Polymer Modified Mortar and Concrete Present Status a Review

R.Ganesh¹, P.Ravikumar²

¹(PG Student, Hindustan Institute of Technology and Science, Chennai, India) ²(Asst. Prof., Hindustan Institute of Technology and Science, Chennai, India)

Abstract: Conventional cement mortar and concrete have water absorption characteristic which intern leads to deterioration in bonding property and affect durability aspects. In this study it is focused what are the various damages caused by water, water repellent requirement and to improve the water resistance property cement mortar and concrete by incorporating different types of polymer during casting process and enhancement of property so for studied in this area is taken up for review. This study will be helpful for the researchers to have comprehensive knowledge in polymer modified system and their effect in properties. **Keywords:** Polymer Modified Mortar and Concrete, Silicone Resin.

I. Introduction

Penetration of water and humidity into facades, buildings and architectural constructions consisting of mortar, concrete, natural stones or bricks is one of the major reasons for damages to their structure and substrate. Water causes these damages either by direct contact, natural weathering or as a result of insufficient foundation of walls. Additionally, the negative impact of water can even be enhanced as it functions as carrier of water soluble salts or pollutants from air . Over the past decade building protection has gained much importance and is nowadays often taken into consideration already during the construction phase. This trend is further supported by general technological advancements such as the development of the dry-mix technology. State of the art powdery hydrophobizing additives have become an integral component of various dry-mix formulations. Concrete structures and manufactured concrete products are frequently exposed to environmental attack. Water and salts cause the major part of all damages in construction work. This damage is estimated to be in a range of several billions of Euros per annum. Silicone-based water repellents can be used as an admixture to avoid application errors during post treatments of concrete.Hydrophobic additives are frequently used to minimize visual defects and physical damage caused by water penetration in the porous nature of cement based materials. Test results are presented on new silicone hydrophobic powders which produced a very substantial reduction in water absorption. Efflorescence was therefore much reduced, and retention of colour in a pigmented mix after weathering was greatly improved. For many years, the application of water repellent agents based on silicone technology has been the preferred method for protecting masonry facades and building surfaces against moisture entry and weathering thereby increasing their service life. The first protection formulations successfully marketed were based on liquid hydrophobisation systems that were to be applied externally on finished constructed parts or facades. Over the past decade, the importance of building protection has been increasing steadily. Nowadays, it is often taken into consideration already during the construction phase. This trend is further supported by general technological advancements such as the development of the dry-mix technology.

Hydrophobisation agents have been the media of choice in order to protect masonry facades and building surfaces against moisture and destruction by weathering thereby leading to an increased lifetime.Hydrophobizing systems to be applied externally on the final constructed parts and outside structures were the first to successfully enter the market. However, although external hydrophobisation still accounts for the major share in the above mentioned applications, integral hydrophobisation enjoys increasing popularity and acceptance. In other words building protection is already taken into consideration during the actual construction phase. On the other hand dry mortars have gained importance in the construction industry over the past decades as they lead to increased productivity and improved quality. In order to improve product quality and to meet all kinds of specific requirements, dry mortars are modified with polymer binders and special powdery additives such as hydrophobizing agents (water repellents). At present metal salts of fatty acids are widely used as water repellents in dry mortars and represent the largest group of hydrophobizing additives. Particularly in regard to long term performance, metal salts of fatty acids exhibit some weaknesses. With this paper we would like to introduce newly developed powdery hydrophobizing additives. These additives are composed of silane/ siloxane blends based on an inorganic carrier to be easily applied to drymix systems. As powdery water repellents they provide superior performance compared to metal salts of fatty acids and are easy to handle and dose. Due to their unique chemical design they provide outstanding water repellence and excellent beading along with true long term performance and sustainably protect buildings and architectural constructions.

1.1 Damages caused by water –uptake:

Most damages to buildings are caused by water e.g. through natural weathering. Air pollutants such as SO2 or NOx accelerate the decomposition processes. To suppress, or, even more desirable, to totally prevent the decay of structures building protection in form of waterproofing or water-repellent treatment is used. Most building materials are porous and water can penetrate into these pores. At lower temperatures this water can freeze to ice. As a consequence cracks may occur within the building material because ice has a larger volume than water. In nature, this is a common phenomenon, e.g. hard rock turns into sand in the course of time. In the presence of water salts and mineral binders that are contained in the substrate areTesting daysTesting daysSubjected to conversion.

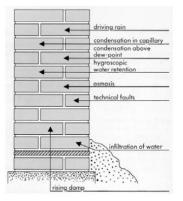


Figure.2.1 Ways of water uptake

1.2 Undesirable consequences of water ingress

- Cracks due to water freezing
- Efflorescence
- Transport of salts (corrosion)
- Dirt retention
- Peeling off of decorative coatings
- Rising/penetration dampness
- Reduced insulating properties

In order to effectively control humidity in the masonry, different water absorption mechanisms need to be considered. Construction defects, destroyed joints, cracks and non-existing insulation give access to moisture. Via defective or non-existing horizontal insulation, moisture can rise in capillary form in the masonry. Capillary action in the porous substrates leads to a fast and high water uptake in masonry. This process is accelerated through the condensation of air humidity when the temperature falls below the thaw point in cold areas, as well as the condensation of water vapour when the temperature rises above the thaw point. Infiltration of ground water might additionally occur in the basement area if insulation is insufficient. Salt blooming is the most apparent moisture-induced damage. Salts which are contained in the building material are dissolved by penetrating water and reach the surface where the water evaporates and the salts crystallise. Salts in the masonry are hydrophilic centres which may cause damp zones.

Water is one of the major causes for structural damage to building materials in the course of time. The results range from total destruction to expensive restoration of the affected buildings. The attack of mould and fungus is not only unpleasant but also poses a health risk.

