PROPERTIES OF NATURAL POLYMER MODIFIED MORTAR

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ANKUR GOYAL
(ROLL NO. 801422004)

UNDER THE SUPERVISION OF

Dr. PREM PAL BANSAL
Associate Professor,
Civil Engineering,
Thapar University, Patiala

DEPARTMENT OF CIVIL ENGINEERING

THAPAR UNIVERSITY

PATIALA-147004

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DECLARATION

I hereby declare that this dissertation titled **"PROPERTIES OF NATURAL POLYMER MODIFIED MORTAR"** is an authentic record of the work carried out as per the requirement for the award of degree of **Masters of Engineering** in **Structural Engineering** in the Civil Engineering Department of **Thapar University, Patiala** under the guidance of **Dr. Prem Pal Bansal, Associate Professor**, Department of Civil Engineering, Thapar University, Patiala during July 2015 to July 2016. The matter embodied in this report has not been submitted in part or full to any other university or institute for the award of any degree.

Date: 14th July 2016

Ankur Goyal

(801422004)

CERTIFICATE

This is to certify that the above statement made by the student concerned is correct and true to the best of my knowledge and belief.

Dr. Prem Pal Bansal

Associate Professor

Department of Civil Engineering

Thapar University, Patiala

Countersigned by

Dr. Naveen Kwatra

Professor & Head

Department of Civil Engineering

Thapar University, Patiala

Dr. S. S. Bhatia

Dean of Academic Affairs

Thapar University, Patiala

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Ankur Goyal

(801422004)

ABSTRACT

Green construction material plays an important role in sustainable development. Brundtland Report (1987) about sustainability has driven the global concept of sustainable development as well as the sustainability of infrastructure. Since concrete has become the most popular construction material in the world, sustainable concrete will determine the sustainability of infrastructure. Several efforts have been done to achieve the sustainable concrete. Methods to achieve the objectives can be (for example) the use of less energy in making concrete, reduction of CO_2 emission by using natural additives, reduction in use of natural aggregates via replacement by recycled aggregates. One of the modern concepts to make concrete a green construction material is, “Triangle of Virtuous Concrete Principle”. The “Triangle of Virtuous Concrete Principle” requires the three parameters of sustainable development, infrastructure development and carbon footprint reduction simultaneously. Connecting the three aspects in the “Triangle of Virtuous Concrete Principle”, concrete will truly become virtuous and green construction material.

Sustainable concrete needs ‘extra’ life-time that means longer durability. Hence, concrete shall be stronger, denser, and more durable. For the last few decades, polymer cementitious materials have been added to concrete to improve its performance and to enhance its properties. For application, polymer added into mortar or concrete which is called polymer mortar or polymer concrete. When polymer added together with cement and also aggregate into mortar or concrete, it is called polymer modified mortar or polymer modified concrete. Polymer modified cementitious material exhibits improved binding properties and adhesion to aggregates; therefore it is useful for concrete repairing and retrofitting in modern construction.

In Polymer Modified Mortars (PMM) aggregates are bound by a matrix phase resulting in superior properties compared to the conventional mortar.

Since most of the polymers are derived from petroleum, which is a non-renewable resource it will end someday. Today’s energy matrix is mainly based on fossil fuels like petroleum oil, coal and natural gas, which covers more than 80% of total worldwide energy consumption.

Alternatives to petroleum-based products are one of the main interests of researchers. Natural oils occur in nature, can be extracted and are renewable. Natural oils such as soybean, corn, linseed, castor and seaweeds, when synthesized produce natural polymers. They are renewable, offer comparable performance and of low cost when compared with petroleum-based polymer matrices. These materials have also environmental advantages over petroleum-based materials.

In this study, polymer modified mortar is designed by using natural polymer from seaweeds. The research is conducted in two phases, pilot study and main-experiment.

Pilot Study aimed to investigate the compressive strength of natural mortar modified with seaweed gel (Eucheuma Cottonii) and seaweed powder (Eucheuma Cottonii). From the pre-experiment results it was observed that mortar modified with seaweed powder gave better compressive strength. Therefore, seaweed powder was selected for main experiment.

The main experiment was conducted by modifying mortar with seaweed powder as an additive in varying compositions of 0.5%, 1%, 1.5% and 2% of cement by weight.

Compressive strength was evaluated for this mortar at 7 days and 28 days of curing. Split tensile strength was also evaluated at 28 days curing. Durability properties were also tested for water sorptivity and Rapid Chloride Permeability Test (RCPT).

