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New Generation Polymer Technology Available to be Used in Plaster and Cementitious Fibre and Non-Fibre Spray On and Grout Systems

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NEW GENERATION POLYMER TECHNOLOGY AVAILABLE TO BE USED IN PLASTER AND CEMENTITIOUS FIBRE AND NON-FIBRE SPRAY ON AND GROUT SYSTEMS

Allison Golsby

ABSTRACT: Polymer plaster forms part of a group of spray on products that use polymers to supplement or replace cement as a binder in grout systems. The types include but are not limited to polymer plasters, polymer-impregnated concrete, polymer concrete, and polymer-Portland-cement concrete. Polymer plaster and concrete has historically not been widely adopted due to the high costs and difficulty associated with traditional manufacturing techniques. However, recent progress has led to significant reductions in cost, meaning that the use of polymer plaster and concrete is gradually becoming more widespread.This paper will focus on addressing aspects of the use of polymers.

INTRODUCTION

Engineered Cementitious Compounds (ECCs), unlike common fibre reinforced concrete, is a family of micromechanically designed material. As long as a cementitious material is designed/developed based on micromechanics and fracture mechanics theory to feature large tensile ductility, it can be called an ECC. Therefore, ECC is not a fixed material design, but a broad range of products under different stages of research, development, and implementations. The ECC material family is expanding. The development of an individual mix design of ECC requires special efforts by systematically engineering of the material at nano-, micro-, macro- and composite scales.

Some polymers can be added plasters or concretes and used to supplement or replace an original binder. The types include polymer-impregnated concrete, polymer concrete, and polymer-Portland-cement concrete, as well as applications using gypsum and other cementitious products. In these ECCs, thermosetting resins are used as the principal polymer component due to their high thermal stability and resistance to a wide variety of chemicals. ECCs can also be composed of aggregates may include silica, quartz, gypsum, granite, limestone, and other high quality material. The aggregate must be of good quality, free of dust and other debris, and dry. Failure to fulfil these criteria can reduce the bond strength between the polymer binder and the aggregate.

ECC may be used for new construction or repairing old concrete. The adhesive properties of ECCs allow patching of both polymer and conventional cement-based and non-cement based compounds. The low permeability and corrosive resistance of ECCs allows it to be used in civil, road and mining applications, such as sewer structure applications, drainage channels, electrolytic cells for base metal recovery, geomechanics, Ventilation Control Devices (VCDs) and other structures that contain liquids, toxic or corrosive chemicals. It is especially suited to the construction and rehabilitation of manholes due to its ability to withstand toxic and corrosive sewer gases and bacteria commonly found in sewer systems. ECC does not require coating or welding of PVC-protected seams.

ECC has historically not been widely adopted due to the higher costs and difficulty associated with traditional manufacturing techniques. However, recent developments in polymer production and ECC assembly has led to significant reductions in cost, meaning that the use of polymer concrete is gradually becoming more widespread.

RELATIONSHIP TO THE MINING INDUSTRY

Portland cement and gypsum based products are currently the most widely used construction materials in underground mining. The historical characteristics of Portland cement include:

- Low cost,
- high stiffness,
- high compressive strength,
- non-flammability,

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- ease of fabrication,
- whilst low tensile strength,
- brittleness, and
- long -term durability.

Reinforcing cement with steel provides increased tensile strength and the incorporation of fibres increases its toughness (resistance to crack propagation). Polymers increase ECC tensile and flexural strength and reduces its brittle nature by increasing toughness. In this paper field of ECC will be reviewed.

Geopolymer cements are inorganic hydraulic cements and are based on the polymerization of minerals (Davidovits, Davidovits, and James 1999). The term more specifically refers to alkali-activated alumino-silicate cements, also called zeolitic or polysialate cements. They are used in construction, with high-early strength applications, and waste stabilisation. These cements do not contain organic polymers or plastics.

BRIEF HISTORY

The ancient history of using natural polymers, like asphalt to modify mortars, goes back to the Babylonians, Egyptians and ancient India.

