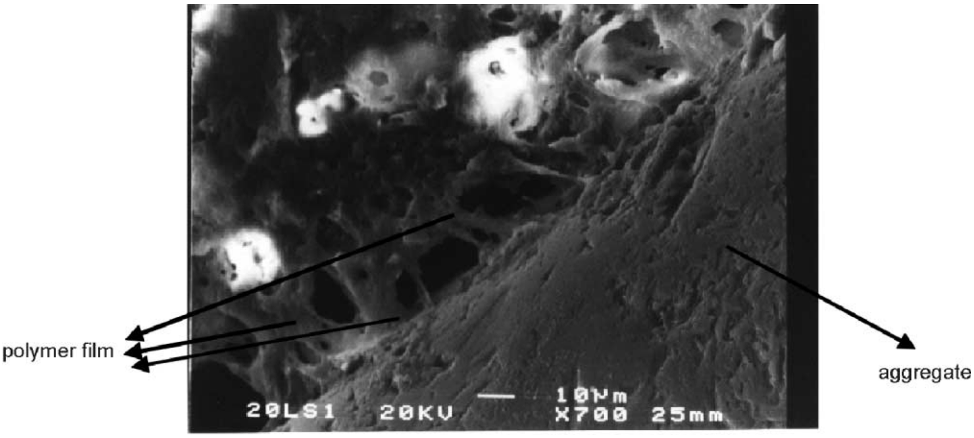

Fig. 8. Transition zone of sample modified with 10% SB1-etched sample.

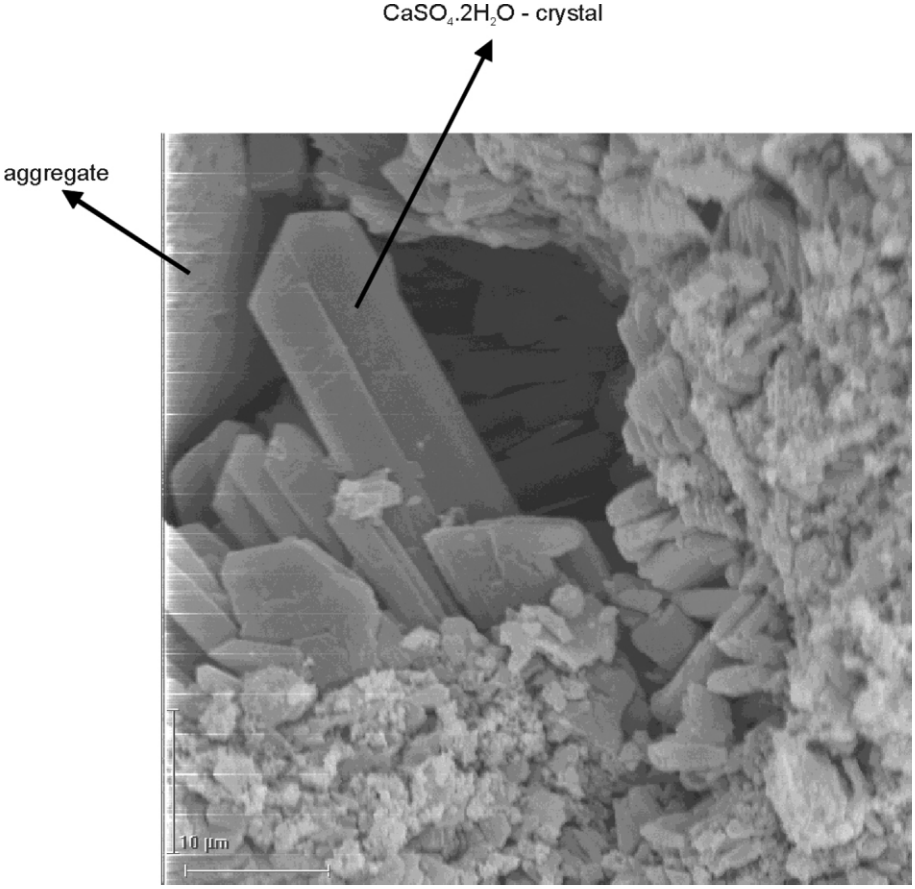

Fig. 9. Transition zone of unmodified sample after corrosion.

are visible at the interface. Due to the low C_3A content of the slag cement, no ettringite is visible.