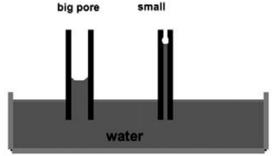


Figure.1.1 Capillary action

1.3 Protection against water Hydrophobizing agents

Being aware of all the damages that can be caused by water and moisture the requirements for a good protection can be described as Reduction of water absorption, Effective protection from heavy wind and driven Rain, High penetration depth of the water repellent, Prevention of efflorescenc, Protection against de-icing salts, Reduction of dirt build-up, No adverse effects on the appearance of the substrate, No significant reduction of the vapour permeability.

1.4 Hydrophobizing agents in dry mortar formulations

Nowadays advanced dry mortar products are available to the construction industry. In contrast to jobsite mortars modern drymix mortars are produced in special factories. Drymix technology can be described as highly controlled process of pre-blending and batching of all the necessary ingredients. Over the past decades drymix technology has been displacing the job-site technology since it provides numerous advantages which are crucial for modern and efficient construction works. Different types of mortar can be produced with well-defined properties to achieve reproduceable performance of high quality. Only water needs to be added at the site. A high level of consistency and reliability is achieved and the overall construction process becomes more productive and cost-efficient.

For superior hydrophobicity and durability high performance water repellents based on blends of silane/siloxane eventually in combination with organic components were developed. Since the active matter of powdery additives itself often is of liquid nature it is converted into a powder by "attaching" it to an inorganic carrier such as silica, carbonates or talc to make it easily applicable to dry-mix systems.

Silane/siloxane based powdery water repellents provide superior performance compared to metal salts of fatty acids and are easy to handle and dose. Due to their unique chemical design they provide outstanding water repellence and excellent beading along with true long term performance resulting in sustainable protection of buildings and architectural constructions. The areas of applications include their use in drymix for masonry mortars, high cement content mortars, renders, plasters, tile grouts and joint fillers.

1.5 Requirements for Water Repellents

The main function of water repellents is to prevent liquid water from penetration into the building materials. To achieve long term performance water repellents need to penetrate beyond the surface layer into the interior substrate of the porous material. By forming distinct chemical bonds with the substrate, subsequent washing out can be avoided. UV stability and good resistance against weathering and high alkalinity are basic requirements for the good performance of a water repellent treatment. The optical appearance of the substrate, such as colour and hue, should not be affected. The formation of visible, sticky films is also not acceptable. Transmission of water vapour needs to be guaranteed to achieve good respiration properties of the building. In summary, water repellent treatments should:

- Reduce liquid water absorption
- Prevent water absorption during driving rain with heavy winds
- Achieve a high penetration depth
- Prevent the formation of efflorescence
- Protect against de-icing salts
- Reduce soiling and biofilm formation and
- Not influence the appearance of the substrate.

1.6AlkoxySilanes and Alkoxy Silicone Resin

The porous structure of construction materials based on ordinary Portland cement leads to high sensitivity to capillary water absorption. Control of water absorption is, therefore, key to reducing various kinds of water-induced damage such as efflorescence, staining, scaling, due to freeze-thaw cycles, chemical attack and corrosion to reinforcing steel. Post treatment of silane/ siloxane water repellent has demonstrated to be a reliable, long lasting solution to minimise water penetration within inorganic construction material. In the last 5-10 years, silane, siloxane or silicone resin-based started to be used as what is known as integral water repellent in mortar and concrete. This is now an established technology, of which the benefits are well accepted. As the technology is nowadays gaining increased interest, it is important to pursue more fundamental studies to better understand the impact of these hydrophobers on the cement hydration processes.

II. Clasification Of Polymer Modifiers

Polymer-based admixtures are classified into four main types, i.e., polymer latex (or polymer dispersion), redispersible polymer powder, water-soluble polymer and liquid polymer.

2.1 Polymer Latexes (or Dispersions)

Latexes (or dispersions) which consist of very small (0.05-5 pm in diameter) polymer particles dispersed in water are usually produced by emulsion polymerization. Natural rubber latex and epoxy latex are not produced by such emulsion polymerization. The natural rubber latex is tapped from the rubber trees, Heveabrasiliensis, etc., and then concentrated to have the proper total solids. The epoxy latex is produced by emulsifying an epoxy resin in water by use of surfactants. Polymer latexes are generally classified into the following three types by the kind of electrical charges on polymer particles, which is determined by the type of surfactants used in the production of the latexes: cationic (postively charged), anionic (negatively charged) and non- ionic (uncharged). In general, the polymer latexes are copolymer systems of two or more different monomers, and their total solids including polymers, emulsifiers, stabilizers, etc. are 40-50% by mass.

2.2RedispersiblePolymer Powders

Redispersible polymer powders as polymer-based admixtures are manufactured by a two-step process. Firstly, polymer latexes as raw materials are made by emulsion polymerization, and spray-dried to obtain the polymer powders. Before spray-drying, the latexes are formulated further with some ingredients such as bactericides, spray-drying aids and antifoaming agents. Anti-blocking aids such as clay, silica and calcium carbonate are added to the polymer powders during or after spray-drying to prevent 'caking' of the powders during storage.