Slant Shear test was also performed to check the bond strength of 28 day cured conventional mix repaired with fresh Polymer Modified Mortar and then cured for 7 days.

XRD analysis was also performed on the samples to check the products formed during the hydration reaction. The results from this analysis are used to interpret the results of mechanical and durability tests.

The research has shown that natural polymer modified mortar with mix composition of seaweed powder of 1% of cement by weight exhibited the maximum enhancement in the compressive strength and split tensile strength and significant improvement in the durability properties and bond strength.

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CHAPTER 1

INTRODUCTION

1.1 General

Polymer Mortar (PM) is a cementing composite, made of inorganic and organic aggregates bonded together by a thermo set resin binder, which substitutes the cement. PM was first developed in the 1950 and became widely known in the 1970's. The composition of PM is determined by its applications, and its strength is influenced by ratio of aggregate to resin content. PM is used very efficiently in precast components. Indeed, polymer concrete has previously been mainly used for industrial flooring, repairing of damaged concrete structures and underground pipes. In comparison with conventional Portland cement concrete, Polymer Mortar offers many advantages, such as higher strength, better chemical resistance and improved fracture toughness.

Globally, buildings are responsible for a huge share of energy, electricity, water and materials consumption. The building sector thus has a great potential to deliver significant cuts in emissions at little or no cost. Buildings account for 18% of global emissions today or the equivalent of 9 billion tones of CO_2 annually. According to the United Nations Environment Program, if new technologies in construction are not adopted during this time of rapid growth, emissions could double by 2050. Green buildings aim to reduce the environmental impact of building. Since construction almost always degrades a building site, thereby building is not at all preferable to green building, in terms of reducing environmental impact. The second rule is that every building should be as small as possible. The third rule is, not to contribute to sprawl, even if the most energy-efficient, environmentally sound methods are used in design and construction.

Green buildings represent a novel concept as a step towards developing a healthier and wholesome surrounding environment by reducing emissions and promoting the reuse and recycling of materials.

1.2 Need for Natural Polymers

Thermo set polymers are derived from petroleum which is a non-renewable resource and it will end someday. Today’s energy matrix is mainly based primarily on fossil fuels like petroleum oil, coal and natural gas, which accounts for more than 80% of total worldwide energy consumption. Petroleum oil represents more than one third of this consumption according to the International Energy Agency. Petroleum products are derived from crude oil and are processed in oil refineries. The majority of petroleum is converted into several classes of fuels.

Chemical admixture additions of both organic and inorganic forms have been used in the ancient period along with mortar. The organic additions were natural, mostly of plants/animal origin and the inorganic ones were the natural and artificial pozzolanic materials. Thus the roots of the today’s chemical admixture addition during construction are from the ancient period. The difference is that in the ancient period the materials used were in the natural form whereas the present day materials are manmade synthetic materials are used. The materials used in the ancient period were environment friendly, stable in a wider range of environmental conditions whereas the present synthetic materials are stable within the specified conditions, this could be one of the possible reasons why ancient structures are still in good shape, confirming the durability of these structures which used natural biopolymers from selected plant & fruit extracts. In the ancient times, the clays of different varieties, lime, pozzolana were mainly used to bind the stones. The lime being produced from different raw materials depending upon their availability like sea shells and conch were used in the places close to sea, whereas Kankar was used in places where there was good quality clay and limestone. The pozzolanic materials used were mainly natural pozzolans. The natural biopolymers were used to improve the properties of plasters, mortars and clays in the fresh as well as hardened state to improve the durability of the structures. These biopolymeric additions also exhibited biocidal and insecticidal properties leading to increased resistance of the constructed structure to bio-corrosion/termite resistance and other environmental deteriorating effects.

Alternatives to petroleum-based products are one of the main interests of researchers. Natural oils occur in nature, can be extracted and are renewable. Natural oils such as soybean, corn, linseed, castor when synthesized produces natural polymers. Plant oils, which are predominantly made up of triglyceride molecules, are ideal replacement material to manufacture bio-based polymeric matrix as they are renewable, offer comparable performance and of low cost when compared with petroleum-based polymer matrices. These materials have also environmental advantages over petroleum-based materials making them an attractive alternative.