The concrete history timeline according to Auburn 2000 and Brown 1996:

- 9000 BC – Cement floor discovered in Israel in 1985
- 3000 BC-Egyptian Pyramids. The Egyptians were using concrete over 5000 years ago to build pyramids.
- 300 BC - 476 AD-Roman Architecture. The ancient Romans used a material that is remarkably close to modern cement to build many of their architectural marvels, such as the Colosseum, and the Pantheon. The Romans also used animal products in their cement as an early form of admixtures.
- 1824-Portland Cement Invented.
- 1836-Cement Testing. The first test of tensile and compressive strength took place in Germany.
- 1889- The first concrete reinforced bridge was built.. Alvord Lake Bridge is over two hundred years old.
- 1903-The first concrete high rise was built.
- 1908-Thomas Edison designed and built the first concrete homes.
- 1913-The first load of ready mix was delivered.
- 1915-Coloured Concrete. L.M. Scofield, products included colour hardeners, colourwax integral colour, sealers, and chemical stains.
- 1930-Air Entraining Agents. Air entraining agents were used for the first time in cement to resist against damage from freezing and thawing.
- 1938-Concrete Overlay. Latex was added to Portland cement, aggregate, and other materials to make a covering for ship decks.
- 1950's-Decorative Concrete Developed. The Bomanite process was developed, the original cast-in-place, coloured, textured and imprinted architectural concrete paving.
- 1970's-Fiber Reinforcement
- 1980's-Concrete Countertops
- 1990-Concrete Engraving
- 1992-Tallest Concrete Building
- 1999-Polished Concrete

Europeans in the Middle Ages, used ox blood and egg white to increase the durability of lime mortars. The modern history of man-made modifiers starts in the late forties, with the development of butadiene styrene, polychloroprene and acrylic latex in modified mortars and concrete. The main application of latex polymer modified cements at that time was for concrete repair. The use of polymers in the fabrication of bridges and parking garage overlays was developed in the early seventies.

The prime function of the polymer was to reduce concrete permeability and increase resistance to chloride penetration, toughness and adhesion. Dry polymer modifiers, so called redispersable powders, based on Ethyl-Vinyl Acetate (EVA), polyvinyl acetate-vinyl arboxylate, (VA/VeovVa), acrylics, styrene-acrylics and others were introduced in the early eighties. Dry polymer modifiers allow the formulation of one-component systems.

Initially dry polymer modifiers were inferior in many aspects to early polymers.

DESCRIPTION OF POLYMERS

A polymer is a high molecular weight molecule, usually a linear chain of many repeat units. All plastics fall under the category of polymers, but also natural products such as cellulose, proteins, DNA etc. The repeat units are called monomers, and these are polymerised in a wide variety of processes. The polymers we are referring to in this paper are dispersions and their spray-dried, dispersible versions. Dispersible polymers are produced in a process called emulsion polymerisation – the monomers are emulsified and reacted in water, and the end result is a dispersion of small particles (typically 100 nm to several microns in diameter, containing up to 10,000 polymer chains) in water, stabilised by surfactants or colloids such as polyvinyl alcohol.

In this application, the water evaporates, the particles come closer to each other and fuse (film formation) and can bind other ingredients (such as sand or limestone) together in the process. Depending on the nature of the monomers and their other properties, the dispersions can be used in a wide variety of applications, such as water-based paints, adhesives, carpet backing, paper and cardboard coatings, and in construction products. The last application area – construction – is the area from which the use of such polymers in mining, has been derived.
The polymer dispersions are used as admixtures to cement mortars in two-component products.

Initial findings, using this combination, were obtained as far back as the twenties and early thirties. A milestone in the mortar modification was reached with the invention of dispersible polymer powders, by the Munich-based company Wacker Chemie AG. Their first polymer powder was launched in 1957 under the trade name VINNAPAS®.