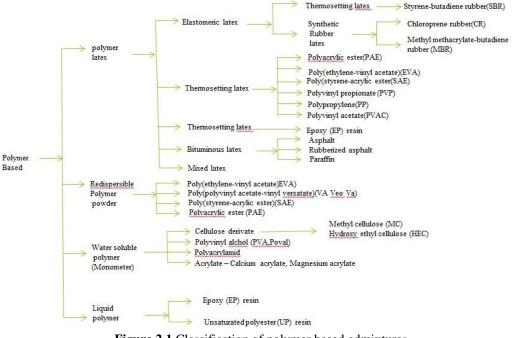


Figure 2.1 Classification of polymer based admixtures

2.3 Water-Soluble Polymers

Water-soluble polymers as polymer-based admixtures are water-soluble powdered polymer, e.g., cellulose derivatives, polyvinyl alcohol (poval), polyacrylamide, etc., and are added in the form of powders or aqueous solutions to cement mortar or concrete during mixing. When added in the powder form, it is advisable to dry-blend the polymers with the cement- aggregate mixtures, and then to mix them with water. Their main effect is to improve workability. The acrylates, such as calcium acrylate and magnesium acrylate, which are added in monomer form during mixing are included within this category because they are water-soluble.

2.4 Liquid Polymers

Liquid polymers as polymer-based admixtures are viscous polymeric liquid such as epoxy resin and unsaturated polyester resin, and are added with the hardener or catalyst, and accelerator to cement mortar or concrete during mixing. However, the liquid polymers are less widely employed as polymer-based admixtures compared with the other admixtures such as polymer latexes, redispersible polymer powders and water-soluble polymers.

III. Principles Of Polymer Modification

Although polymer-based admixtures in any form such as polymer latexes, water-soluble polymers and liquid polymers are used in cementitious composites such as mortar and concrete, it is very important that both cement hydration and polymer film formation (coales- cence of polymer particles and the polymerization of resins) proceed well to yield a monolithic matrix phase with a network struc- ture in which the cement hydrate phase and polymer phase interpenetrate. In polymer-modified mortar and concrete structures, aggregates are bound by such a co-matrix phase, resulting in superior properties compared with conventional cementitious composites.

3.1Modification with Polymer Latexes

Polymer latex modification of cement mortar and concrete is governed by both cement hydration and polymer film formation processes in their binder phase. The cement hydration process generally precedes the polymer film formation process by the coalescence of polymer particles in polymer latexes. In due course, a co-matrix phase is formed by both cement hydration and polymer film formation pro- cesses. The co-matrix phase is generally formed according to the simplified model.Some chemical reactions may take place between the particle surfaces of reactive polymers such as polyacrylic esters (PAE) and calcium ions (Ca^{2+}), $Ca(OH)_2$ solid surfaces, or silicate surfaces over the aggregates. Such reactions are expected to improve the bond between the cement hydrates and aggregates, and to improve the properties of hardened latex-modified mortar and concrete.

3.2Modification with Redispersible Polymer Powders

The principle of modification of cement mortar and concrete with redispersible polymer powders is similar to that of latex modification, except that it also involves the redispersion of the polymer powders. Mostly the redispersible polymer powders are used by dry mixing with the cement and aggregate premixtures, followed by wet mixing them with water. During the wet mixing, the redispersible polymer powders are re-emulsified in the modified mortar and concrete, and behave in the same manner as the latexes for polymer-based admixtures.

1.2 Modification with Water-Soluble Polymers

In the modification with water-soluble polymers such as cellulose derivatives and polyvinyl alcool, small amounts of the polymers are added as powders or aqueous solutions to cement mortar and concrete during mixing. Such a modification mainly improves their workability because of the surface activity of the water-soluble polymers, and prevents the 'dry-out' phenomena. The prevention of the 'dry-out' is interpreted in terms of an increase in the viscosity of the water phase in the modified cement mortar and concrete and a sealing effect due to the formation of very thin and water- impervious films in them. In general, the water-soluble polymers contribute to little improvement in the strength of the modified systems.

1.3 Modification with Liquid Polymers

In the modification with liquid thermosetting resins, considerable amounts of polymerizable lowmolecular weight polymers or prepolymers are added in a liquid form to cement mortar and concrete during mixing. The polymer con- tent of the modified mortar and concrete is generally higher than that of latexmodified systems. In this modification, polymerization is initiated in the presence of water to form a polymer phase, and simultaneously the cement hydration occurs. As a result, a co-matrix phase is formed with a network structure of interpenetrating polymer and cement hydrate phases, and this binds aggregates strongly. Consequently, the strength and other properties of the modified mortar and concrete are improved in much the same way as those of the latex-modified system.

3.5 Alkoxysilanes and alkoxy silicone resin

Silanes are molecules based on one silicon atom which bears four substituents. Alkyl trialkoxysilanes, are used to formulate water repellents, either for post-treatment or admixture as they have good reactivity towards inorganic, silanol-rich surfaces. Upon hydrolysis and condensation, silanes create a resinous network which can bind covalently to the surface of inorganic materials. The aliphatic chain (i.e. isobutyl or octyl chain) confers the hydrophobic character to the treated substrate and resistance against alkaline environment. Silicone resins are obtained by a sequence of controlled hydrolysis and condensation reactions of individual or mixtures of silanes. Silicone resin with alkoxy groups and hydrophobic alkyl groups can be designed such as to diffuse within the cement matrix and react with the pore's surface. The reaction leads to a chemical anchorage to the treated materials, while the alkyl group provides the hydrophobic character to the treated surface. Neat silanes, siloxanes or silicon resins used as water repellent active materials need to be further formulated to enable their effective use. Preparation of oil-in-water emulsion of silanes enables their easy incorporation and dispersion in cement, mortar or concrete slurries. Silane-based hydrophobic additives formulated as an emulsion was used as

an 'integral water repellent' in cement paste and mortar, in order to examine the influence of bulk waterproofing treatment on the cement hydration process using both micro and macro structural analysis of cement hydrates.