1.3 Selection of Materials

Effective production of Polymer Modified Mortar could be attained by carefully inspecting, selecting, controlling and proportioning all the necessary ingredients, which go into making of mortar. The ingredient materials with specific requirements are discussed as below:

1.3.1 Cement

Cement is the basic ingredient for making mortar and for the development of polymer modified mortar PPC should be utilized from both workability as well as strength point of view as it contains flyash which increases the strength and workability. Any variation in cement content causes the compressive strength of concrete to fluctuate more than any other single material.

1.3.2 Water Cement Ratio

A well established fact in the cement industry speaks that excessive water content leads to reduction in strength of cement mortar, but insufficient water content incurs a poor workability. Hence, a method for determining the optimum water content and influence of w/c ratio on cement mortar is obviously desirable. Quality control unit involves tight control of w/c ratio for concrete constituents. But in the case of cement mortar, more water is deemed requisite by the mason to make the mixture workable enough for easy mixing and placement. Therefore, it is appropriate to study the influence of w/c ratio for mortar strength.

1.3.3 Fine aggregates

The characteristic property and quality of fine aggregates affect the properties of concrete in fresh as well as in hardened state. Redistribution of aggregates after compaction often creates homogeneity in the concrete mix system due to the influence of vibrations. This can lead to strength gradients. The presence of aggregates greatly increase the robustness of concrete, above that of cement, which otherwise is a brittle material and thus making concrete a true composite material. The grading of fine aggregate regulates the workability of concrete at a particular water content of the concrete mix as the specific surface of these fine aggregates is relatively much higher than that of coarse aggregates. Sand which has fineness modulus below 2.5 produces concrete which is too sticky and due to this sticky behavior it is very difficult to compact. However, the sand which has fineness modulus of about 3.0 gave the optimum compressive strength and workability.

1.3.4 Admixtures

The admixtures which are generally used in concrete manufacturing can be classified into two categories namely chemical admixture and mineral admixtures.

Chemical admixtures

Chemical admixtures are materials in the form of powder or fluids that are added to the concrete to give it certain characteristics not obtainable with plain concrete mixes. In normal use, admixture dosages are less than 5% by mass of cement and are added to the concrete at the time of batching/mixing. The common types of admixtures are as follows.

- Accelerators speed up the hydration (hardening) of the concrete. Typical materials used are $CaCl_2$, $Ca(NO_3)_2$ and $NaNO_3$. However, use of chlorides may cause corrosion in steel reinforcing and is prohibited in some countries, so the nitrates may be favored. Accelerating admixtures are especially useful for modifying the properties of concrete in cold weather.
- Retarders slow the hydration of concrete and are used in large or difficult pours where partial setting before the pour is complete is undesirable. Typical polyol retarders are sugar, sucrose, sodium glucomate, glucose, citric acid, and tartaric acid.
- Air entraining agents add and entrain tiny air bubbles in the concrete, which reduces damage during freeze-thaw cycles, increasing durability. However, entrained air entails a trade off with strength, as each 1% of air may decrease compressive strength up to 5%. If too much air becomes trapped in the concrete as a result of the mixing process, de-foamers can be used to encourage the air bubble to agglomerate, rise to the surface of the wet concrete and then disperse.
- Plasticizers increase the workability of plastic or "fresh" concrete, allowing it be placed more easily, with less consolidating effort. A typical plasticizer is lignosulfonate. Plasticizers can

be used to reduce the water content of a concrete while maintaining workability and are sometimes called water-reducers due to this use. Such treatment improves its strength and durability characteristics. Superplasticizers (also called high-range water-reducers) are a class of plasticizers that have fewer deleterious effects and can be used to increase workability more than is practical with traditional plasticizers. Compounds used as superplasticizers include sulfonated naphthalene formaldehyde condensate, sulfonated melamine formaldehyde condensate, acetone formaldehyde condensate and polycarboxylate ethers.

- Pigments can be used to change the color of concrete, for aesthetics.
- Corrosion inhibitors are used to minimize the corrosion of steel and steel bars in concrete.
- Bonding agents are used to create a bond between old and new concrete (typically a type of polymer) with wide temperature tolerance and corrosion resistance.
- Pumping aids improve pumpability, thicken the paste and reduce separation and bleeding.

1.4 Constituent Admixture Used

Carrageenans

Carrageenans are a family of linear sulphated polysaccharides that are extracted from red edible seaweeds (eucheuma cottoni). They are widely used, for their gelling, thickening, and stabilizing properties.

