Polymer Process Engineering

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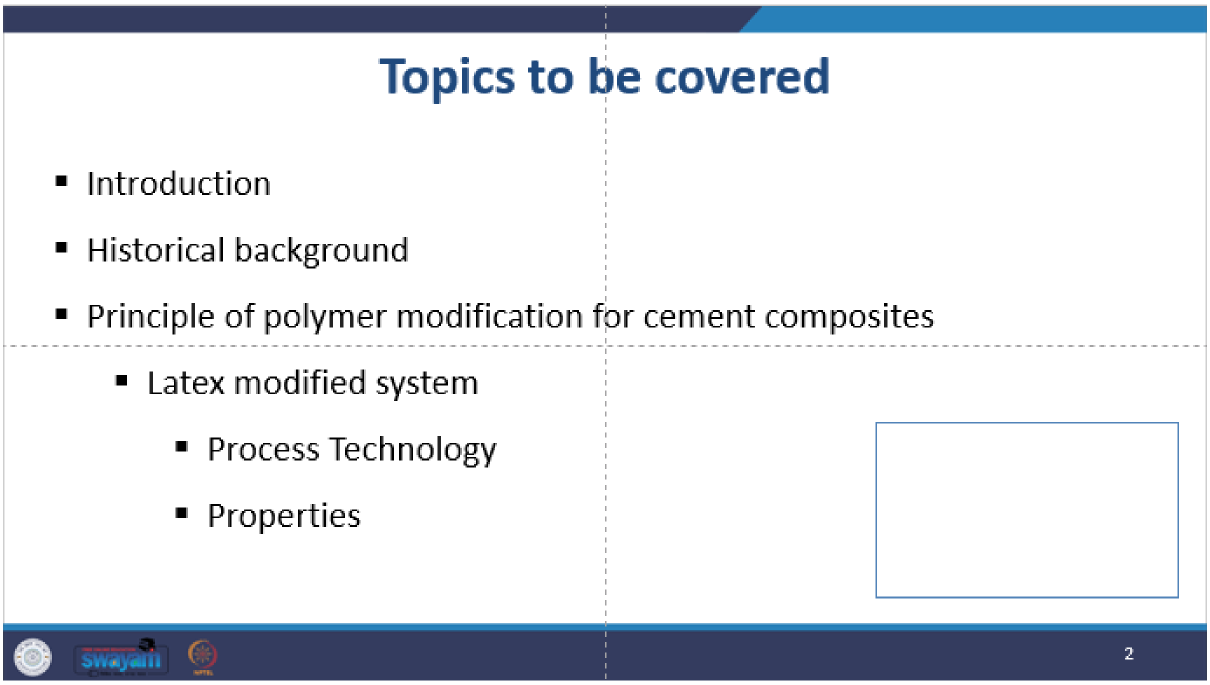
Lecture 57

Polymer Applications in Building Materials

Hello friends, welcome to the polymer applications in building materials under the edges of polymer process engineering. Here we are going to cover about the brief introduction, then historical background and we will discuss about the principle of polymer modification for various cement composites. I will discuss about the latex modification system and then the process technology apart from this we will discuss the different properties.



Now mortar and concrete made with the Portland cement they have been widely used in the construction industry for over 200 years. However, they have a disadvantage including decay hardening, low tensile strength, large drying shrinkage and low chemical resistance. The polymer additives they have been introduced to mitigate these drawbacks in a technique called polymer modified or polymer cement, mortar or concrete.

Introduction

- Mortar and concrete made with portland cement have been widely used in construction for over 170 years.
- However, they have disadvantages including delayed hardening, low tensile strength, large drying shrinkage, and low chemical resistance.
- Polymer additives have been introduced to mitigate these drawbacks in a technique called polymer-modified (or polymer-cement) mortar or concrete.

The polymer additives this included the latexes, re dispersible polymer powders, water soluble polymers, liquid resins and monomers. The polymer modified mortars and concretes they have a monolithic co-matrix where the organic polymer matrix and cement gel matrices are blended together and the properties of the polymer modified mortar and concrete are determined by this co-matrix structure. In systems modified with the latexes, re dispersible polymer powders and water-soluble polymers, water drainage during cement hydration leads to the formation of a film or membrane. A system modified with the liquid resins and monomers the addition of water triggers cement hydration and polymerization of the liquid resin or monomers.

History

Time Period	Material Used	Novel Development
1923	Natural rubber latexes	First patent for a polymer-hydraulic cement system issued to Cresson involving paving materials with natural rubber latexes and cement as a filler
1924	Natural rubber latexes	Lefebure published a patent introducing the concept of polymer latex-modified mortar and concrete using natural rubber latexes

Let us talk about the brief history. In 1923 the natural rubber latex being used and the first patent for a polymer hydraulic cement system is issued to christen involving the paving materials with natural rubber latexes and cement as filler. In the very next year in 1924 again the natural rubber latex and Liffber published a patent introducing the concept of a polymer latex modified mortar and concrete using natural rubber latex. Again in 1925 pertaining to the natural rubber latex Kirkpatrick patented a similar idea. In between 1920 and 1930 the development of polymer modified mortars and concretes using natural rubber latex being carried out.

History

Time Period	Material Used	Novel Development
1925	Natural rubber latexes	Kirkpatrick patented a similar idea
1920s-1930s	Natural rubber latexes	Development of polymer-modified mortars and concretes using natural rubber latexes
1932	Synthetic rubber latexes	Bond's patent suggested the use of synthetic rubber latexes for polymer-modified systems

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In 1932 the synthetic rubber latex came into existence and Bond's patent suggested the use of synthetic rubber latexes for the polymer modified system. In the similar year pertaining to the synthetic resin latex the polyvinyl acetate latex being produced and Rodwell's patent claimed that the application of synthetic resin latex to modified system. In 1940s the synthetic latex the chloroprene rubber poly acrylic esters latex being developed and the patent published on polymer modified system using the synthetic latexes. In the similar arena the polyvinyl acetate modified mortar and concrete been developed and active development of polyvinyl acetate modified mortar and concrete. In the late 1940s onward, there are various polymers being developed and increased use of polymer modified mortar and concrete in various applications.

Time Period	Material Used	Novel Development
1953	Polyvinyl-acetate-modified mortar	Geist et al. reported a detailed study on polyvinyl-acetate-modified mortar, providing valuable suggestions for later research
1960s	Styrene-butadiene rubber, polyacrylic ester, poly (vinylidene chl.-vinyl ch.)	Increased use of these polymers in practical applications

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In 1953 polyvinyl acetate modified mortar was developed and Geist they have reported a detailed study on polyvinyl acetate modified mortar. This provides a valuable suggestion for later research. In the 1960s the styrene-butadiene rubber poly acrylic ester polyvinylidene chlorine vinyl increase the use of this polymer in practical applications. In the 1960s the unsaturated polyester resins they are within prominent use and they developed the the ester create system modified with the unsaturated polyester resin. In 1965 and 1973, people widely used epoxy resins and finally, they patented a system based on epoxy resin.