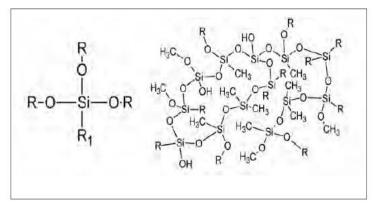


Figure 3.1 Structure of an alkyl trialkoxysilane and schematic representation of a silicone resin

3.5.1 Siloxanes

Siloxanes and silicone oils are oligomeric or polymeric molecules basedon Si-O-Si chains. Because of their low intermolecular forces these oilsare liquid even at high molecular weight and over a wide temperature range. Technically interesting is also the fact that silicone oils are good insulators. The surface tension of silicone oils depends on molecular weight, increasing from 15.7 mN/m for hexamethyldisiloxane to about 22mN/m for medium and high molecular weight oligomers and polymers. This is much lower than those for organic oils, i.e., with carbon chains, which are usually in the range of 30-35 mN/m. Also to be mentioned istheir high thermo stability.In organo-modified siloxanes some of the methyl groups at the siliconatoms are substituted by other organic groups

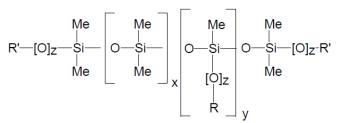


Figure 3.2 Generic structure of organic siloxanes

In construction applications organo-modified siloxanes are mainly used forhydrophobisation of neutral and natural substrates. They also areapplicable for treatment of aged concrete with a lowered pH value due tocarbonation. The main applications for these products are façadetreatment and protection against rising damp. Due to their higher reactivitycompared to that of monomeric silanes, siloxanes do not need a catalystfor curing. On high alkaline substrates the curing process of siloxane is sofast that it does not allow the molecule to penetrate very deep into thesubstrate.

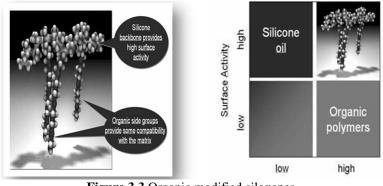
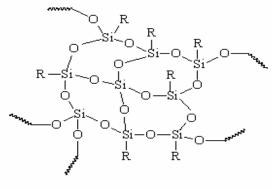


Figure 3.3 Organic modified siloxanes

3.5.2 Silicone Resine

Silicone resins are highlybranched polysiloxanes of highemolecular weight. They provide excellent beading properties butalso have some disadvantages as low alkaline stability, and poorsolubility properties. These products must be diluted to 5-10% solids in solvents to achieve a good impregnation depth. Emulsified products hardly can perform as well because of insufficient penetration into the substrate.



R= Me, OH, H.

Figure 3.4 Structure of silicone resin

3.5.3 Chronological Formulation Development

Over the last decades silicone based water repellent systems have gone through a constant process of change driven by legislative and commercial aspects. The first representatives appeared in the 1960s when high molecular weight silicone resins dissolved in organic solvents, mainly alcohols, containing approx. 60 -70 % of active material were developed for this application. Learning from the drawbacks of these products, low molecular weight oligomericsiloxanes were developed in the 1970's. For the protection of concrete, alkoxysilanes gave the best results and they were commercially available for this application since approximately 1980. Later on, combination products of silanes and low molecular weight siloxanes were marketed as more generally applicable products. For the preparation of ready-to-use products these systems had to be diluted with white spirits or alcohols. Depending on the system and the substrate type, the active matter of the formulated products ranged from 5 to 100 %. For environmental reasons the market asked for "green products" with a lower content of volatile organic compounds (VOC), ideally without any solvents. As a consequence, water based emulsion products were developed. Top performing products, like an emulsionbased on organo modified siloxanes/silanes, were curable without additional catalyst. Paste-like water repellents completed the productrange for external treatment since early 2000 providing alternativetreatment methods. During the last years new developments have focused on products for dry-mix mortar systems. Today a broad range of powder based silanes and modified siloxanes in which the water repellents are applied on an inorganic carrier are available.

3.5.4 Mode of Action

What the discussed silicone compounds have in common is that in theirstructure they all carry hydrophobic alkyl chains and hydrophilic SiOR groups (with R = methyl, or ethyl). The hydrophobicity mainly depends on the length of the alkyl group. Longer alkyl chains give also good resistance against alkalinity as they set up a steric shield for the Si-O-Si bonds which are prone to hydrolysis. When applied to the substrate, the alkoxy groups of these products react with water or humidity to form a non-stable silanol intermediate which will spontaneously polycondensate to form a hydrophobic film. At the reactive OH-groups from the silanols can form irreversible bonds with the mineral substrate. These can be regarded as an anchorage system between the hydrophobic film and the building substrate. Hence, by treatment with silicone compounds the building material becomes hydrophobised as a result of a chemical modification and newly formed bonds. The performance and durability of the water repellent treatment depends on the penetration depth of the silicone material and the active content of the applied product.

The different penetration depths attained by one and the same product on substrates of different alkalinity show that there is a reaction with the mineral substrate (Fig. 10). In the chemical reaction of the alkoxy groups of the silanes/ siloxanes with the hydroxyl groups of the mineral substrates, the alkalinity has a catalytic effect [4]. Due to the large differences in surface tension of water and silicones (72 mN \square m-1and 22 mN \square m-1, respectively) water cannot penetrate the impregnated areas. It is important that the application of silicone based products does not block the substrate pores and that the formed water repellent film remain permeable for water vapour. In contrast to a coating layer, the breathing activity of the construction material

remains entirely unaffected. Organosilicone compounds are characterised by their excellent ability to penetrate very deeply into the substrate. Furthermore, they do not form any damaging substances and the surface does not become sticky over time.