Carrageenans are large, highly flexible molecules that curl forming helical structures. This gives them the ability to form a variety of different gels at room temperature. They are widely used in the food and other industries as thickening and stabilizing agents.

Eucheuma Cottonii (powder) is used in this research because they contain agarans and carrageenans which helps in emulsification of its form thus strengthening the structure. Eucheuma Cottonii is polysaccharide that contains kappa carrageenan. It has advantage as emulsifier, suspensor, condenser, and stabilizer.

It is also noted that Cottonii (powder) have rheological properties as gelling and thickening agents that which can perform as epoxy resin in polymer modified mortar. According to the advantage of seaweed, this natural polymer modified mortar is expected to perform excellent bonding mechanism, strength, and durability as the key factor to achieve sustainability.

1.5. Advantages of Natural Polymer Modified Mortars

Of various polymer-modified mortar and concrete, , polymer powder -modified mortar and concrete have superior properties, such as high tensile and flexural strengths, excellent adhesion, high waterproofness, high abrasion resistance, and good chemical resistance, compared to ordinary cement mortar and concrete. Durability issues in normal mortar have been a major problem for many years and large amount of funds are required to rehabilitation of aging infrastructure. Polymer modified material possesses good durability properties and lower porosity and capillaries thus can be used for repairing works. Their construction requires lower maintenance costs in its service life than conventional concrete. Polymer modified cementitious material has good binding properties and adhesion to aggregates, therefore it is useful for concrete repairing and retrofitting in modern construction.

1.6. Applications of Natural Polymer Modified Mortars

Due to possession of superior properties like high tensile and flexural strengths, excellent adhesion, high waterproofness, high abrasion resistance, and good chemical resistance, compared to ordinary cement mortar and concrete. Accordingly, they are widely used in many specialized applications in which the ordinary cement mortar and concrete have been employed to a lesser extent till now. In these applications, the , polymer powder -modified mortar is widely used rather than the latex-modified concrete from the viewpoint of a balance between their performance and cost. Typical applications of the , polymer powder -modified mortar and concrete are listed below.

Recently, polymer powder-modified mortar has been increasingly used in much the same applications as ordinary mortar and concrete.
Although more expensive compared to latex-modified mortar and concrete, liquid resin-modified mortars and concretes appear to be getting increased acceptance in the construction industry.
This may be because they give more rapid hardening, higher thermal stability, and better water resistance over the latex-modified systems.

Typical Applications of Polymer-Modified Mortar.

Floorings and Pavements	Floors for houses, warehouses, schools, hospitals, offices, shops, toilets, gymnasiums and factories, passages, stairs, garages, railway platforms, .
Adhesives	Tile adhesives, adhesives for floorings, walling materials and heat-insulating materials, adhesives joining new cement concrete or mortar to old cement.
Repair Materials	Grouts for repairing cracks and delaminations of concrete structures, patching materials for Damaged concrete structures, rustproof coatings for corroded reinforcing bars, etc.

Figure 1.1 Application of Polymer Mortar in Flooring and Repairing

In Japan, polymer-modified mortar is most widely used as a construction material for finishing and repair work, but polymer-modified concrete is seldom employed because of a poor cost-performance balance. This trend is similar to that in other advanced countries. As stated above, about 60,300 m^3 per year of polymer modified concrete is employed for the repair work for damaged concrete structures in U.S. In U.K., about $500 million are spent each year on the repair of the concrete structures. Thus the polymer-modified mortars and concretes are currently becoming low-cost, promising materials for preventing chloride-induced corrosion and repairing damaged reinforced concrete structures.

1.7 ORGANIZATION OF DISSERTATION

Many researchers put their theory for use of cement based polymer composites but very less work specifically regarding to the naturally modified polymer has been done. So the aim of the study is to study the effect on mechanical and durability properties of mortars when modified with natural polymer.

Organization of dissertation has been organized in the following five chapters:

Chapter 1: This chapter deals general introduction and history of Polymer Modified Mortars.

Chapter 2: This chapter deals with review of literature work and the need for the present study.

Chapter 3: This chapter details the experimental programme. In this properties of various material used in work have been discussed.

Chapter 4: This chapter is about the results and discussion of the work carried out.

Chapter 5: It details the summary and conclusions of the work carried out.

