

## **New Trends in Concrete-Polymer Composite Materials and Systems**

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### **ABSTRACT**

Appropriate combination of polymers and classical construction materials provides opportunities for innovative applications and systems, for improved performance and for increased durability. Particularly in restoration and retrofitting, polymer based materials highly contribute to sustainable construction activity. This paper highlights the innovations, new approaches and durability assessments, presented at the International Symposium on Polymers in Concrete in Guimarães, Portugal, 2006. Emphasis is put on microstructure formation, modification by means of hardener free epoxy resin, by polymers in solution or by recycled particles, bond assessment and improvement, durability of bond under moisture and temperature effects, concrete protection by means of coatings.

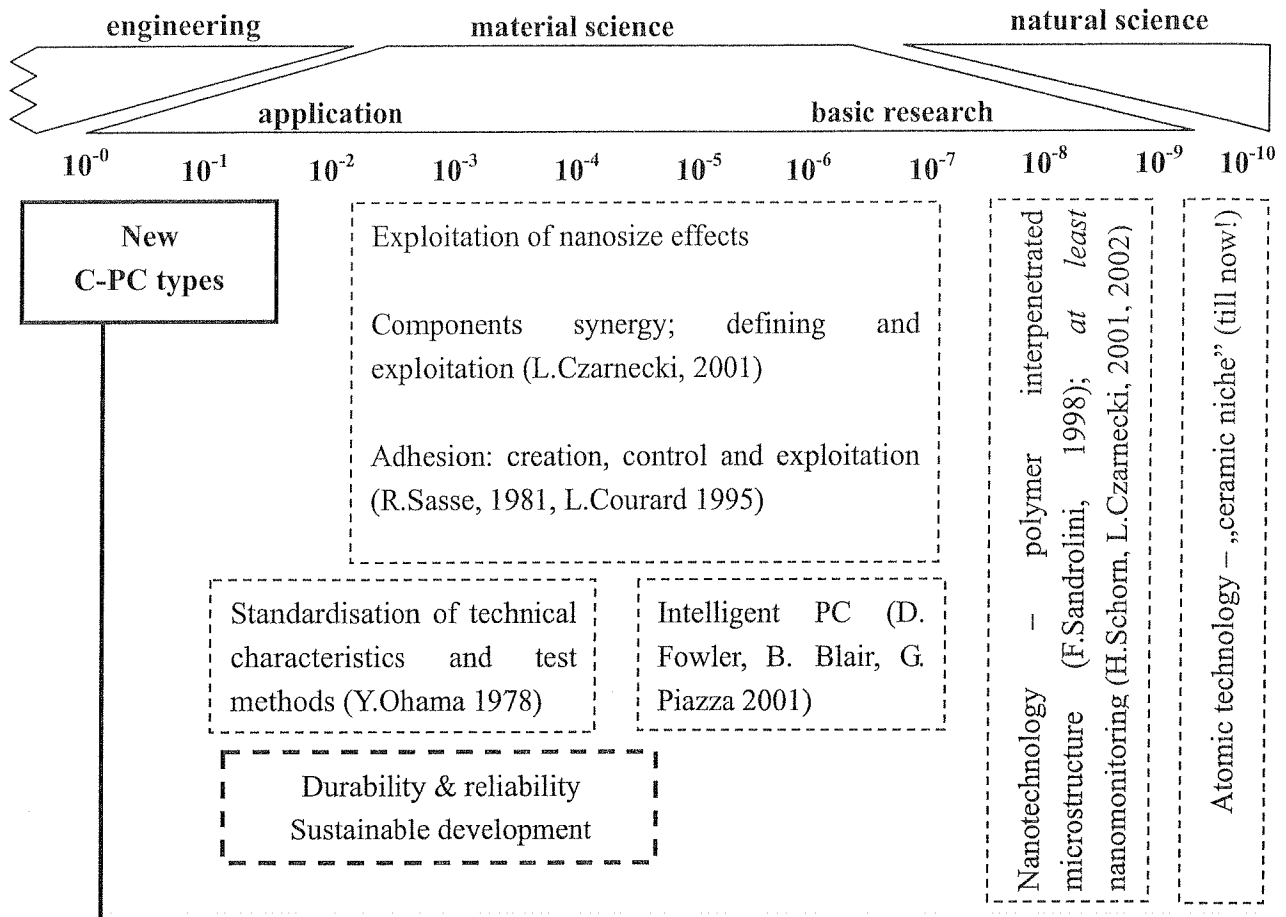
**KEYWORDS:** concrete, polymer composite materials, polymer.