3.5.5 Hydrophobising Agents In Dry Mortar Formulations

Today advanced dry mortar products are widely used in the construction industry. Dry-mix technology can be described as a highly controlled process of pre-blending and batching of all the necessary ingredients. It provides numerous advantages which are crucial for modern and efficient construction work. Different types of mortar can be produced with well defined properties to achieve reproducible performance of high quality. Only the water has to be added on site. A high level of consistency and reliability is achieved and the overall construction process becomes more productive and cost-efficient. For superior hydrophobicity and durability high performance water repellents based on silanes/ oligomericsiloxanes, sometimes in combination with organic components, were developed. Since the active ingredient of these compounds is often a liquid, it is converted into a powder by "attaching" it to an inorganic carrier such as silica, carbonates or talc to make it compatible with and easily integrated to the dry-mix systems. Silane/siloxane based powdery water repellents provide superior performance compared to metal salts of fatty acids and are easy to handle and dose. They provide an outstanding water repellency and an excellent beading effect along with true long term performance resulting in sustainable protection of buildings and architectural constructions. The areas of applications include their use in dry-mix for masonry mortars, high cement mortars, renders, plasters, tile grouts and joint fillers.

IV. Test Procedure For Polymer Modifiers

Test procedures for measuring colloidal and polymeric properties of polymer modifiers are frequently used for quality-control purposes to ensure a supply of a consistent product. The tests can also be used to assess the suitability of polymer modifiers for specific uses.

4.1 Nonvolatile or total solids content

Nonvolatile content is the polymer content of the latex, together with any ingredient that is nonvolatile at the temperature at which the test is run. Nonvolatile content is important in that it is the major factor in determining the cost of the product. It is determined by weighing a small representative sample of the latex, drying it under certain conditions, and weighing the residue. The residue is expressed as a percentage of the original mass. Although there are several acceptable published methods, different values may be obtained by different test methods. The main difference is in the temperature and time used to dry the latex. If there is a dispute, the generally accepted method is ASTM D 1076.

4.2 pH value

The pH value of a material is a measure of hydrogen-ion concentration and indicates whether the material is acidic or alkaline. ASTM D 1417 gives the method for testing pH of latexes. The pH range of a latex varies significantly, depending on the type of latex. For styrene-butadiene copolymer latexes used with hydraulic cement, it is usually 10 to 11; for acrylic copolymer latexes, it is usually 7 to 9; and for vinyl acetate homopolymer and copolymer latexes, it is usually 4 to 6. Walters (1992b) showed that with styrene-butadiene copolymer latexes, no significant change in flow, wet and dry density, and permeability properties of the PMC occurred when the pH value was varied from 4 to 10.

4.2 Coagulum

Coagulum is the quantity of the polymer that is retained after passing a known amount of the latex through a certain sized sieve. The sieve sizes used in ASTM D 1076 are 150, 75, or 45 mm (formerly No. 100, 200, or 325 mesh). The test measures the quantity of polymer that has particles larger than intended, usually formed by particle agglomeration or skin formation. Typical coagulum values are less than 0.1% by mass.

4.3 Viscosity

Viscosity is the internal resistance to flow exhibited by a fluid. Viscosity can be determined in many ways and the viscosity of a fluid can vary depending on the test method. Particle size can be determined by several methods, and it is possible that each method will give a different result. The methods require the use of equipment such as electron microscopes, centrifuges, and photospectrometers. Particle size is dependent, to a large degree, on the levels and types of surfactants.

4.5Surface Tension

Surface tension is related to the ability of the latex to wet or not to wet a surface and is determined using a tensiometer. The lower the value of surface tension, the better the wetting ability of the latex. This

property affects the workability or finishability of a latex-modified mixture. The surface tension is dependent, to a large degree, on the levels and types of surfactants. A typical value for a styrene-butadiene copolymer latex is about 40 dynes/cm, while that of water is about 75 dynes/cm.

4.6Minimum Film-Forming Temperature

Minimum filmforming temperature (MFFT) is defined as "the lowest temperature at which the polymer particles of the latex have sufficient mobility and flexibility to coalesce into a continuous film (Concrete Society 1987)." The type and level of monomer(s) used to make the polymer control the MFFT and it may be reduced by the addition of plasticizers. A plasticizer is a chemical added to brittle polymers to increase flexibility. Latex-modified hydraulic cement mixtures, the MFFT should be lower than the application temperature. In some cases, however, satisfactory performance has been obtained with the application temperature below the MFFT of the latex because the cement reduces the effective MFFT of the latex. ASTM D 2354 describes a method for measuring MFFT.