Time Period	Material Used	Novel Development
1960s	Unsaturated polyester resin	developed the "Estercrete" system modified with unsaturated polyester resin
1965, 1973	Epoxy resins	Donnelly and Duffi43lp patented systems based on epoxy resins
1959	Urethane prepolymer	System modified with urethane prepolymer patented

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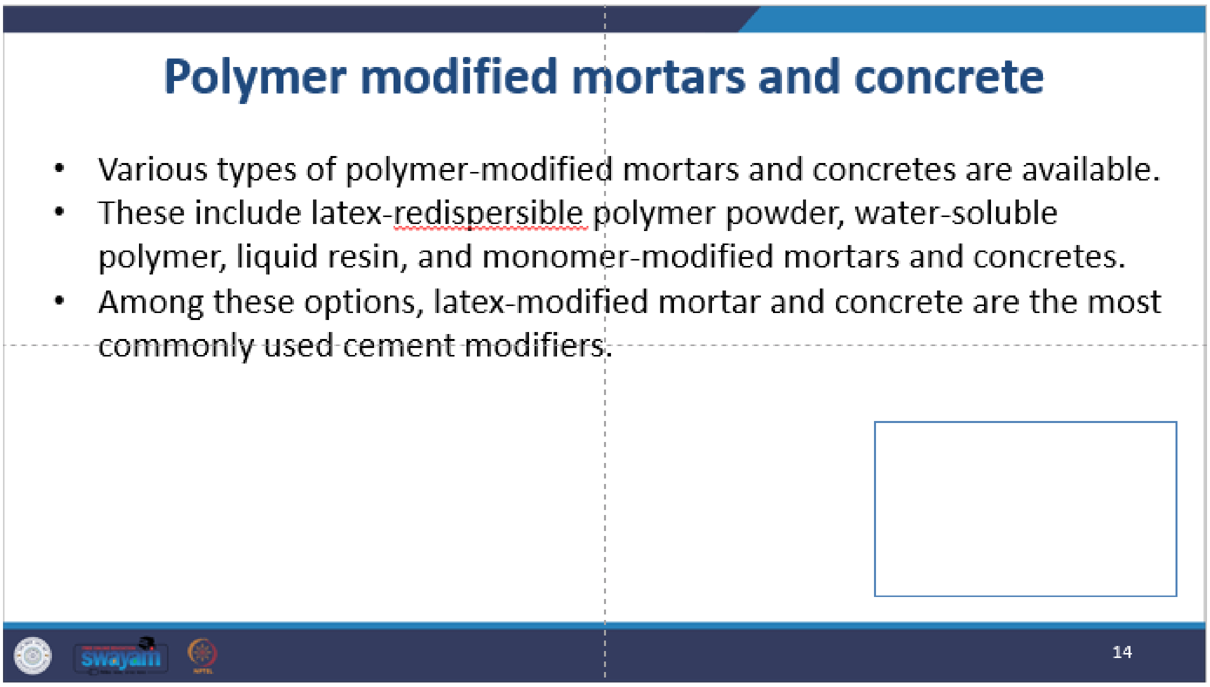
In 1959 the urethane pre-polymer was developed and the system was modified with the urethane pre-polymer patented. Early 60s methyl cellulose found a very prominent role and methyl cellulose is used as a water-soluble polymer modifier and adhesive polymer-modified mortars for ceramic tiles. In 1974 the polymer-modified system was reviewed and Relay and Reis they wrote a summarized review of the polymer-modified system. In the 1970s the polymer modified mortar and concrete research and development being carried out and the development pertaining to the extensive research and development conducted worldwide. In the 80s polymer modified mortar and concrete dominance being there and polymer-modified mortar and concrete became the dominant material in the construction industries.

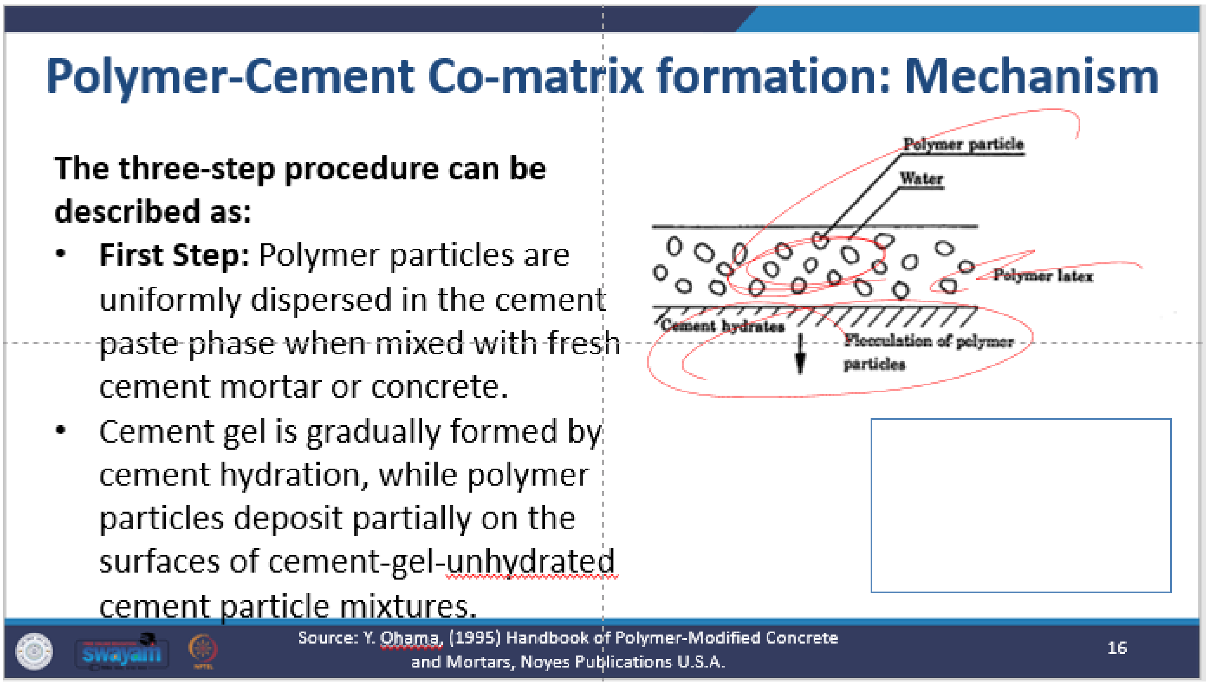
History

Time Period	Material Used	Novel Development
1970s	Polymer-modified mortar and concrete research and development	Extensive research and development conducted worldwide
1980s	Polymer-modified mortar and concrete dominance	Polymer-modified mortar and concrete became dominant materials in the construction industry