### **1 INTRODUCTION**

Cement concrete and polymers have long been considered to be complementary construction materials. Polymeric materials were used for finishing and protection. Cement concrete was the load bearing structural material. However, it was soon recognized that the synergetic action between polymers and classical building materials offered great opportunities for improvement and for a wide range of new and innovative properties and applications in construction and other industries. Today the use of polymers is part of an intensive search for more performing and sustainable construction materials<sup>[1]</sup>.

The framework of research trends and the state-of-the-art in concrete-polymer composites (C-PC) technology was presented by L. Czarnecki<sup>[2,3]</sup> at the International Symposium on Polymers in Concrete in Guimarães, Portugal, 2006, and is visualized in the scheme of Fig.1. ISPIC 2006 highlighted contributions on: microstructure building; concrete modification by means of epoxy without application of a hardener, by means of polymers in solution and by means of recycled particles; bond assessment and durability of bond under thermal and moisture actions; epoxy bonded external reinforcements; concrete protection; polymer impregnated

textile reinforcement for concrete.



1995	J.Sustersic	Steel Fibre Reinforced Concrete & Polymer Fibre Reinforced Concrete
	F.Sandrolini	recycled polymer/ recycled filler
1998	D.Kruger	lightweight PCC
	Y.Ohama	green PCC
	V.Vidaurre	void-free PC
2001	M.Kawakami	ultralight PCC
	Y.Ohama	self-repairing PCC
	H.Joo, Y.Ohama	slag PCC
2004	D.Jolley,	fly ash PCC
	D.Kruger	
	E.Knapen,	sound absorbing PCC
	D.Van Gemert	
	T.San-Jose	Glass Fibre Reinforced Polymer – Polymer Concrete
2005	Idea acc.	– monomer vapour impregnated concrete
	D.Fowler	– PC-PCC multilayer composites
		– containment vessels for toxic/hazardous wastes (PC, PIC)
		– PC panels – steel or aluminium framing members

Figure 1. Map of C-PC research trends <sup>[3]</sup>

## 2 MICROSTRUCTURE FORMATION

### 2.1 Polymer dispersions

Usually, polymer-modified cement concrete or mortar is prepared by mixing polymer dispersions or redispersible polymer powders with the fresh mixture. The influence of polymer modification on the microstructure is twofold. Due to the presence of the polymers and surfactants, a retardation of the cement hydration is observed. On the other hand, due to the film formation or due to the interaction between the cement hydrates and the polymer particles, the tensile strength of the binder matrix as well as the adhesion strength between the aggregate and the binder phase are enhanced.

The mutual influences between the cement hydrates and the polymer particles and film can be incorporated in an integrated model of structure formation, presented by Beeldens e.a. <sup>[4]</sup>. This model is based on the three-step model of Ohama, but stresses the positioning of the processes on the time scale and the interaction between the different components.

When a dry curing period is included, cement hydration and polymer film formation coincide and encapsulation of unhydrated cement particles is possible. Further, the formation of an interstitial phase, consisting of inorganic and organic precipitates in the bulk phase is pointed out. For an optimal benefit of polymer modification, the amount of these phases should be limited since those polymers are contributing less to the final properties of the material. Based on this integrated model, optimal curing conditions are pointed out.