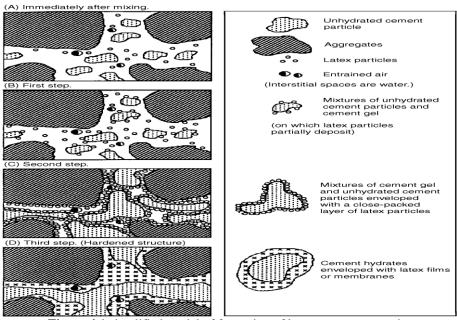


Figure 4.1 simplified model of formation of latex-cement comatrix

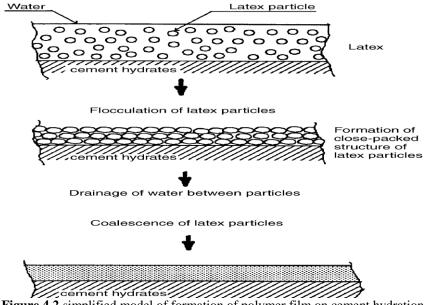


Figure 4.2 simplified model of formation of polymer film on cement hydration

						fix dolle on poryllier file		
SI. no	Author	Year	Types of polymer used	Variable	Test conducted	Result obtained	Curing	Observation
1.	Etsuo Sakai et al	1994	EVA(Emulsion) EVA(Powder)	Ordinary Portland cement with	Particle diameter,	The bending and compressive strengths for each dosage of polymer in PMC with		When either a polymer emulsion or a powdered polymer is mixed with cement, spherical polymer particles
				specific gravity 3.16.	Viscosity, pH, Solid density.	water: cement ratio constant. It shows that compressive strength decrease with an increase of the dosage of polymer. This phenomenon may due to the existence of soft polymer in the hardened cement which has the same effects pores. On the other hand, bending strength increases with an increase of dosage for		independently fill the interface between the cement particles, and hydrates produced after hardening crowd around the polymer particles. When powdered polymer is mixed with either cement paste or alkali solution, it disperses and displays the same behaviour as in the case where an ordinary polymer emulsion is used. The reason for the increase of bending strength of PMC is explained by the action of the polymer particles distributed
						low dosages, and then it begins to decrease of higher dosages. This increase of bending strength at low dosages is considered to be due to the effect of the distributed polymer particle.		in the hardened cement as reinforcing particles. The diminishing of the mean free path results in the complication of the propagation course of crack in the hardened cement. For the composite mechanism of PMC it is necessary to consider the particulate reinforced composite type.
2	R.Ollitraul t-Fichet et al	1998	Acrylic polymer emulsion with 50% (BA) 48.5% Methylmethacr ylate (MMA) and 1.5% Methylmethacr ylic acid (MAA) with addition of 0.36% of anionic stabilizer. The mean size of polymer particle was 180mm. The pH of the medium was 9.65. Viscosity of 64 cP for a dry- matter content of 47%.	Ordinary Portland Cement (CPA- CEMI 52.5 PMES CP, Lafarge) with Bogue composition of 66.0 of C3S, 18.3% of C3S, 18.3% of C3A, 6.3% of C4AF, and 5.0% of gypsum. Water cement ratio was 0.1.	Microscopi, Xray diffraction, thermal analysis, Porosemitri.	I.Irpartially obstructs the fine pore network inside the hydrates; 2.Irfill the large pores 3.Ir forms membrane than encapsulates the cement grains. The effect combine to decrease the permeability and hydration rate. The XRD patterns show more unhydrateresudece and less portlandite in the PMC than in the PFC which confirms the retardant effect of the polymer. There is no noticeable difference between PMC and PFC in respect of porcomentri which means the size of the polymer particles (200m) is too large to affect the fine porosity significantly.	28 days water curing at 23°C, in 50% relative humidity.	SEM observations show that the PMC microstructure is characterized by a shell configuration of polymer-containing hydrates, polymer granule beads, and non-hydrated cement grain. The retardant effect of the polymer is marked, which can be due to the polymer membrane that encapsulates the cement grains.
3	MUK Adridi et al	2002	Ordinary Pordand cement and Toyotra standard sand specified in Japanese industrial standard. Poly(vinyl acteate-vinyl carboxylate), Poly(ethylene – vinyl acetate), EVA emultion and Styrene- Butadiene Rubber (SBR)	Sand = 1:3(by weight), P/C (Calculated on the basis of total solids in powdered and aqueous cement modifiers)of 0%,5%,10%,15%. and 20%	Initial and final setting time, Flexural strength of mortar, Compressive strength of mortar.	Mortar constituents, i.e. cement hydrates and sand grains of UMM, being loosely joined with each other having ultimate lesser adhesion among themselves and lover chemical resistance as compared to those of PPMMs and APMMs. The PPMMs and APMMs are compactly joined, have ultimate improved adhesion among themselves and higher chemical resistance due to the presence of polymer films which reinforce the gel network. Such fully developed, coherent polymer films in PPMMs and APMMs seems to interweave the cement hydrates and sand grains, thus holding the mortar constituents more compactly, simultaneously making elastic inter connections by filling or reinforcing the capillaries and cavities.	3,7,28 days immerse d in water at 200C	Mortar constituents of UMM are loosely joined with each other due to the absence of polymer films, thus having a structure with comparatively lower mechanical and durability characteristics. By constant
4.	J. Novacek et al	2004	Oleate, Stearate, Mixed Products(Oleate + stearate), silane / siloxane, Hydrofobizedpo lyvinylacetate based binders.	Monofunctionalsil iconne based hydrofobixer 0.5%, Water repellent polymer binder (PVA based)v1.2%	Frost-proof, Complex endurance test,Compreh ensive lading test(CLT),Wh ole cubature water up-take after 24 hours,Compr essivestrengt h,Tensile strength.	Progression of compressive strength after 0.20 and 40 cycles of CLT.	Water curing 10 min, 20 min, 30 min, 60 min, 4h, 6h, 24h, 48h, 72 hours.	The research was focused on water repellents based on silicone. The material properties of these repellents were compared with properties of waterproof metallic soaps and substances based on hydrophobised polyvinyl cetates.
5.	M.Quadre lli et al		1.Siloxane, 2.Alkoxysiloxa ne, 3. Modified silanes / siloxanes, 4. Alkoxysilane and stearates, Cemen t, sand, filler	Premixed cement, sand, filler. The water repellent(dosage =0.2 - 0.5 %). Premix % of the total of water is added.	The Water absorption	Additive 1 the saturation was reached after about 24 h. Additives 3 and 4 even after 48 h the water up-take was still as low as approx _w . 50% of the maximum uptake.	Before testing specimen left for 2 days at 230c and 90% relative humidity	The hydrophobizinng agent based on modified silanes/siloxanes is the superior water repellent for dry mortar formulation being universally applicable and providing excellent water repellence as well as outstanding beading performance.
6.	L.K Agarwal et al.	2007	Epoxy emulsion based on diglycidyl ether of bisphenol-A and Amino- amide based hardener Ordinary OPC 43 grade and quartz sand No. 10	Cement sand ratio 1:3 by mass Water cement ratio was adjusted to have a flow between 110 and 120 mm	Flexural strength, compressive strength, and water absorption, Carbonation and chloride ion test	The compressive strength of controlled mortar specimen 39.5 MPa at 28 days and 45.0 MPa at 90 days. The compressive strength of PMM is less than that of water cured control specimen when the polymer cement ratio is more than 20%. The flexural strength of controlled mortar specimen is 7.8 MPa at 28 days	28 days at 230c, in 50 % relative humidity.	The flexural strength of epoxy modified mortar samples 30% polymer cement ratio is about 10% higher as compared to wetcured samples in case of air cured samples the case of air cured samples the samples and epoxy modified mortar is about 60%. Epoxy modified mortar is about 60%. Epoxy modified mortar behave better than acrylic modified mortar under flexural loading. Polymer modification can significantly improve the toughness of the mortar. Epoxy based mortar is about 60%. So you would be the resistance to penetration of carbon dioxide. 30% polymer-cement ratio. The decrease in water absorption is about 45% and 55% for acrylic and epoxy emulsion modified mix, respectively. Epoxy emulsion based mortar is a potential material that can be used for repair works in humid and industrial environments.