So the polymer modified mortars and concrete various types of polymer modified mortar and concrete they are available nowadays. This includes the latex, re dispersible polymer powder, water soluble polymer, liquid resin and monomer modified mortars and concrete. So among these options the latex modified mortar and concrete are the most commonly used cement modifiers. There are various type of things like polymer latex, elastomeric latex, thermoplastic latex, thermosetting latex, bituminous latex, mixed latex, then re dispersible polymer powders, water soluble polymers, liquid resins, monomers. In polymer cement co-matrix formation let us talk about the mechanism.



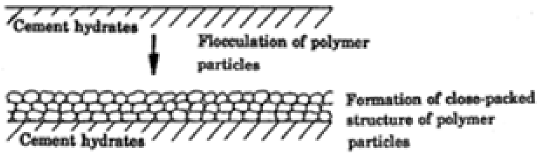
There are three-step procedures this can be described like first step polymer particles are uniformly dispersed in the cement paste phase when mixed with the fresh cement mortar or concrete. This is a cement hydration and flocculation and these are polymer particles. This is the polymer latex. Now cement gel is gradually formed by cement hydration while polymer particles deposit partially on the surface of the cement gel un-hydrated cement particle mixtures. The calcium hydroxide reacts with the silica surface of aggregates to form a calcium silicate layer and the calcium hydroxide crystals are formed at the contact zone between the cement hydrates and aggregates in presence of polymer latex.



In the second step the polymer particles they are confined in capillary pores due to drainage and development of cement gel structure. The polymer particles flocculate and form a continuous close packed layer on the surface of cement gel un-hydrated cement particle mixture and adhere to the mixture and aggregate surface. The larger pores in the mixture are filled by adhesive and auto adhesive polymer particles. The chemical reaction may occur between the reactive polymer particle surfaces and calcium ions and calcium hydroxide crystals or silicate surfaces. Let us talk about the third step.

Polymer-Cement Co-matrix formation: Mechanism

- **Second Step:** Polymer particles are confined in capillary pores due to drainage and development of the cement gel structure.
- Polymer particles flocculate and form a continuous close-packed layer on the surfaces of cement-gel-unhydrated cement particle mixtures and adhere to the mixtures and aggregate surfaces.



Source: Y. Ohama, (1995) Handbook of Polymer-Modified Concrete and Mortars, Noyes Publications U.S.A.

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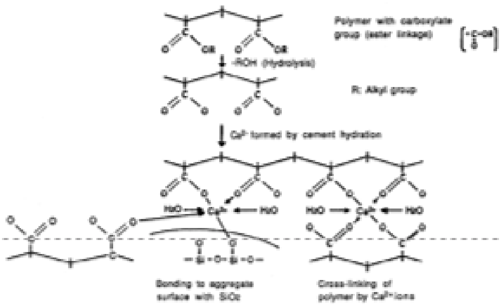
The polymer particle coalescence takes place into the continuous film or membrane as water is withdrawn by the cement hydration. Now drainage of the water between the polymer particles and coalescence of the polymer particles. Now film or membranes bind cement hydrates together and form a monolithic network where the polymer phase interpenetrates throughout the cement hydrates.

Polymer-Cement Co-matrix formation: Mechanism

- Larger pores in the mixtures are filled by adhesive and autohesive polymer particles.
- Chemical reactions may occur between reactive polymer particle surfaces and calcium ions, calcium hydroxide crystals, or silicate surfaces.



Source: Y. Ohama, (1995) Handbook of Polymer-Modified Concrete and Mortars, Noyes Publications U.S.A.

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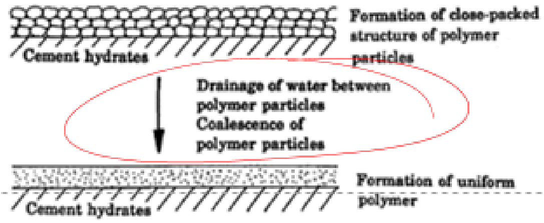
Now the structure acts as a matrix phase for latex modified mortar and concrete binding aggregates to the hardened material. Now let us talk about the latex modification.

Polymer-Cement Co-matrix formation: Mechanism

- **Third Step:** Polymer particles coalesce into continuous films or membranes as water is withdrawn by cement hydration.
- Films or membranes bind cement hydrates together and form a monolithic network where the polymer phase interpenetrates throughout the cement hydrate phase.



Source: Y. Ohama, (1995) Handbook of Polymer-Modified Concrete and Mortars, Noyes Publications U.S.A.

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The latex modification greatly improves the properties of ordinary cement mortar and concrete. The hardened cement paste typically has an agglomerate structure leading to micro cracks and poor tensile strength. The latex-modified mortar and concrete bridge micro cracks with polymer films preventing cracks propagation and developing a strong cement hydrate aggregate bond. Increasing the polymer content or polymer cement ratio enhances the effect increasing tensile strength and fracture toughness. The excess air entrainment and the polymer inclusion disrupts the monolithic network structure and reduce the strength despite some effective chemical reactions.

Effect of Latex Modification

- Latex modification greatly improves the properties of ordinary cement mortar and concrete.
- Hardened cement paste typically has an agglomerated structure, leading to microcracks and poor tensile strength.
- Latex-modified mortar and concrete bridge microcracks with polymer films, preventing crack propagation and developing a strong cement hydrate-aggregate bond.
- Increasing the polymer content or polymer-cement ratio enhances the effect, increasing tensile strength and fracture toughness.

Source: Y. Ohama, (1995) Handbook of Polymer-Modified Concrete and Mortars, Noyes Publications U.S.A.