Estimation of the minimum quantity of polymer to develop a continuous network, the continuity threshold of polymer phase in concrete” has been proposed by P. Łukowski<sup>[5]</sup> using the percolation theory (Fig. 2). The minimum content of polymer in relation to Portland cement has been estimated as equal to 6% by mass. This result is in very good agreement to both experimental and stereological results. The treatment of percolation phenomena as the transformation of a discontinuous structure into a continuous one seems to be an effective method for analysis of the polymer composite microstructure.

a)



b)

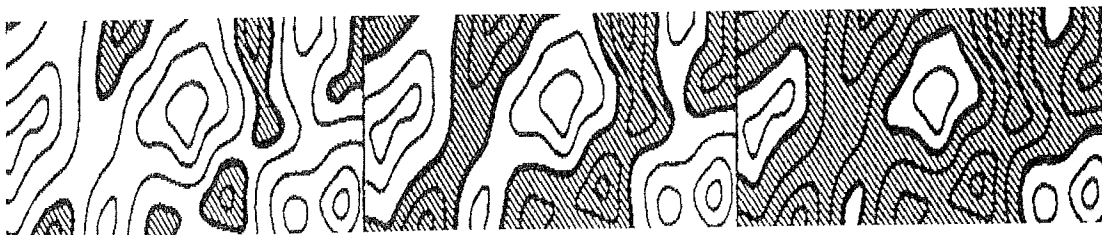
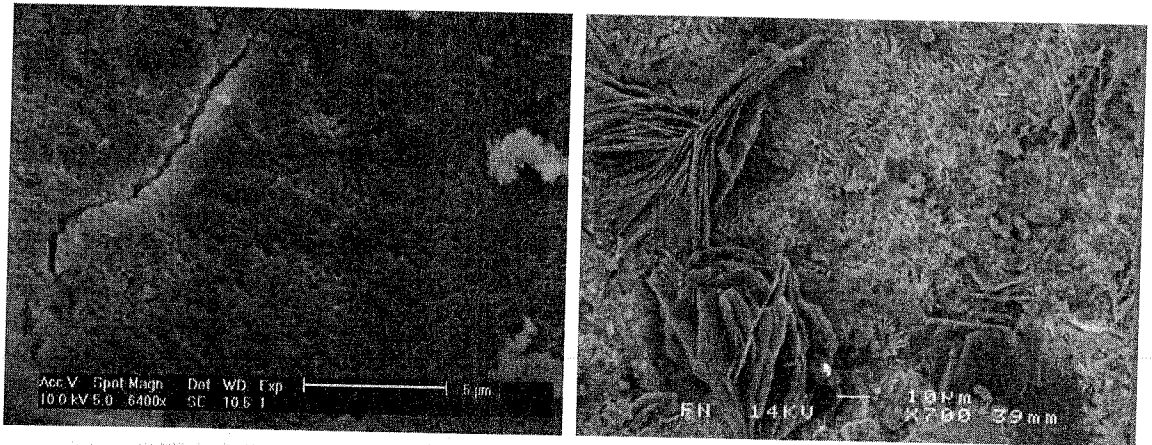


Figure 2. (a) Microstructure of acrylic-cement composite; polymer amount (from left to right): 0%, 5%, 10%; SEM 2000x and (b) schematic presentation of percolation transformation (shaded areas are elements with continuous connection)

## 2.2 Water-soluble polymers <sup>[6]</sup>

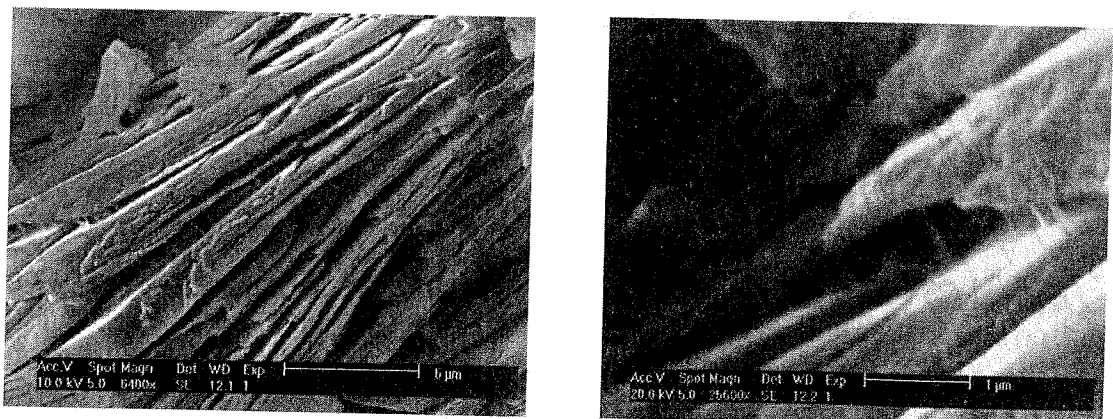
When water-soluble polymers are added instead of polymer dispersions, the polymer molecules are supplied on a molecular scale, improving the approach of the relatively large cement grains by the polymers. In the absence of surface active agents, these water-soluble polymers tend to require a lower proportion in order to be comparably effective as polymer dispersions for some applications.