Polymer powders are spray-dried dispersions. The production of these powders is not simple: dispersions which will form continuous and, in some cases, tacky films at room temperature. They have to be converted into free-flowing and storage stable, water-free powders. Before the spray-drying process is run, a water soluble protective colloid (for example polyvinyl alcohol) is added, which surrounds the dried emulsion particles to keep them separate and to protect them against premature coalescence. Once the applicator (or pump) adds water to the mortar on site, the polymer disperses and the mortar is practically indistinguishable from a mortar modified with dispersion.

Since the seventies, there has been an increasing trend towards the substitution of mortar additives in dispersion form, with polymer powders. This allowed the producers of a construction mortar to add the polymer to the cement or plaster mixes in their pre-blended, bagged form, whereas the liquid dispersion needed to be added on site. This process has the advantage that the amount of polymer could be controlled, and that the logistics of bringing product to a site became a lot easier, especially underground applications.

Since then the use of these dry versions in construction mortars has been growing steadily. The modification of cement based mortars with thermoplastic film forming polymers for a variety of applications is very common today in the Australian construction industry.

Examples for these applications are thin-bed tile adhesive mortars and tile grouts, self-levelling flooring compounds, renders, cement paints, concrete repair mortars, injection grouts, and even concrete itself.

CURRENT USE IN PLASTER AND CEMENT-BASED PRODUCTS

The addition of polymer powders to mineral binders, both cement and gypsum, hydrated lime or high alumina cement, improves a range of properties of hardened and fresh mortar. They include:

- increased open time for adhesives,
- better cohesion for sprayed products,

- better rheology once placed on the target surface (either more flowing, or the opposite to keep the product in place),
- improved adhesion to critical substrates,
- increased flexibility and deformability,
- crack-free curing,
- increased abrasion resistance,
- water-proofing,
- In some cases a higher compressive strength,
- better freeze/thaw resistance where it is relevant.

HOW POLYMER POWDERS WORK

At low polymer dosage, the polymers help bind together the other constituents of the ECC, mostly the fillers, just as the cement does in concrete. The polymers are often found in discernible local domains as well as in enhanced concentrations at the surface of a mortar, or between the mortar and the substrate the mortar was applied to, increasing the adhesion, especially if the substrate is not porous but smooth and dense.

Electron micrographs are used to investigate the structure of a mortar containing polymer powders in their cement matrix. In Figure 1, the dried polymer can be clearly seen. The polymer powder works as a second binder in the cementitious system. The polymer is concentrated in the voids where the water was during the drying process. As the water evaporates or is used to hydrate the cement, the polymer particles form a film – a polymer domain (compare arrows). The tensile adhesive strength of such a resin domain is higher than the tensile adhesive strength of a cementitious mortar. Therefore the domains act like a reinforcing material to enhance the adhesion between the mortar and the dense tiles, as shown in Figure 1.