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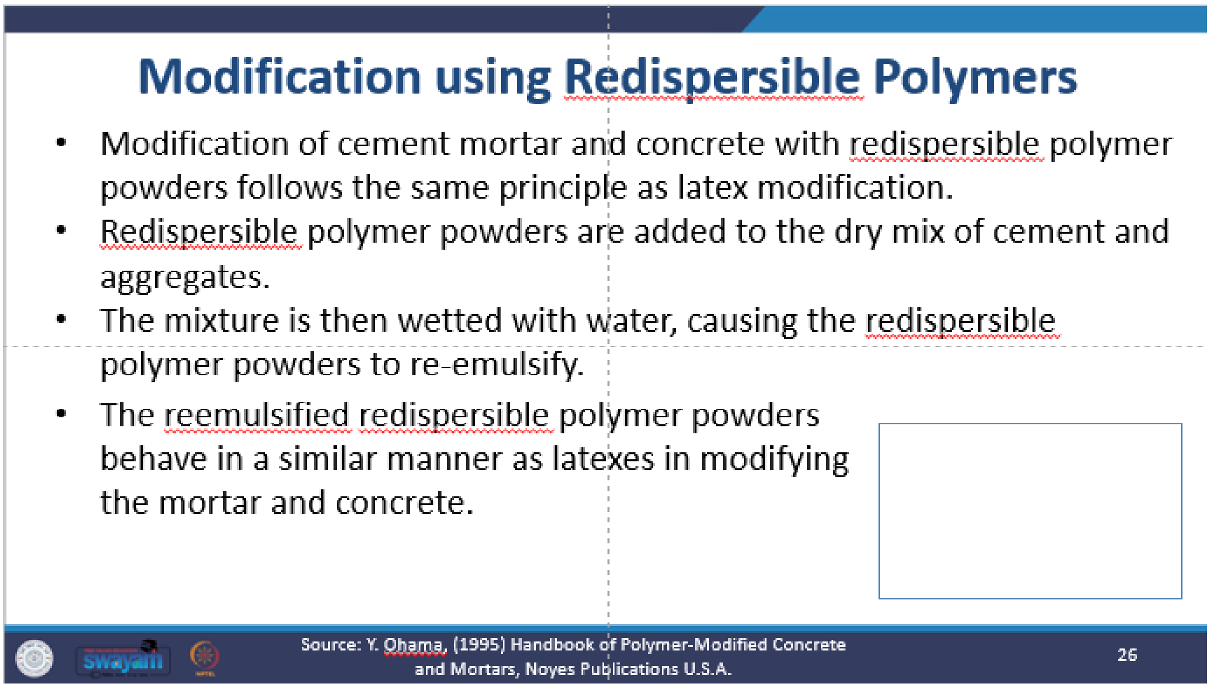
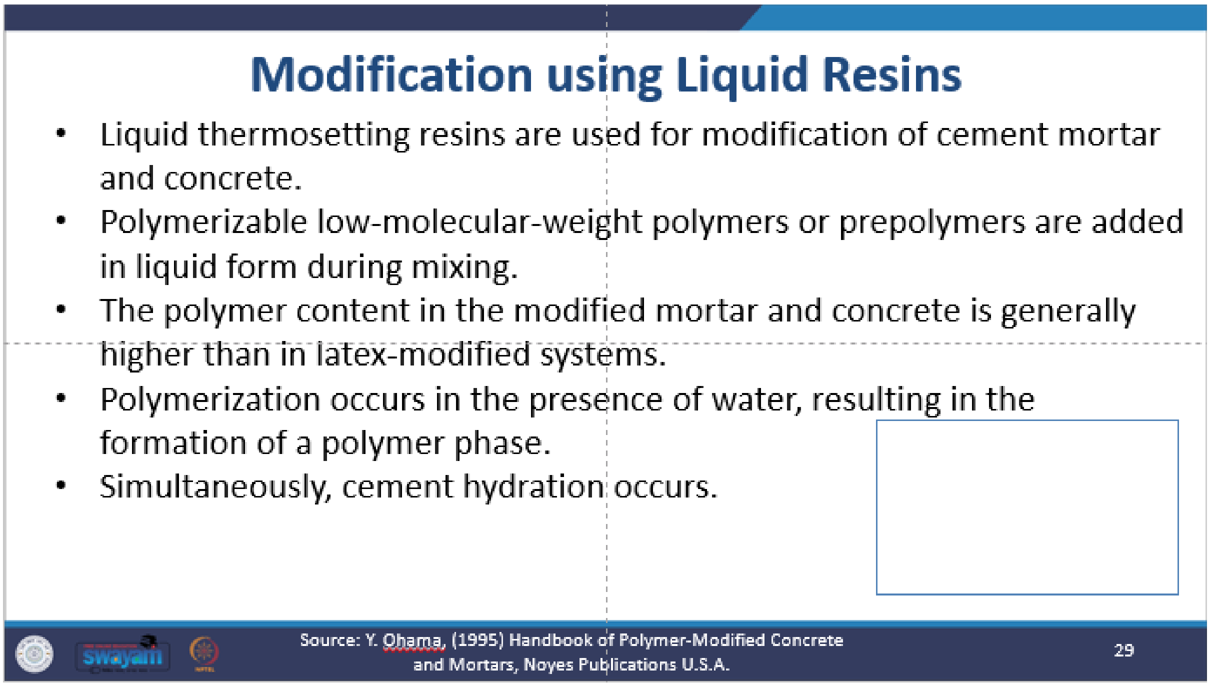
The polymer film or membrane this improve the waterproofness resistance to chloride ion penetration moisture transmission carbonation and oxygen diffusion chemical resistance and freeze durability. The specific surface area of cement gel an indicator of hydration this can be accelerated or retarded by latex addition at the initial stage. Say after 28 days cure the specific surface area of all paste is comparable. This suggesting the polymer modification does not significantly affect the cement hydration. The pore structure of latex modified system is influenced by the type of polymer and polymer cement ratio.



Increasing the polymer cement ratio decreases the total porosity or pore volume improving the impermeability resistance to carbonation and freeze thaw durability. Modification of cement mortar using re-dispersible polymers. Now, modification of cement mortar and concrete with re-dispersible polymer powder follows the same principle as per the latest modification. Re-dispersible polymer powder they are added to the dry mix of cement and aggregates. The mixture is then wetted with the help of water causing the re-dispersible polymer powder to re-emulsify.

The re-emulsified re-dispersible polymer powder behave in a similar manner as latex in the modifying the mortar and concrete. Let us talk about the modification using water soluble polymers. Water soluble polymers like cellulose, derivatives and a polyvinyl alcohol they are used for modification of cement mortar and concrete. Now, these polymers are added in a small amount as powder or aqueous solution during mixing. The main benefit of this modification is improved workability and prevention of dry out phenomena.



The water soluble polymer increase the viscosity of the water phase in the modified cement mortar and concrete. The formation of thin water impervious film provides a sealing effect and water soluble polymers generally do not significantly improve the strength of the modified system. Let us talk about the modification using liquid resin. Liquid thermosetting resins are used for modification of cement mortar and concrete. Polymerizable low molecular weight polymers or pre-polymer they are added in liquid form during mixing.