The microstructure of cement hydrates formed at the air void surfaces is strongly influenced by polymer modification, as shown in Fig. 3. Because of their strong affinity to the gas-water phase, the presence of the water-soluble polymers is expected at the air void surfaces. Water molecules are bound to the polymer particles until sufficient forces are exerted, e.g., by cement hydration. Unmodified mortar beams have a smooth internal pore surface at the micrometer scale. The air void surfaces of mortars modified with methylcellulose (MC) are characterized by an abundant efflorescence of  $\text{Ca}(\text{OH})_2$  crystals, surrounded by needle-like C-S-H. The  $\text{Ca}(\text{OH})_2$  plates are formed parallel towards each other and they are almost undistorted. Methylcellulose has a high swelling capacity and can swell to forty times its dry volume in water. The presence of methylcellulose at the air void surfaces results in a very aqueous environment which promotes crystal formation.



**Figure 3. Air void surface in unmodified (left) and 1% MC-modified mortar (right)**

In Fig. 4, a stack of layered and undistorted  $\text{Ca}(\text{OH})_2$  crystals is shown, formed inside an air void. Polymer bridges are detected between the  $\text{Ca}(\text{OH})_2$  layers, which act as an additional bond, gluing the layers together. Because  $\text{Ca}(\text{OH})_2$  crystals are the weak link in the binder matrix and the surfaces of those crystals form preferred cleavage sites, the strengthening by polymer bridges may result in an improvement of the overall strength of the binder matrix.



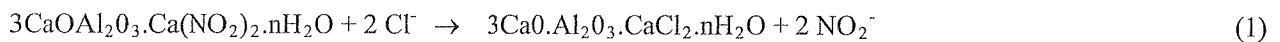
**Figure 4. Polymer bridges between a stack of layered  $\text{Ca}(\text{OH})_2$  crystals in 1% MC-modified mortar**

### 3 HARDENER-FREE EPOXY WITH NITRITE-TYPE HYDROCALUMITE

Conventional epoxy-modified mortars and concretes have an inferior applicability due to the two-component mixing of the epoxy resin and hardener, the toxicity of some hardeners like polyamine or polyamide, and the obstruction of cement hydration by the polymer. However, even without hardeners the epoxy resin can harden in the presence of the alkalis or hydroxide ions produced by the hydration of cement in the epoxy-modified mortars. Such new epoxy-hydraulic cement systems provide an increase in the flexural strength and a marked improvement in the carbonation or chloride ion penetration resistance.

In hardener-free epoxy-modified mortars with polymer-cement ratios of 20% or less, the hardening degree of the epoxy resin is 50 to 90 %, and unhardened epoxy remains. It is considered that the unhardened epoxy resin may be sealed with hardened epoxy resin phase in the epoxy-modified mortars. The epoxy resin phase forms self-capsuled epoxy resin. The self-capsuled epoxy resin can be broken at cracking of the epoxy-modified mortar under loading. The unhardened resin in the self-capsuled epoxy phase may fill microcracks, thus providing a self-healing capacity to the mortar.