CHAPTER 2

LITERATURE REVIEW

2.1 General

In spite of their extensive use, cement mortar and concretes present a number of shortcomings such as low tensile and flexural strengths, low failure strain, delayed hardening, susceptibility to frost damage, low bonding strength in repair applications, and poor resistance to aggressive agents. Some of these drawbacks can be overcome by the incorporation of an organic polymer or resin in mortar mass, instead or in conjunction with Portland cement binder. These relatively new materials, the concrete-polymer composites (CPC), offer a number of advantages that justify their growing use and application.

This chapter summarizes the background related to polymer materials and their performance as compared to ordinary cement concretes. The review also deals with the concepts and processes technologies associated with mortar-polymer composites, their development and progress over the last decades, and the standardization work that has been made regarding them in the industry.

The progress of CPC-science can be assessed by the relevant amount of international activities, published papers, awarded patents and standardization works that have been developed in the last few decades. The relevant activities addressing this subject are reported, in the following sections.

Considerable volume of information and studies is presently available on concrete polymer composites.

The contributions made from relevant activities (conferences and meetings, published reports, users' guides and standardization works), along with the practical experience gained within the growing industry that applies polymers to concrete technology, constitute the basis of polymer modified mortar in applied science, which is at present only limited by the ingenuity of the concrete user.

2.2 Review of the Previous Work

In the following content, the previous work relating to the effect of different polymers on the cement mortar mix has been mentioned.

2.2.1 SBR and VAE latexes

Ghai et al. (2016) studied the effects of addition of polymers namely; styrene-butadiene-rubber latex (SBR) and vinyl-acetate-ethylene polymer (VAE) in the mortar matrix. The polymer modified mortars (PMM) were prepared by adding different percentage of polymers to the conventional cement mortar (CCM) matrix. Cement to sand ratio of 1:2 was used for casting the specimens. Two types of mortars modified with SBR and VAE polymers were prepared. The mortar matrices were modified by addition of 5%, 10%, 15% and 20% polymer by weight of cement. The mixes had a constant w/c ratio of 0.56. The addition of SBR and VAE polymer to the mortar matrix was designated as S11, S21, S31, S41 and V11, V21, V31, V41 respectively. The mix details are provided in Table 2.1

TABLE 2.1 Polymer-Modified Mortars at w/c ratio of 0.56

S.No.	Mix Designation	Polymer/Cement Ratio (%)	Water/Cement Ratio
1	CON	0	0.56
2	S11	5	0.56
3	S21	10	0.56
4	S31	15	0.56
5	S41	20	0.56
6	V11	5	0.56
7	V21	10	0.56
8	V31	15	0.56
9	V41	20	0.56

Cubical specimens of size 70.6mm×70.6mm×70.6mm, of SBR and VAE polymer modified mortars (PMM) were casted and tested for compressive strength as per ASTM C 109-93. Beam specimens of size 40mm×40mm×160mm were casted to investigate the flexural strength by performing the central-point loading test as per ASTM C 348-02. Cylindrical specimens of size 100mm×200mm were also casted to investigate the Young's modulus of the polymer modified mortar as per ASTM C 469-02.

The compressive strength of SBR modified mortars first increased and then decreased with the increase in percentage addition of SBR and the maximum increase (7.46%) was observed at 15% addition of polymer. The addition of VAE with cement mortar caused reduction in the compressive strength of VAE modified mortars at all compositions.

With 15% addition of polymer by weight of cement, the flexural strength of SBR and VAE modified mortars was observed to increase by 44.89% and 23.46%, respectively. With any further addition of these polymers, the flexural strength was found to reduce.

The results for Modulus of Elasticity (MoE) of SBR modified mortars, showed that the MoE value increased by 12.45% with a 10% polymer addition. A further addition of polymer resulted in reduction of MoE values.

The MoE value of VAE modified mortar decreased at a higher rate as compared to the ordinary mortar and decreased up to 44.68% at 20% polymer addition.

2.2.2 Jute Fibers

Chakraborty et al. (2013) studied the physical and mechanical properties of polymer modified mortar reinforced with the jute fibers. Polymer modified alkali treated jute fiber as a reinforcing agent was prepared using different compositions of jute reinforced cement mortar as shown in Table 2.2.

Flow behaviour of the freshly prepared cement mortar (which indicates its workability) is estimated by a flow table test in accordance with IS 1727. The bulk density (both wet and dry), water absorption, and apparent porosity of the water cured mortar samples were estimated according to ASTM C 948.