The polymer content in modified mortar and concrete is generally higher than latex modified system and the polymerization occurs in presence of water resulting in the formulation of polymer phase and simultaneously cement hydration occurs. The modified system this forms a co-matrix phase with a network structure of interpenetrating polymer and cement hydrate phase. The co-matrix phase strongly binds aggregates. We can have improved strength and other properties as per the observed in the modified mortar and concrete that may be similar to the latex modified system. Let us talk about the modification using monomers.

Modification using Monomers

- Modification of cement composites with monomers is similar to liquid resin modification but involves the addition of monomers instead of liquid resins.
- Monomers are mixed with cement mortar and concrete in significant quantities.
- Polymerization and cement hydration occur simultaneously during or after curing.

Source: Y. Ohama, (1995) Handbook of Polymer-Modified Concrete and Mortars, Noyes Publications U.S.A.

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The modification of cement composites with monomer is similar to liquid resin modification but involves the addition of monomer instead of liquid resin. Monomers are mixed with cement mortar and concrete in significant quantities and polymerization in the cement hydration occurs simultaneously during or after curing. The aim is to create a monolithic matrix that binds aggregates. Generally this modification approach has not been successful due to poor properties of the modified system. There are various challenges attributed to this one.

Materials used in latex modified system

- The materials used in latex-modified mortar and concrete are the same as those in ordinary cement mortar and concrete.

1. Cements:

- Ordinary portland cement is widely used.
- Other types such as high-early-strength, ultrahigh-early-strength, sulfate-resisting, moderate-heat, white, blended, high alumina, and ultrarapid-hardening cements are also employed.
- Air-entraining cement should not be used due to latex addition.

Source: Y. Ohama, (1995) Handbook of Polymer-Modified Concrete and Mortars, Noyes Publications U.S.A.

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These challenges include interference with the cement hydration, degradation of monomers by cement alkalis and difficulty in achieving uniform dispersion during mixing. Let us talk about the materials used in the latex modified system. The materials used in the latex modified mortar and concrete are the same as those in the ordinary cement mortar concrete. First and foremost is the cement. We can use the ordinary Portland cement which is being widely used.

Materials used in latex modified system

2. Polymer Latexes:

- Polymer latexes consist of small polymer particles (0.05-5 pm) dispersed in water.
- They are produced by emulsion polymerization.
- Reactor agitation and heating with initiators cause chain polymerization.
- Unreacted monomers are removed by stripping.
- Latexes may be concentrated or diluted, and additives like preservatives and stabilizers are included.

Source: Y. Ohama, (1995) Handbook of Polymer-Modified Concrete and Mortars, Noyes Publications U.S.A.

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The other types such as high early strength ultra high early strength sulphate resisting moderate heat, white cement, blended cement, high alumina and ultra rapid hardening cement they are also employed. Ear-entraining cement should not be used due to the latex addition. Then talk about the polymer latexes. The polymer latexes consists of small polymer particles maybe say 0.05 to 5 p.m. They are dispersed in water. They are usually produced by emulsion polymerization, reaction reactor agitation and heating with initiator they can cause the chain polymerization and unreacted monomer they are removed by stripping. Latexes may be concentrated or diluted and additives like preservatives and stabilizers are being added. Ultra rubber latex and epoxy latex have different production processes. The polymer latex this can be cationic, anionic, non-ionic based on the electrical charges on the particles and they are copolymer system with the total solid content of 40 to 50 percent by weight.

Materials used in latex modified system

- **General requirements for polymer latexes as cement modifiers:**

a) High chemical stability towards active cations (Ca2+ and A13+) released during cement hydration.

b) High mechanical stability under severe conditions, including mixing and pumping.

c) Low air-entraining action with appropriate antifoaming agents during mixing.

d) No negative impact on cement hydration.

Source: Y. Ohama, (1995) Handbook of Polymer-Modified Concrete and Mortars, Noyes Publications U.S.A.