Nitrite-type hydrocalumite [ $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{NO}_2)_2\cdot n\text{H}_2\text{O}$ ] is a corrosion inhibiting admixture or anticorrosive admixture which can adsorb the chloride ions ( $\text{Cl}^-$ ) causing the corrosion of reinforcing bars and liberate the nitrite ions ( $\text{NO}_2^-$ ) inhibiting the corrosion as expressed by the formula:



**Table 1. Quality levels of hardener-free epoxy-modified mortars with calumite at polymer-binder ratio of 10 %**

Test item	Quality requirements in JIS A 6203	Test results
Flexural strength (MPa)	> 8.0	9.8 ~ 10.3
Compressive strength (MPa)	> 24.0	43.7 ~ 50.8
Adhesion to mortar (MPa)	> 1.0	1.0 ~ 1.2
Water absorption (%)	< 10.0	1.3 ~ 1.6
Water permeation (g)	< 15.0	1.3 ~ 1.5
Length change (%)	0 to 0.150	0.07 ~ 0.10

It provides excellent corrosion-inhibiting property to the reinforcing bars in concrete. Consequently, polymer-modified mortar with superior corrosion inhibiting property and durability is expected when combining the use of nitrite-type hydrocalumite and hardener-free epoxy-resin, with beneficial use as an effective repair material for deteriorated reinforced concrete structures [7]. A testing program was executed with various nitrite-type hydrocalumite contents and polymer-binder ratios. The following conclusions could be drawn from the experiments:

- to maintain a constant consistency, the water-binder ratio of hardener-free epoxy-modified mortar with calumite must be increased lightly with increasing calumite content or polymer-binder ratio. This is ascribed to the porous layered structure of calumite, and to the absence of surfactants in the epoxy resin;
- increasing calumite content improves the corrosion inhibiting property of hardener-free epoxy-modified mortars, but decreases compressive strength, adhesion to mortar substrates and waterproofness, and

increases drying shrinkage. Increasing the polymer-binder ratio improves flexural strength, adhesion to mortar substrates and waterproofness.

At calumite contents up to 10 % of cement binder and polymer-binder ratio of 10 % the hardener-free epoxy-modified mortar satisfies all the quality requirements specified in JIS A 6203, as given in Tab.1.

#### 4 BOND ASSESSMENT

The adhesion between repair material and concrete substrate is one of the most important factors that affect the reliability and durability of repair. A high adhesion allows higher tolerance on non-compatibility of properties of both materials [8]. This is also reflected in the European Standard EN 1504-10 (2003) and ACI Concrete Repair Manual (2003), where the bond quality is the main requirement on the repair system. Adhesion depends on various phenomena taking place in the interfacial zone. Among others, the quality of the concrete substrate resulting from surface treatment belongs to the most important factors. This implies that before any repair operation, an effective assessment of the concrete substrate has to be performed. Besides the surface preparation of concrete, evaluation of the cohesion of the superficial concrete is requested for adhesion and durability reasons.