Fig. 10 presents a similar transition zone of a sample modified with SB1. The attack on the interface zone is clearly visible, but the crystals which are formed are much smaller. This could again point out an encapsulation or a binding of the polymer film with the cement hydrates and/or aggregates. The presence of polymer in the interfaces improves the cohesion of the material, and thus retards the microscopic erosion. Although sulphate corrosion is not stopped, the rate of corrosion showed to be smaller than in non-modified concrete. The non-

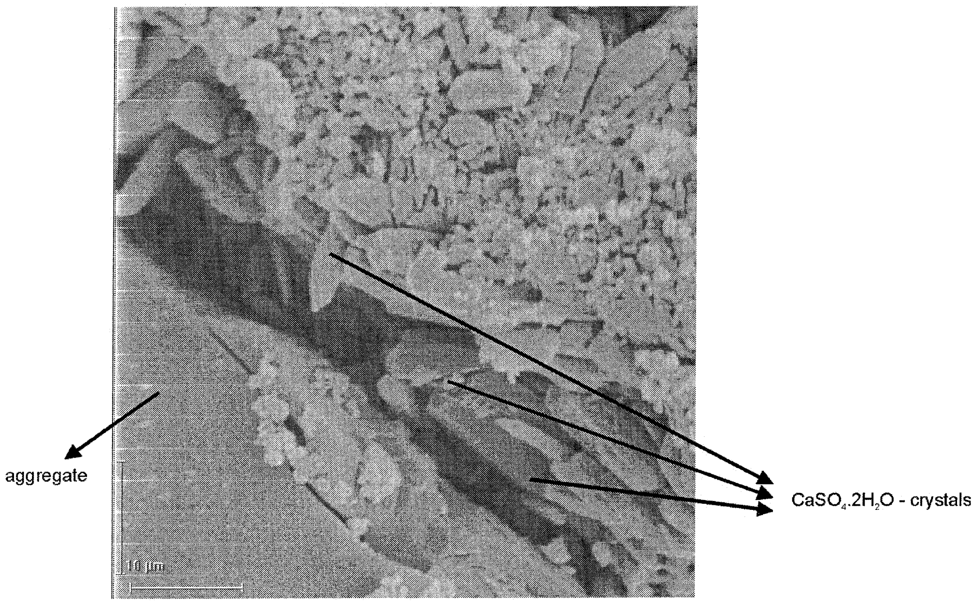

Fig. 10. Transition zone of sample modified with 8% SB1 after corrosion.

continuity of the polymer film seems to be the main reason for the further sulphate induced corrosion. The effect of continuity or discontinuity of the polymer film, and the relation between chemical and biogenic sulphur attack, are the subject of further research.

6. Conclusions

Polymer modification of cement mortar or concrete generates an interpenetrating network of polymer film and cement hydrates in which the aggregates are embedded. SEM study clearly revealed the presence of a polymer film at the aggregate-mortar interface. The density and porosity of the polymer film varied with the type of polymer emulsion. Not only the type of monomer is important but also the minimum film forming temperature and the type and amount of surfactants and defoamer added in the emulsion.

Mechanical tests showed an increased flexural strength and a comparable or slightly reduced compressive strength of the modified mortars for most types of emulsions used. Two types of latex, however, gave insufficient results due to a very large porosity: PA and SA. This was also visible from the tests on the pure polymer film.

A retardation of the cement hydration is noticed. This could point out partly or completely the encapsulation of unhydrated cement particles by polymer film, which results in a simultaneous film formation and cement hydration.

The SEM investigation revealed the restriction on the growth of large crystals by polymer modification. This is also visible in the corroded samples: at the interface of the unmodified samples, large $Ca(OH)_2$ crystals are formed. For the modified samples, the crystals are also formed, but are reduced in size. Further investigation will focus on the durability of the samples.

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