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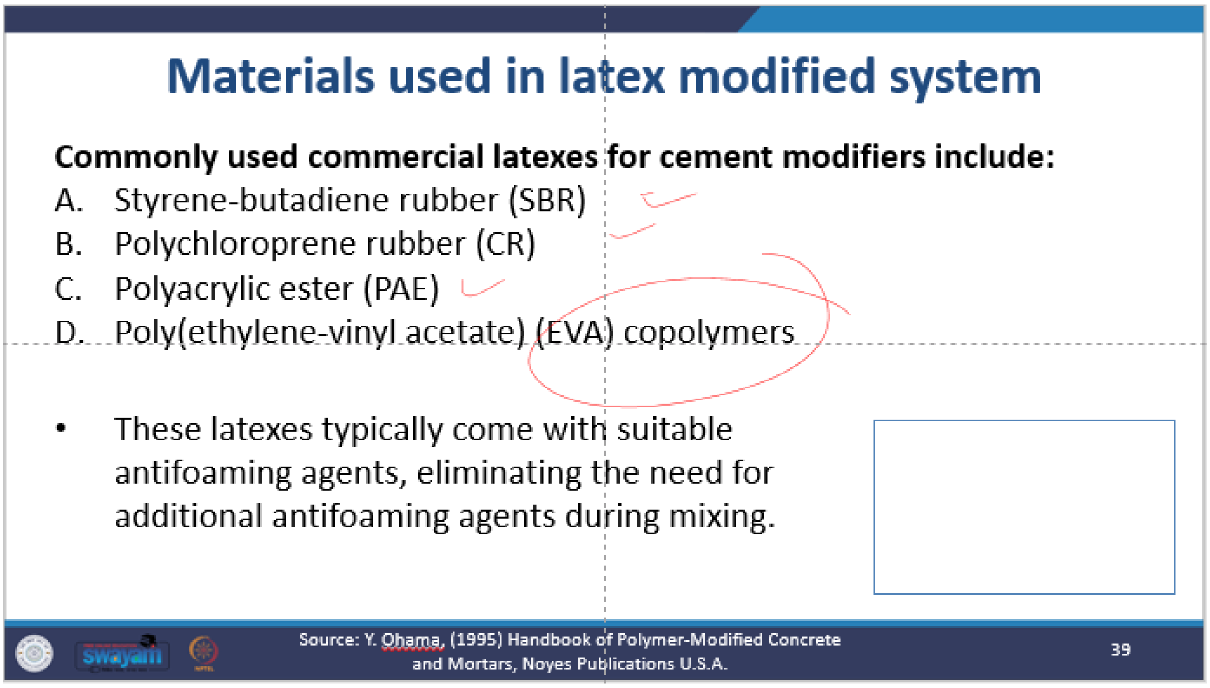
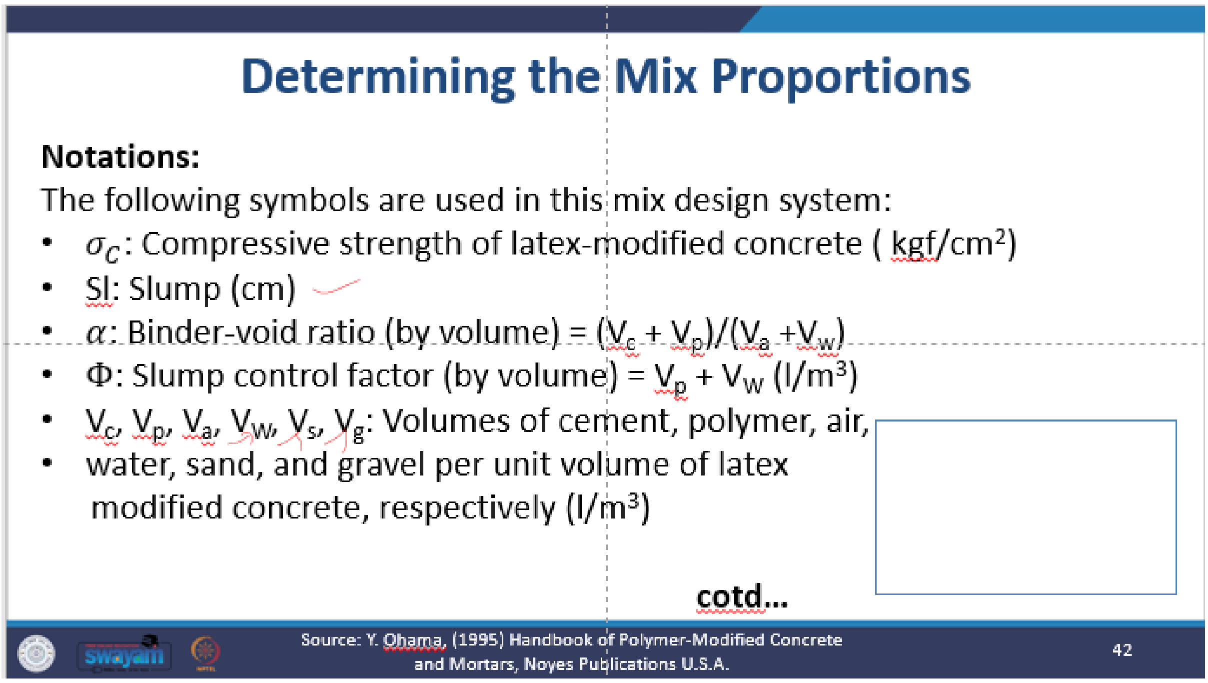
Most commercially available latexes for cement modifiers are based on elastomeric and thermoplastic polymers. Polyvinyl acetate latex and polyvinylidene chloride polyvinyl chloride latex they are generally not recommended as cement modifier in Japan due to poor water resistance and chloride ion liberation respectively. There are general requirements for polymer latexed as a cement modifier. One is that high chemical stability towards active cation Ca++ or Al3++ they are released during the cement hydration. High mechanical stability under severe condition including mixing and pumping.

Low air entraining action with appropriate anti-foaming agent during the mixing and there should be no negative impact on cement hydration. The formation of continuous polymer film in mortar or concrete achieved by lower minimum film forming temperature and strong addition to cement hydrates and aggregates. Excellent water resistance, alkali resistance, weatherability of the polymer films formed in mortar and concrete and thermal stability to withstand the temperature variation during the transportation and storage like free throw stability in cold climates or high temperature storage ability in hot climate. The commonly used commercial latexes for the cement modifier this includes styrene butadiene rubber, polychloroprene rubber, polyacrylates esters, polyethylene vinyl acetate EVA copolymers. These latexes typically come with a suitable anti-foaming agent eliminating the need of additional anti-foaming agent during mixing.



The latex modified mortar and concrete use the same type of aggregate as ordinary cement mortar and concrete. This includes the river sand and gravels, crushed sand and stones, silica sands, artificial lightweight aggregates. The silica sands and siliceous crushed stones these can be used for corrosion resistance purposes. Aggregates with the excessive water content should be avoided to achieve the desired polymer cement ratio. The aggregate should be clean, sound and have a proper grading and the selection of aggregate depends on the factors such as application, thickness, cover in reinforced concrete and type of and density of reinforcement.