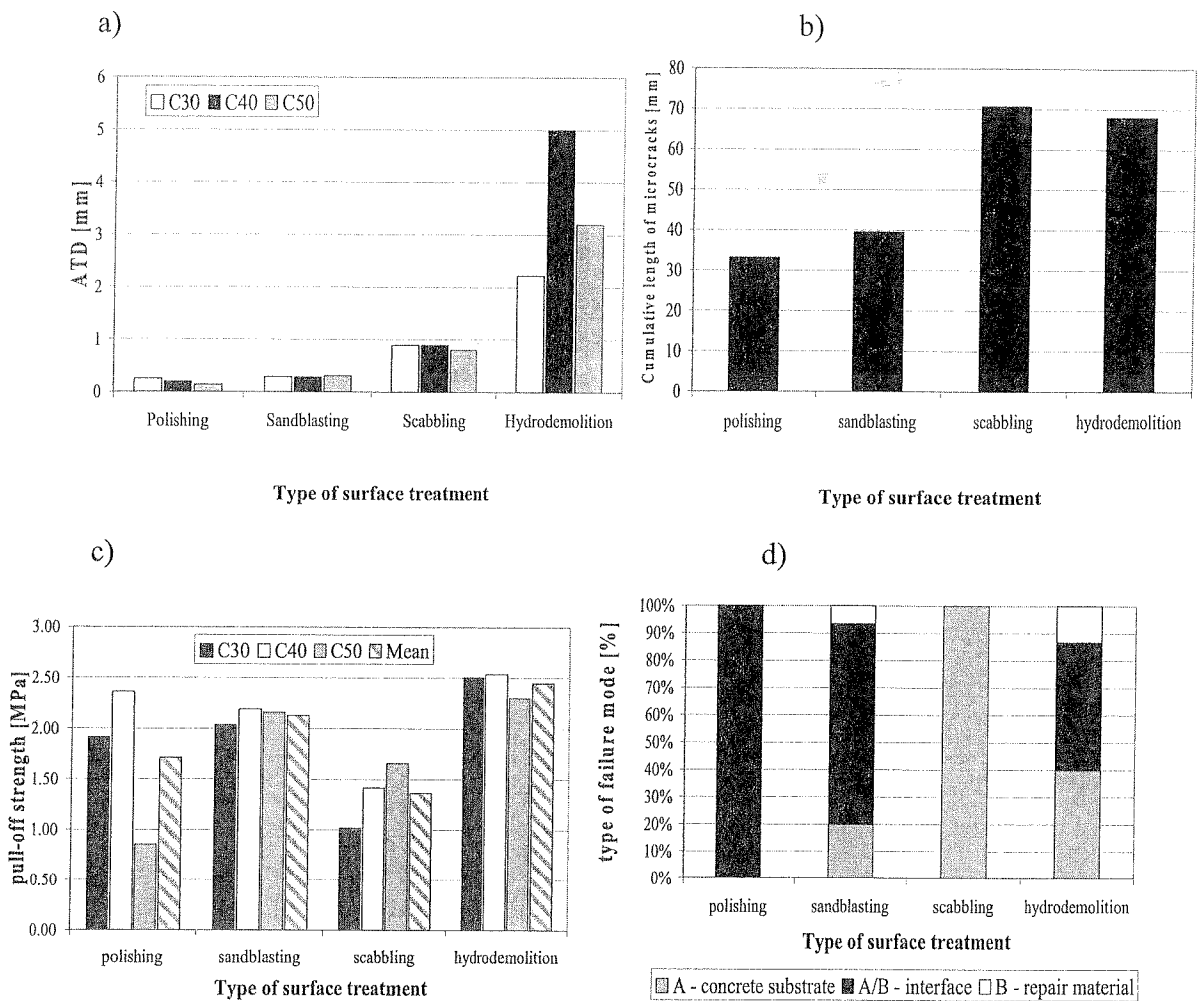
Many authors describe the influence of the surface preparation technique on the superficial cohesion of concrete or the adhesion. However, research on the real effects of the surface preparation technique just started with the quantification of superficial microcracking or roughness. The investigation described in the ISPIC'06 paper by Courard et al. [9] concerned the influence of concrete substrate strength and preparation technique efficiency. Three types of concrete (C30, C40 and C50) and four types of surface preparation have been combined in twelve different concrete slabs. The quality of the superficial concrete has been characterized according to different destructive and non destructive techniques: surface roughness (Average Texture Depth test according to EN 13036-1:2000), compressive strength, superficial cohesion (pull-off test), Impact Echo measurements and cracking quantification (microscopical observations). A self-compacting polymer-cement mortar has been applied and adhesion has been evaluated by means of pull-off tests.

The following conclusions may be drawn from the present investigations concerning the concrete substrate evaluation and the adhesion of repair systems:

- the quality of concrete substrate surface (roughness and microcracking) strongly depends on the surface preparation technique used (Fig. 5a,b); microcracking was observed mainly in the superficial zone of concrete (2 cm) and the number and orientation of microcracks depend on type and "aggressiveness" of the treatment; additionally relatively low effect of concrete strength on the surface quality was observed;
- bond strength (Fig. 5c) after hydrodemolition and sandblasting is greater than the threshold minimum values for laboratory performance, while it is close to the limit for polishing and scabbling; in the case of polishing, all failures during pull-off test appeared at the interface between concrete substrate and repair mortar (Fig. 5d). Scabbled (needle hammered) surfaces present ruptures near to the interfacial zone, due to microcracks;
- there is no clear relationship between the class of concrete strength and the pull-off strength. The concrete strength class had no influence on bond strength for sandblasting or hydrodemolition but it had an effect in the case of polishing and scabbling; the concrete strength had no effect on the failure mode in the pull-off test.