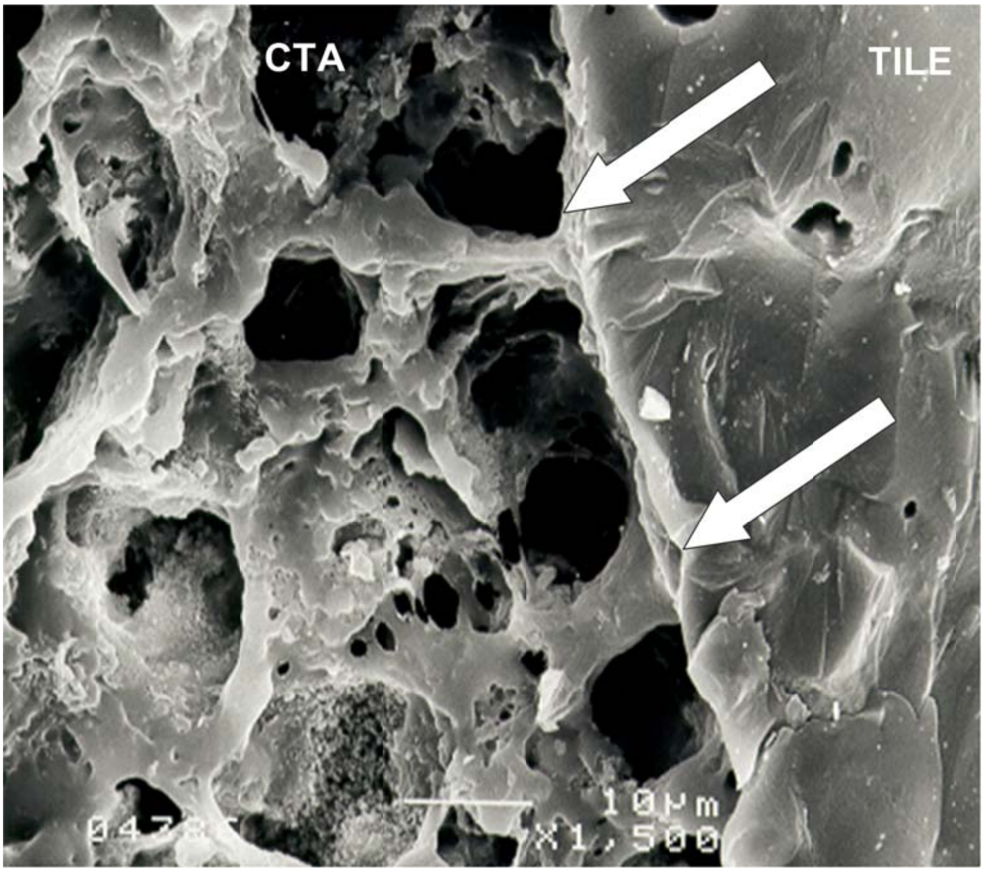

Figure 1: ceramic tile adhesive (CTA), modified with VINNAPAS® polymer powder, on porcelain tile x1500 (Wacker Chemie AG)

At a higher dosage the volume of polymer starts to dominate the cement, and at very high dosages, such as used in water-proofing membranes, the polymers form the matrix, and the cement can be considered as the reinforcement.

Graphic examples of the properties conferred by the polymers can be seen in Figures 2 and 3.

Figure 2 shows the deformation in a three-point bending test of a cementitious mortar where the level of polymer modification was varied between 0% and 15%. The Figure shows the substantial increase in deformation the mortar can sustain before breaking. This mortar is used to make flexible cementitious tile adhesives and mining grouts.

Figure 3 shows examples of cement-polymer mixtures at the same polymer: cement ratio, where the inherent flexibility of the polymer was changed. This illustrates the ability to control the properties of the mortar by controlling the type of polymer used. There are many polymers available.

Figure 4 is a photograph of the dry-spray shotcrete application modified by these types of polymers in a mine. The modification resulted in a marked improvement of the water-proofing properties of the shotcrete, even though the percentage of polymer was not high enough to create continuous film of polymer in the concrete. Instead the polymer domains allowed the shotcrete to cure crack-free to the extent that the shotcrete itself was water-proof.

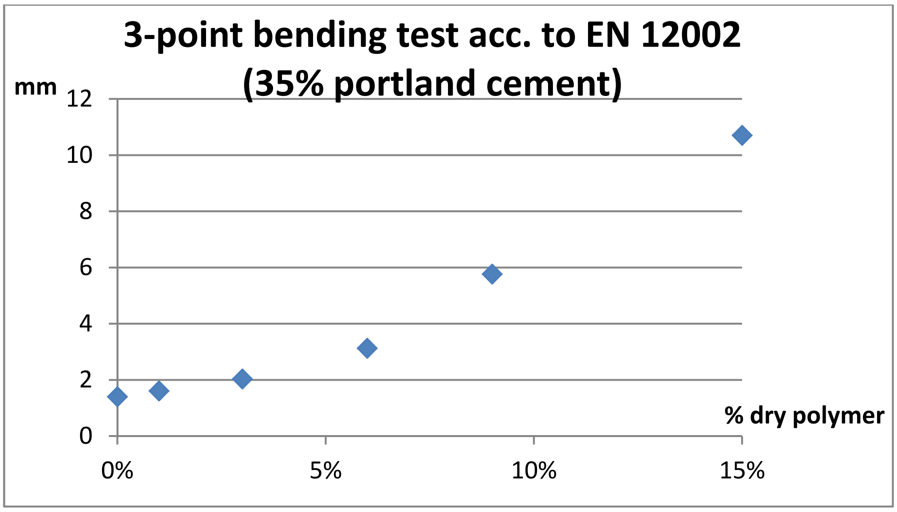

Figure 2: 3 point bending test acc. to EN 12002 (35% Portland cement) (Wacker Chemie AG)