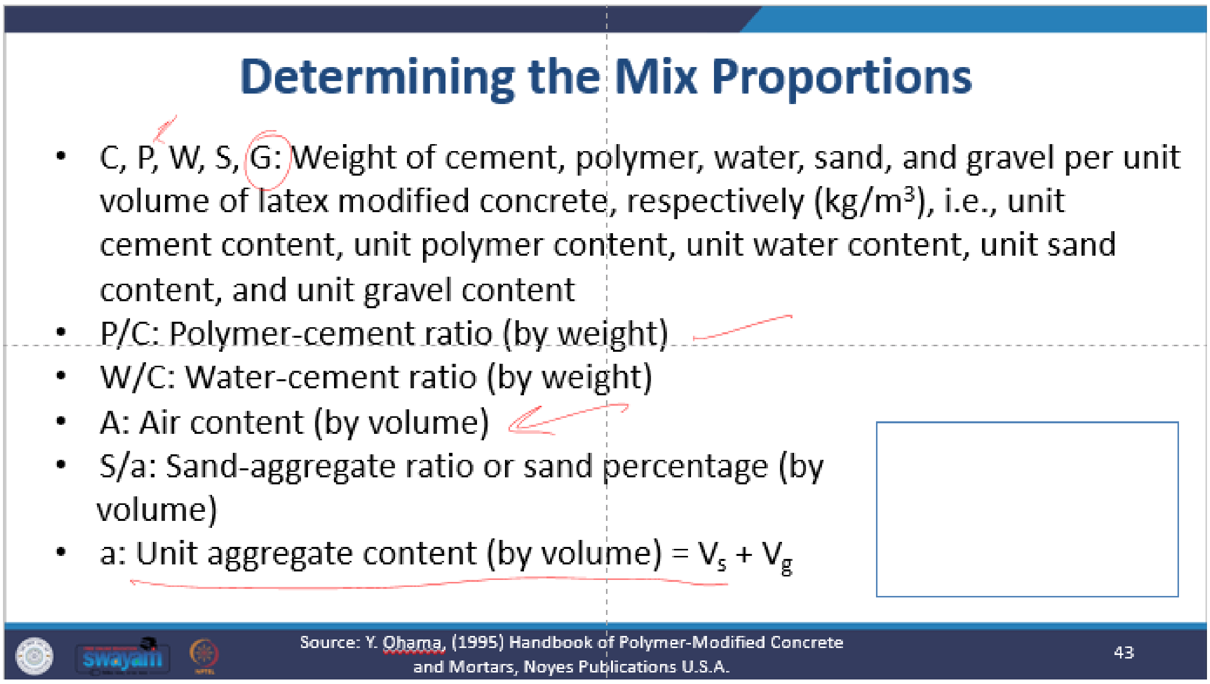
$\alpha = (V_c + V_p)/(V_a + V_w)$

$\Phi = Vp + VW \ (l/m^3)$

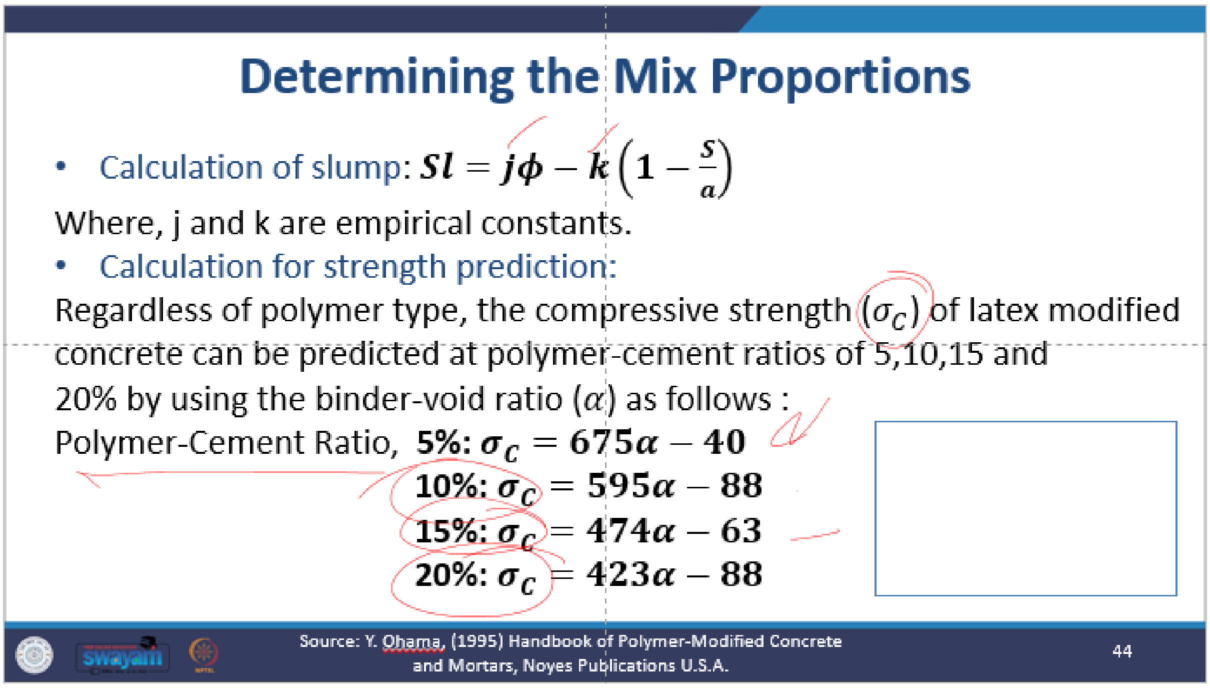
V_c, V_p, V_a, V_W, V_s, V_g: Volumes of cement, polymer, air, water, sand, and gravel per unit volume of latex

modified concrete, respectively (l/m^3)

Let us talk about the determining the mixed properties. There are several notations being used and these some of the symbols used in the mixed design system like theta c that is the compressive strength of latex modified concrete and the units are kilogram force per centimeter square. Then SL slump then the units are in centimeter. Then alpha that is a binder wide ratio by volume that is a v c plus v p over v a v w phi that is a slump control factor this is by volume that is v p plus v w. Now v c, v p, v a, v w, v s, v g these are the volumes of the cement, the polymer, the air, the water, the sand and the gravels per unit volume of the latex modified concrete respectively.