These conclusions lead to the following consideration: microcracking is really an essential parameter in the evaluation of the quality of the concrete substrate before repairing. However, it remains a very difficult property to clearly evaluate, necessitating long preparation and laboratory investigations: an on-site test like

surface permeation, as already used in metal welding technology, should be soon developed in order to simplify concrete surface assessment.



**Figure 5. Average texture depth (a), mean cumulative crack length (b), pull-off strength (c) and fracture mode (d) for repair systems after various surface treatments of concrete substrate**

The pull-off test is commonly used to test the bond strength. However, non-destructive methods (NDT) are preferred for this purpose, especially in the case of large-area structures. A majority of NDT methods mentioned in EN 1504-10 and ACI Concrete Repair Manual for repair efficiency assessment are based on propagation of stress waves. Particularly, the ultrasonic method and the impact-echo method are recommended. In the selection of an NDT method, many factors should be taken into account, e.g. type and size of defects at the interfacial zone, type of repair material (cement or polymer), thickness of overlay, roughness of concrete substrate. The usability of impact-echo and ultrasonic methods for the assessment of the quality of various repair systems was analysed by Garbacz<sup>[10]</sup>.

## 5 DURABILITY

The performance of concrete and the durability of structures are now, more than ever, subject to intensive research. Special attention has been drawn to the durability of epoxy resins and fiber-reinforced polymers (FRP), the durability of concrete coatings and the use of hydrophobing agents in concrete.

The durability of bonds with polymers, especially when they are subjected to severe environmental conditions, is still not well known. This issue strongly hinders their wide spread use as the lifetime of the bond can not be well



defined. Lettieri et al. <sup>[11]</sup> studied the effect of aging, both natural and artificial, of three cold-curing epoxy resins. The mechanical, thermal and colour properties are analysed after exposure to both an environment with 70 °C and 75% RH and natural weathering. The accelerated aging, with both high temperature and high levels of relative humidity, led to different behaviours of the epoxy resins under study. Results show that a plasticization effect occurred due to water absorption in two of the resins studied.

Lettieri et al <sup>[11]</sup>. observed that the post-cure counteracted in part the decrease of the glass transition temperature ( $T_g$ ) due to the plasticization effect of water. The changes seem to be reversible and follow the cyclic climatic conditions. Furthermore it was observed that the higher temperatures achieved, during the warmer months, are apparently sufficient to promote variations of the properties of these resins.

In a similar study, two commercial epoxy composites, carbon fiber reinforced polymer (CFRP) and glass fiber reinforced polymer (GFRP), and three epoxy adhesives were subject to both a natural and artificial environmental loading. Specimens were exposed to 40 °C and 90 % RH for six months. Tensile tests were performed on the composite materials before and after the exposition to artificially simulated severe environments. Again the combination of humidity and temperature can be severe for the properties of thermosetting resins as the glass transition temperature of the resins is approached as reported by Frigione et al <sup>[12]</sup>.