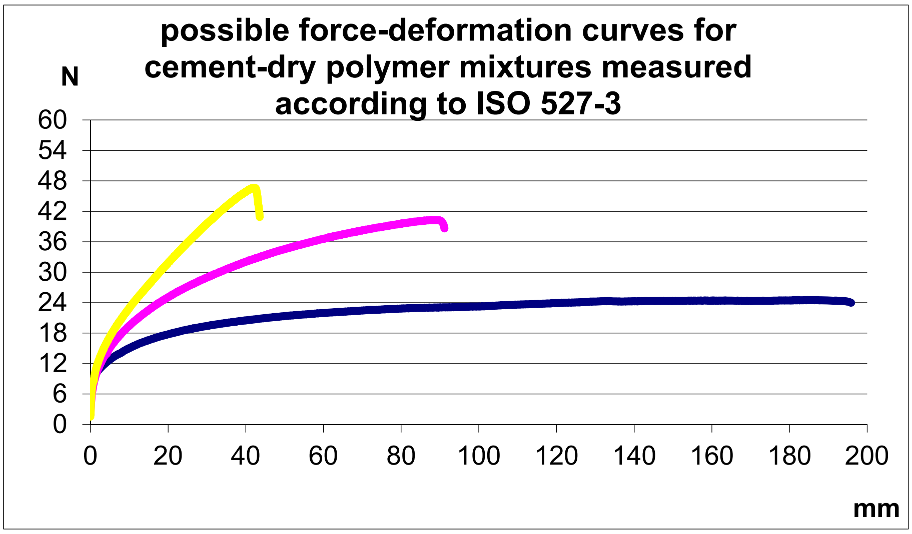

Figure 3: possible force-deformation curves for cement-dry polymer mixtures measured according to ISO 527-3 (Wacker Chemie AG)

Figure 4: ECC application (Wacker Chemie AG)

CASE STUDY

Despite concrete in general not being a widely used product in underground coal compared to hard rock – much less specialised fibre concrete, there have been uses dating back many years.

Fibre in concrete can be divided into two sections:

- Macro fibre – any type of fibre that is generally in excess of 30mm in length. The first Macro fibre was made of steel, which is still used in civil applications however; "plastic macro fibre" is the preferred additive in just about 100% of hardrock shotcreting in Australia. The use of course concrete and macro fibre in underground coal mines has been very limited. The limiting factors include: the size of pumping equipment, logistics to site and the poor adhesion relationship between coal and general concrete).
- Micro fibre – again "plastic" fibre dominates this market with the fibre length ranging from 6mm to about 15mm. This type of fibre is compatible with the dry gunite pumping systems which are the primary source of concrete and plaster spraying in U/G coal. The additional benefit of micro fibre is that it is relatively easy to integrate it into pre bagged dry mix products.

In the 1990's Thin Skin Liners (TSL's) was an experimental product that many manufactures focused on. Micro fibres were an integral part of these TSL's. They all lacked structural integrity. The TSLs were simple surface and crack sealers. The TSL market has diminished greatly with several products morphing into very thin crack sealers, without fibre to improve crack penetration.

More recently high strength ductile cement based products have made their way in to the market using micro fibres – the term Thin Structural Liners has been adopted for these products. These TSL's are highly refined engineered pre bagged products. The TSLs are designed so the cement based matrix works in unison with the characteristics of the micro fibres. This allows for a unique "strain hardening" cracking system to occur. Basically, the matrix is designed to micro crack thus transferring the load to the fibres. As the fibres increase the load bearing ability the matrix continues to micro crack over the entire loaded area thus bringing into play many more fibres. This strain hardening effect permits the matrix to have a high compressive strength (40MPa +) and exhibit high flexural ductility of around 10% plus high tensile strength of 5% plus.