Table1: Summary of various work done on polymer modified mortar and concrete

Polymer Modified Mortar and Concrete Present Status a Review

7	V.Spaeth et al	2008	Two Silicone based agents (dihydroxypoly dimethylsiloxan e and n- octyltriethoxysil ane) on the hydrasion Portland cements and to understand the understand	Water to cement ratio of 0.5, addition of 0.5% of silicone-based agents per cement mass and a sand to cement ratio of 3.	Efficient and sustainable treatment preserving the mechanical properties of material. Capillary water absorption and mechanical tests on admixed mortars before ageing were obtained.	The addition of PVA only (n20) decreases the mechanical strength by almost a factor of two. Addition of pure zeolite (n03) does not affect significantly the compressive strength. The incorporation of powdery additive (, 08,9 and 10) does not affect significantly the mechanical properties of mortar cured for 28 days.	Immersio o of the specimen s in water for 24 hours for water absorptio n test. 28 days curing for mechanic al strength.	Impact of the addition of silane and PDMS induces the hydrophobicity of the admixture. Impact of PVA addition does not affect the setting times although it does not delay significantly the maxima of heat flow associated to hydration and the transformation of ettringite to calcium monosulfoaluminate during the acceleration period. Impact of zeolite addition with and without water repellent agents a slight reduction of the induction period and of the setting time. Hydrophobic agents are efficient additives for integral treatments of cementitious materials.
8.	Muhamm ad FarhanAr ooj et al	2011	PVA with the addition of two subsidiary chemicals 1.Acrylic glue AG, 2.Corboxymeth yl cellulose CMC	Concrete mx proportion 1:1.5:3, Size of aggregate Passing BS sieve ½. Water cement ratio 0.5	Tensile and compression test	Highesttensile strength 1200 Psi and compressive strength 12400 Psi in polymer modified concrete with the ratio of 4:4:1 by the weight of PVA, AG and CMC. It was about three time more than the ordinary concrete.	7 days water curing	The tensile strength of ordinary concrete repaired with the above ratio of polymer-modified concrete was 550 Psi, Which was even more than the tensile strength of un-broken sample. It also showed excellent bonding with old concrete.
9.	Markus Roos et al	2012	Silicone resin, Ordinary porland cement	Dosage of 0.05 to 0.1 Wt % of silicone actives. Metal soap: 0.20%	Capillary absorption, Compressive strength, Air content in fresh concrete.	Water uptake: (Reduction after $7d \ge 50\%$. Reduction after 119 d $\ge 40\%$). Air content. Air content with admixtures should not be higher than 2 % referred to control. Compressive strength: Limits reduction after 28 d $\le 15\%$	7 days and 28 day water curing. The specimen partly placed in sodium sulphate solution(100g sodium sulphate/ 900g water)	Organo-modified sloxanes in combination with alkoxy functional silanes are proven to give successful protection against water induced damages on concrete or mortars. The capillary transport of moisture and salts is reduced to a minimum. Low dosages, less influence onn mechanical properties combined with the easy incorporation into the cement matrix make these products very suitable.
10.	Jean- paullecom te et al	2013	Silicone is a generic term describing polymers based on a siloxanes backbone, Polydimethylsil oxanes or PDMS,Alkyltri alkoxysilanes	Sand cement ratio of 3/1 and water/cement ratio of 0.5. Silicone resin- based poder 0.25 5% and 0.5 %	The Water absorption, Measure of the capillary water absorption of reference and motifies mortar blocks by using "Rilem". Tubes affixed to the blocks surface.	Efflorescence can thus be minimized by reducing the capillary water absorption and transfer of through the cement matrix. This sett pore blockers which will decrease the gas permeability of the cement matrix.	28 days and dried overnight at 70 0C	Material based on ordinary Portland cement are to some degree porous, leading to capillary water absorption and consequent damage ranging from efflorescence to sapling and corrosion of reinforcing steel. Hydrophobic additives formulated to combat this were originally based on oleochemicals and metal soap, but powdered silanes and silicone resins offer better performance, gas permeability and weathering resistance, Both additives substantially reduced water absorption compared toann untreated cement mix.
11.	NenadMil enkovic et al	2015	Alkoxysilanes and alkoxy silicone resin. CEM152.5 R LA ordinary Portand cement and CEM III/A 42.5 N LA Blast Furnace Slag (BFS) cement.	Silane emulsion added was 2% of 5% wiw of cement. The hydration process of CEM1 32.5R LA ordinary Portland cement and CEM III/A 42.5 N LA Blast Furnace Slag (BFS) cement (45.7% slag content)	The Water absorption, SEM and XRD Rietveld analysis, DSC –TG analysis and isothermal calorimetry on cement paste.	MOR-3 has a lower mechanical strength as short term (2 days of curing) to that of MOR-1. This difference is decreases ar longer curing time (28 days)	90 days immerse d in tap water at 200 C and 65 % relative humidity.	Additon of IE silane emulsion in mortars leads to a strong reduction of capillary water absorption, indicating reaction of the silanes with CSH. Some impact on rate of hydration is, however, observed, which leads to a drop of about 7% in mechanical strength. The calorimentic measurements show that the hydration of C3S appears to be retarded in the presence of IE silane emulsion and heat production inn CEM-I and CEM-3 is lowered by around 10% when IE silane emulsion is present.