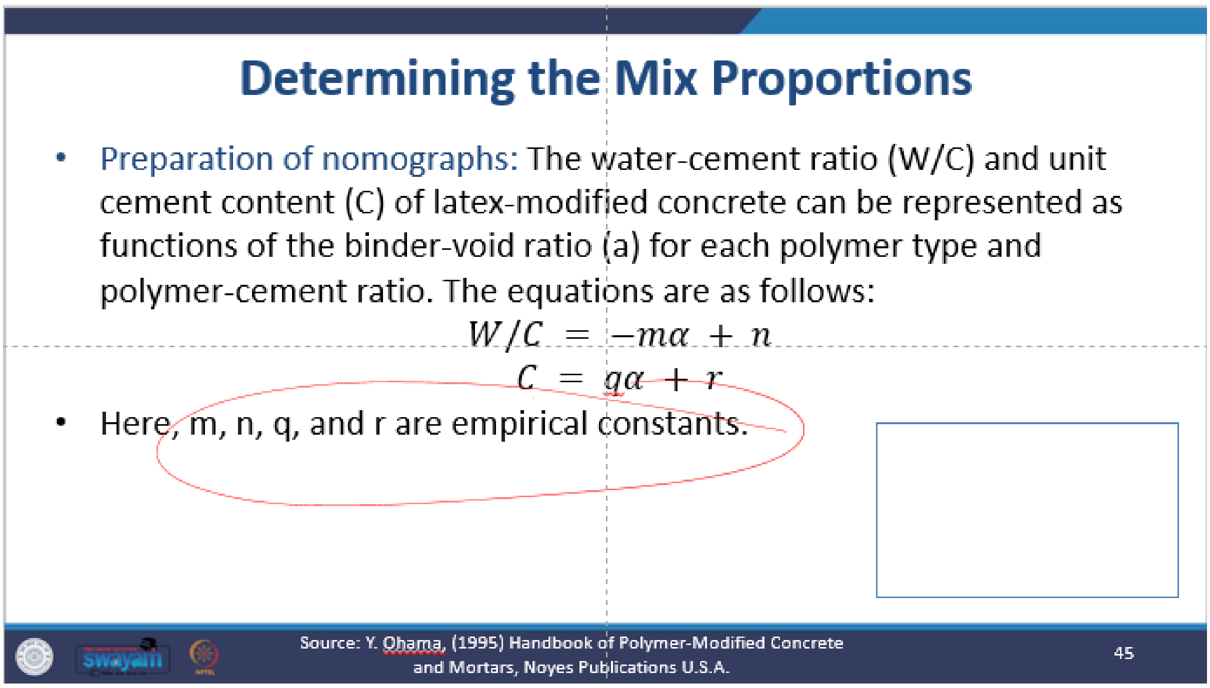


Then C, P, W, S, G weight of cement, weight of polymer, weight of water, weight of a sand and weight of gravel per unit volume of the latex modified concrete respectively that is in kilogram per meter cube. The unit of the cement content, unit polymer content and unit water content and unit sand content and unit gravel content. P over C the polymer cement ratio by weight, W over C water cement ratio by weight, A the air content by volume, S over A that is the sand aggregate ratio or the sand percentage by volume, A is a unit aggregate content by volume that is equal to v s plus v g. Now the calculation of slump S cell is equal to J phi minus k into 1 minus S over A where J and k are the empirical constant. Now if we try to calculate the strength prediction that regardless of polymer type the compressive strength theta c of latex modified concrete can be predicted by the polymer cement ratio of 5, 10, 15 and 20 percent by using the binder void ratio alpha as per the following like polymer cement ratio 5 percent theta c is equal to 675 alpha minus 40, 10 percent theta c is equal to 595 alpha minus 88, 15 percent theta c is equal to 474 alpha minus 63 and 20 percent theta c is equal to 423 alpha minus 88.



Now preparation of nomographs the water cement ratio and the unit cement content of the latex modified concrete can be represented as a function of the binder void ratio A for each polymer type and polymer cement ratio. So, the equation can be W over C is equal to minus m alpha plus n and C is equal to q alpha plus r here m and q and r are empirical constants. Now this particular figure provides the example of nomographs that utilize these equation to estimate W over C and C values. Now the procedure for determining the mixed properties of the latex modified concrete involves different steps like determining the required workability and the primary secondary performance of the concrete based on its application, measure the required slump and determine the compressive strength theta c and secondary properties such as flexural strength, waterproofing, adhesion, etc. Now determination of the polymer cement ratio P over C based on the manufacturer's information and technical data of polymer latexes for cement modifiers.

$$Sl = j\phi - k\left(1 - \frac{S}{a}\right)$$

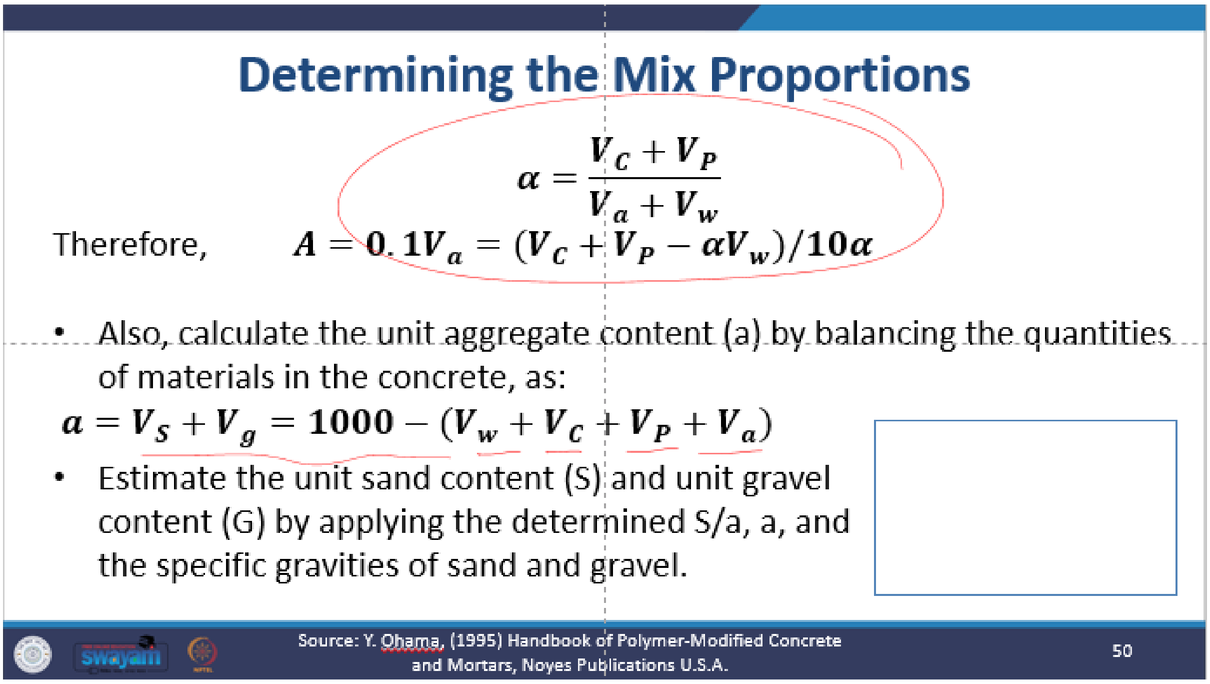


$$W/C = -m\alpha + n$$

$$C = q\alpha + r$$

Here, m, n, q, and ‘r’ are empirical constants.

Simultaneously determine the binder void ratio alpha using an equation of compressive strength prediction. Estimate the water cement ratio W over C and a unit cement content using nomograph and determine the value of A. We calculate the unit polymer content P and a unit water content W by applying the estimated C to the determination of P over C and W over C, respectively and determine the slump control factor phi using the sum of, say V P and V W derived from P W and the specific gravities of the polymer and water. So determine the sand aggregate ratio S over A using the equation of for slump prediction and next step is to estimate the air content A using the estimated values of C P W and these specific gravities of cement polymer and water according to the this particular equation that is alpha is equal to V C plus V P over V A over V W.



$$\alpha = \frac{V_C + V_P}{V_a + V_w}$$

$$A = 0.1V_a = (V_C + V_P - \alpha V_w)/10\alpha$$

$$a = V_S + V_g = 1000 - (V_w + V_C + V_P + V_a)$$

Therefore, A is equal to 0.1 V A is equal to V C plus V P plus minus alpha V W over tan alpha. Also we need to calculate the aggregate content by balancing equation of material the concrete as alpha is equal to V S plus V G is equal to 1000 minus V W plus V C plus V P plus V A. Then next step is to estimate the unit sand content S and the unit gravel content G by applying the determined S over A and A and A specific gravities of the sand and gravel.

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So dear friends in this particular segment we discussed about the application of polymers specifically in the building aspects and for convenience we have included several references which you can utilize as and when required. Thank you very much.