Testing undertaken of the product (PMG 64) used in this case study and the products that are currently on the market are compared in Table 1 below. These tests were conducted at 14 days after application.

From the data in Table 1, PMG 64 has higher flexial strength and crack bridging properties than standard grout.

Table 1: Comparison of case study ECC (PMG 64) to current products (After Moore 2014)

Property	PMG 64	Standard Grout	Phoenelic Resin	PUR
UCS (Mpa)	32	45		
Tensile on Sandstone (MPa)	0.75	0.3	0.74	1.46
Crack Bridging (mm) at 1MPa	1.8	0.4		
Flexial Strength (Mpa)	11	1.2		

An example of the use of such a product was the rib consolidation on the non-walk side of an aging belt road which was starting to spall badly. The entire consolidation was completed from off the stationary belt over a ten day maintenance period. The success of this project has led into the assessment of using such products and techniques as an alternative to secondary support in general as the product costs are similar, the speed of application is much faster with both sides of a 100m pillar roadway being able to be sprayed from a single setup by three men plus a loader in a single shift. Currently, such products are being tested to gauge their effectiveness for pillar confinement and have demonstrated to be tougher in vehicle impact situations which have the potential of extending travel road maintenance periods extensively. The main benefits discovered from this application was that by using the penetration and gluing strengths of these products, that very little needed to be used to give structural strength (around 15 mm over competent coal). The ability to "glue" back into the rib large spalling blocks and put them back to work as support members was a distinct benefit.

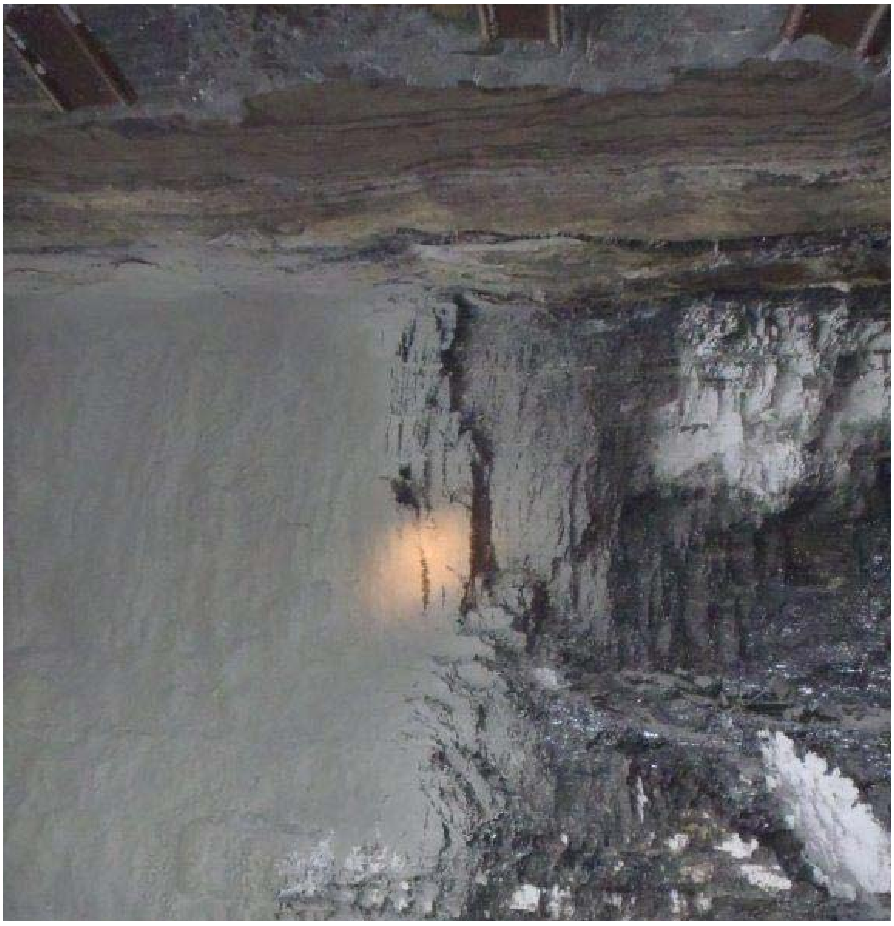

Figure 5: Applied Thin Skin Liner in an underground coal mine (Moore 2014)