Conclusion

- 1) Hydrophobic additives formulated to combat this were originally based on oleochemicals and metal soap, but powdered silanes and silicone resins offer better performance, gas permeability and weathering resistance.
- 2) The addition of the "pure" silicon-based agents was difficult to study since no homogeneous mixture was obtained.

- 3) Additions of oil in water emulsions and powdery agents appear to be an effective method for the introduction of the silicon-based agents and little changes of setting time or physical properties were observed.
- 4) Goldschmidt's newly developed powder products provide durable protection against water penetration, thus preventing buildings and architectural structures from decay related to water ingress. One can select the product that best meets the specific requirements for an individual application.
- 5) The hydrophobizing agent based on modified silanes/siloxanes is the superior water repellent for dry mortar formulations being universally applicable and providing excellent water repellence as well as outstanding beading performance.
- 6) Some impact on rate of cement hydration is, however, observed, which leads to a drop of about 7% in mechanical strength. This effect is less significant for BFS cement. The mechanical strength decrease could not be correlated to a porosity modification.
- 7) The degree of hydrophobation varied depending on the side chain lengths and also on the functionality of the precursors.
- 8) polymer emulsion or a powdered polymer is mixed with cement, spherical polymer particles independently fill the interface between the cement particles, and hydrates produced after hardening crowd around the polymer particles.
- Adding polymer dispersions, redispersible powders, water-soluble polymers or liquid polymers to the fresh mixture produces polymer-modified cement concrete or mortar. Generally, polymers dispersed in water by surfactants
- 10) The retardant effect of the polymer is marked, which can be due to the polymer membrane that encapsulates the cement grains. In cured pastes, the porous volumes are similar in PFC and PMC, although the presence of polymer shifts the pore width distribution toward smaller values

References

- Aggarwal, L. K., Thapliyal, P.C. and Karade, S. R., Properties of Polymer modified mortars using epoxy and acrylic emulsion, Journal of Construction and Building Materials, 2007, Vol-21, No. 2, pp. 379-383
- [2]. Etsuo Sakai * and Jun Sugita Cement Additives Dpt., Denki Kagaku Kogyo K.K. 1-4-1 Yuraku-cho Chiyoda-ku Tokyo Japan 100. Composite mechanism of polymer modified cement 1994.
- [3]. Jean-Paul Lecomte, Dow Corning, DaniLladó, Nubiola, Sabrina Salvati, Dow Corning, Gustavo Rodrigues, Dow Corning, Murilo Ribeiro, Dow Corning. New silicone resin-based hydrophobic powder for the dry mix market 2013.
- [4]. Knapen, E. Beeldens, A. Van Gemert, D. Van Rickstal, F. Modification of cement concrete by means of polymers in solution.Reyntjens Laboratory, Department of Civil Engineering, K.U.Leuven, Leuven, Belgian Road Research Centre, Belgian 2004.
- [5]. Markus Roos,,Sabine Giessler-Blank, Sustainable concrete protection with siloxane based admixtures
- [6]. M. Roos, F. König, S. Stadtmüller and B. Weyershausen Evonik Goldschmidt GmbH, Essen Evolution of Silicone Based Water Repellents for Modern Building Protection 2008.
- [7]. M.A. Islam, M.M. Rahman and M. Ahmed. Polymer-modified Concrete: World Experience and Potential for Bangladesh. Indian concrete journal 2011.
- [8]. M.U.K. Afridi, Y. Ohama, K. Demura, M.Z. Iqbal, Development of polymer films by the coalescence of polymer particles inpowdered and aqueous polymer-modified mortars. Department of Architecture, College of Engineering, Nihon University, Koriyama, Fukushima-ken, 963, Japan Institute of Chemistry, University of the Punjab, Lahore, Pakistan 2002.
- [9]. Muhammad FarhanArooj, SajjadHaydarand Kafeel Ahmad, Development of Economical Polymer-modified Concrete for Repair of Concrete Structures in Pakistan, Institute of Environmental Engineering & Research, UET, Lahore 2011.
- [10]. Nenadmilenkovic, Jean-paullecomte, Christian pierre, Marie-pauledelplancke, examining silane-based integral water repellent and its impact on cement hydration, european coatings journal 2015
- [11]. NOVACEK.J. Brno University of Technology, Faculty of Civil Engineering, Technology Institute of Building Materials and Components 2008
- [12]. Ohama, Y.: Handbook of polymer-modified concrete and mortars, Noyes Publications, 1995.
- [13]. Quadrelli, M., König, F., Roos, M., Stadtmueller, S., Weyershausen, B.: New powdery water repellents for dry mortar application. Dry mortar yearbook 2007
- [14]. R.Ollitrault-Fichet, C.Gauthier, G. Clamen, and P. Boch1, Microstructural aspects in a polymer-modified cement, EcoleSupe rieure de Physique et de ChimieIndustrielles, 10 rue Vauquelin, 75005 Paris, France 1998.
- [15]. V. Spaeth, M.P. Delplancke-Ogletree and J.P. LecomteUniversitélibre de Bruxelles, Faculty of Applied Science, Chemicals and Materials Department, Brussels, Belgium Dow Corning S.A., Seneffe, Belgium. Hydration process and microstructuredevelopment of integral water repellent cement based materials 2008