## **6 POLYMER IMPREGNATED TEXTILE REINFORCEMENT FOR CONCRETE**

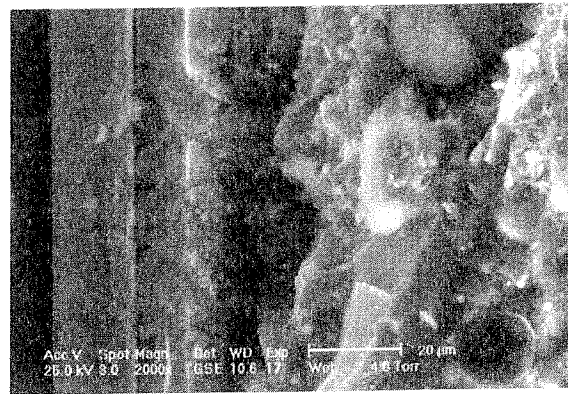
Textile reinforced concrete enhances the possibilities in the design and production of high-strength thin-walled structures. Focus has been put on textiles made of glass, basalt, carbon and high-module polymers. The contribution of the textile reinforcement to the performance of the composite stays far below the expectations, based on the intrinsic qualities of the textile fibres. The bond and load-bearing behaviour must therefore be optimized. The main reason for the low efficiency lies in the inhomogeneous force transmission between the individual filaments in the textile yarns. While the outer filaments are embedded in the cementitious matrix and take most of the load, the inner filaments of the textile contribute only minor to the load transmission, probably only by friction. Different strategies for the improvement of the bond behaviour have been studied, such as the improvement of the cement penetration in the textiles, the use of hybrid yarn structures, and the application of polymers.

Due to the small diameter (150-200 nm) of the particles aqueous polymer dispersions better penetrate into the core region of the roving. Using a polymer-impregnated textile reinforcement in cement matrix gives a bond of fibre-matrix-interface which is primarily realized by hydration products. Polymer particles can interact with hydration products to improve the bond. By impregnating the reinforcement with an uncured polymer, the friction and adhesion between all filaments in the roving is increased due to the presence of polymer particles and consequently the load transfer capacity increases too. The load capacity considerably exceeds that of the untreated reinforcement <sup>[13]</sup>.

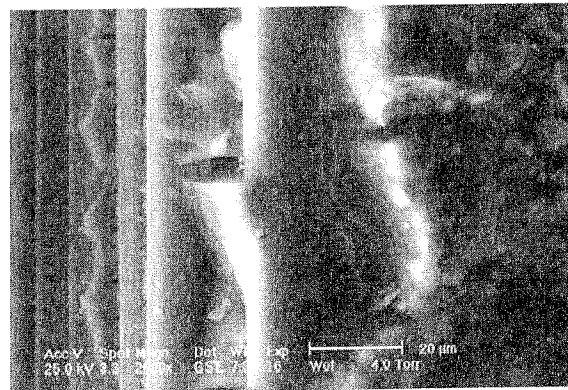
The impregnated uncured textile reinforcement is strongly hygroscopic. After mounting in the fresh concrete the rovings suck in water that contains fine particles of the cement paste. A small part of the polymer particles migrates into the concrete that encircles the roving. With progressing hydration the generated CH- and CSH-phases penetrate in this dispersion liquid and use the stored water for further hydration product formation. Losing this water the polymer particles further converge and coagulate by cohesion between the particles forming compact clusters or they accumulate as single small polymer spheres at the filament surfaces (Fig. 6). Both effects result in a more effective and deeper fill-in zone, and thus a better composite behaviour. Polymer modification of the cement matrix leads to similar processes, but the effect of the polymer is much less pronounced. The penetration of cement hydration products and polymer particles into the roving rapidly



decreases from surface to roving depth (Fig. 10). Therefore, the combination of polymer impregnation of the roving with polymer modification of the matrix will be subject of further investigations.



**Figure 6. Penetration and intermingling of polymer agglomerates and hydration products between textile filaments <sup>[13]</sup>**



**Figure 7. Uncovered filaments in the core zone of a roving, embedded in cement matrix, polymer/cement ratio of 15 % <sup>[13]</sup>**

## 7 CONCLUSION

The use of polymers in construction industry is steadily growing. The synergic action of polymers and cement mortar and concrete offers great opportunities for improvement and for a wide range of new and innovative applications. Society and environment require corrective actions to be taken continuously. The use of polymers should be well-considered to guarantee better performance and improved sustainability.

Polymers are no longer special construction materials that replace classical mineral or organic building materials. They are now one vital component in the production of composite and sustainable building materials. They will further allow the development of new and durable constructions, as well as new and durable restoration and retrofitting techniques.

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