Another successful program was the selection of one of these products to replace all the stoppings in a New South Wales underground coal mine. The priorities for this job were – minimal construction time, minimal thickness for the required rating, a high safety factor and the ability to resist convergence. This program is ongoing today with over 100 new stoppings having been built alongside the existing old non rated block stoppings.

One application example of the product was sprayed in this case study at between 2mm to 5mm, covering 1000m2 in 5.5 hours using 350 20kg bags of the product as shown in Figure 5 below. Less of the product is needed to be applied to achieve a similar outcome to standard grout. So, for the same surface area, less product is required and the total product cost is much lower. The site requires no special machinery, skilled staff to apply the product and less challenging OHS issues for a similar result to Phoenelic Resin and PUR (Polyurethane resin). Phoenelic Resin and PUR are commonly used in underground coal mines.

CONCERNS ABOUT POLYMERS

The success of the above program along with the modernising of the dry gunite systems to make them virtually dustless (which is essential for compliance) and the dust reducing additives now available have made the option of using both fibre reinforced cement and plaster based systems more than viable. Figure 6 shows physical comparisons between ECCs and other composite materials.

Properties	FRC	Common HPFRCC	ECC
Design Methodology	N.A.	Use high Vf	Micromechanics based, minimize Vf for cost and processibility
Fiber	Any type, Vf usually less than 2%; df for steel ~ 500 micrometre	Mostly steel, Vf usually > 5%; df ~ 150 micrometre	Tailored, polymer fibers, Vf usually less than 2%; df < 50 micrometre
Matrix	Coarse aggregates	Fine aggregates	Controlled for matrix toughness, flaw size; fine sand
Interface	Not controlled	Not controlled	Chemical and frictional bonds controlled for bridging properties
Mechanical Properties	Strain-softening:	Strain-hardening:	Strain-hardening:
Tensile strain	0.1%	<1.5%	>3% (typical); 8% max
Crack width	Unlimited	Typically several hundred micrometres, unlimited beyond 1.5% strain	Typically < 100 micrometres during strain-hardening[1]

Note: FRC=Fiber-Reinforced Cement. HPFRCC=High-Performance Fiber Reinforced Cementitious Composites

Figure 6: Comparison between ECC and other composite materials (wikipedia)

CONCLUSIONS

ECCs historically have not been widely adopted because of higher costs and difficulty associated with traditional manufacturing techniques. However, recent developments have led to significant reductions in cost, meaning that the use of polymer concrete is gradually becoming more widespread.

Advantages of polymer concrete include:

- Rapid curing at ambient temperatures
- High tensile, flexural, and compressive strengths
- Good adhesion to most surfaces
- Good long-term durability with respect to freeze and thaw cycles
- Low permeability to water and aggressive solutions
- Good chemical resistance
- Good resistance against corrosion
- Lighter weight (only somewhat less dense than traditional concrete, depending on the resin content of the mix)
- May be vibrated to fill voids in forms
- Allows use of regular form-release agents (in some applications)
- Dielectric
- Less product required compared to similar applications with standard grouts

Disadvantages of polymer concrete include:

- Product hard to manipulate with conventional tools such as drills and presses due to its strength and density. Getting pre-modified product from the manufacturer is recommended

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Wacker Chemie AG, electron microscope (ceramic tile adhesive (CTA), modified with VINNAPAS® polymer powder, on porcelain tile x1500 photo.

Wacker Chemie AG, possible force-deformation curves for cement-dry polymer mixtures measured according to ISO 527-3 photo.

Wacker Chemie AG, ECC application photo.

Moore M, Applied Thin Skin Liner in an underground coal mine 2014 photo.