The mechanical properties like compressive strength were tested using 1000 KN UTM and flexural properties were tested using three point load test.

Table 2.2 Composition of Jute Reinforced Cement Mortar.

Components	Formulation No.						
	1	**2**	**3**	**4**	**5**	**6**	**7**
Cement (kg)	3	3	3	3	3	3	3
Sand (kg)	9	9	9	9	9	9	9
Raw/0.5% alkali treated jute	-	30[a]	30[b]	30[b]	30[b]	30[b]	30[b]
Weight of polymer (dry basis)	-	-	0.257[c]	0.513[c]	1.025[c]	2.050[c]	0.513[c]
Water (ml) (for polymer emulsion)	-	-	1000[d]	1000[d]	1000[d]	1000[d]	1000[d]
Additional water (ml) (for mortar mixing)	1800	1800	800	800	800	800	740

[a] Weight of water soaked raw jute (g).

[b] Weight of alkali treated jute (g).

[c] Weight of polymer of Sika latex in respective formulations on dry basis.

[d] Added water for making polymer emulsion (ml).

Polymer modified alkali treated jute fiber as a reinforcing agent, substantially improves the physical and mechanical properties of cement mortar with a mix design cement : sand : fiber : water ::1:3:0.01:0.6. The workability of the mortar is found to increase systematically from 155 ± 5 mm (control mortar) to 167 ± 8 mm (0.2050% polymer modified mortar). The density of the mortar is increased from 2092 kg/m3 to 2136 kg/m3 with a concomitant reduction of both water absorption and apparent porosity. Optimal polymer content in emulsion (0.0513%) is found to increase the compressive strength, modulus of rupture and flexural toughness 25%, 28%, 387% respectively as compared to control mortar.

Wan Jo et al. (2015) performed the Hydration study of the polymer modified jute fiber reinforced cement paste using analytical techniques. The paper deals with the hydration behaviour of the polymer modified jute fiber reinforced cement paste. In this investigation, different polymer contents in the emulsion (i.e., 0.0257%, 0.0513%, 0.1025% and 0.2050%) were used to prepare the polymer modified jute fiber reinforced cement paste. The hydration characteristic of the cement samples was assessed by monitoring the extent of hydrated cement product. Based on the X-ray diffraction, Fourier transformation infrared spectroscopy, differential scanning calorimetry and thermo gravimetry analysis of the hydrated cement samples, it was revealed that the polymer modified (0.0513%) jute fiber reinforced cement sample produced a greater extent of hydrated cement product as compared to that of the unmodified fiber reinforced cement sample. Therefore, it is demonstrated that the unmodified jute fiber delays the cement hydration reaction, whilst, the use of an optimum polymer content in the emulsion (0.0513%) recovers the hydration delaying action of jute fiber.

2.2.3 Pissava Fibers

Reis et al. (2013) carried out experimental studies to evaluate the feasibility of use piassava (Attalea Funifera Mart) lees as natural reinforcement of polymer mortars with particular regards to fracture and toughening mechanisms. The fracture properties like fracture toughness, fracture energy and elasticity modulus were calculated according to RILEM 50-FMC, RILEM 49TFR and three point bending tests were used to determine the fracture loads. Various weight fractions of fine aggregates of 1%, 2%, 5%, 10% and 15% were replaced by the same weight of piassava lees. A significant reduction of the specific weight of the polymer mortars was observed. The fracture toughness of epoxy polymer mortar when piassava lees substitutes foundry sand by 1% was increased to 17.70%. An increase of 57.1% for 5% piassava lees specimens in the fracture energy when compared to plain epoxy specimens was observed. The modulus of elasticity increased only upto 2% of piassava lees content.

Reis et al. (2014) studied the mechanical behavior of piassava fiber reinforced castor oil polymer Mortars. The aim of this work was to evaluate the use of natural fibers, piassava (Attalea Funifera Mart) scraps from broom industry, as reinforcement of natural polymer based mortars. The biopolymer matrix is manufactured from castor oil obtained by expressing the seed of the plant Ricinus Communis. Mechanical properties of castor oil polymer mortars reinforced with 1 and 2 wt% of piassava fibers lees were analyzed with particular regards to compressive, flexural and fracture properties. The results shown are in Table 2.3.

It can be seen that, piassava fibers act as reinforcement to castor oil polymer mortars. In compression a small decrease in strength, 2.1%, is calculated for 1% of piassava fiber content

Table 2.3 Piassava Fiber Reinforced Castor Oil Polymer Mortars Test Results

Specimens	Compressive strength (MPa)	Flexural strength (MPa)
Plain castor oil PM	37.86	22.11
1% Piassava reinforcement	37.06	19.30
2% Piassava reinforcement	39.52	19.98

and an increase of 4.4% is reported for 2% of piassava fiber content. According to Ribeiro et al. when piassava fibers were used as reinforcement in polyester polymer mortars and tested in compression an increase in strength was observed, 14.3% for 1% piassava fiber content and 10.5% when 2% of piassava fibers were used as aggregate replacement. Comparing to plain castor oil polymer mortar to epoxy a slight decrease, 2.2%, is observed and an increase of 55.2% when compared to unsaturated polyester PM.

Comparing plain castor oil polymer mortars to plain epoxy and unsaturated polyester, plain PM has higher flexural strength. Relating to epoxy PM, castor oil PM has 39.1% higher flexural strength.

2.2.4 Hemp Fibers

Hamzaoui et al. (2014) studied the microstructure and mechanical performance of modified mortar using hemp fibers and carbon nano tubes. Mechanical performance of modified mortar using hemp fibers were studied following various processing conditions. Hemp fibers combined with carbon nanotubes (CNT) were introduced in mortar and their effect was studied as function of curing time. The cement phase was replaced by different percentages of dry or wet hemp fibers ranging from 1.1 wt% up to 3.1 wt% of the cement weight whereas carbon nanotubes were dispersed in the aqueous solution.

Experimental results showed that compressive and flexural strengths of wet fibers modified mortar are higher than those for dry hemp-mortar material by 12.35% and 16% respectively. The achieved optimal percentage of wet hemp fibers is 2.1 wt% allowing a flexural strength higher than that of reference mortar. The addition of an optimal CNT concentration (0.01 wt%) combined with wet hemp has a reinforcing effect which turns to be related to an improvement of compressive and flexural strengths by 10% and 24%, respectively.

Mostefai et al. (2015). **s**tudied the Microstructure and mechanical performance of modified hemp fiber and shive mortars. In this work, he investigated the effect of hemp fiber and shive addition on modified mortars microstructure and mechanical performance. The mortar formulation was adjusted with different percentages and lengths of either hemp fibers or shives. Workability of fresh modified mortars was carried out using two main techniques including maniabilimeter and flow table experiments. Micro structural effects were revealed using X-ray µ-tomography where the pore content and 3D spatial arrangement and content of hemp was investigated. Mechanical performance was derived from bending and compression testing at different curing times. Mechanical strength was found to depend positively on hemp length, curing time and negatively on hemp content. This statement holds for both shiv and fiber modified mortars irrespective of loading type. When comparing the average strength for 7 days and 90 days, the observed improvement of compressive strength was better achieved with hemp fiber addition (69% higher than the reference against 58% for shiv modified mortar) but results in a limited increase in bending strength (only 38% higher than the reference against 58% for shiv modified mortar). Optimal mortar formulations involving either hemp fibers or shives have to be planned with fillers at least of 20 mm in length and weight contents no more than 2%.

2.2.5 Linseed oil

Nunes et al.(2014) studied the hydrophobic lime based mortars with linseed oil. Linseed oil was added to lime and lime metakaolin mortars with compositions shown in Table 2.4 in order to impart hydrophobic properties and investigate its resistance to weathering agents involving water transport.

Table 2.4 Mortar identification, composition by weight and air content of fresh mixture

Mortar code	Composition	Mortar code	Water/binder ratio	Air content (%)
L	Lime:sand (1:3)	-	1.04	2.6
LO	Lime:sand (1:3)	1.5	1.08	5.4
LM	Lime:metakaolin:sand (0.75:0.25:3)	-	.96	2.2
LMO	Lime:metakaolin:sand (0.75:0.25:3)	1.5	1.02	4

Different properties of the mortars with 6 months of age were evaluated: open porosity, pore size distribution, water absorption by capillarity, mechanical strength, carbonation reactions, microstructure and durability assessed by testing the resistance to sodium chloride accelerated ageing test. Significant durability improvement of both lime and lime metakaolin mortars enriched with linseed oil was achieved: remarkable capillarity reduction and consequently higher resistance to NaCl cycles. Linseed oil had a different effect on the two studied mortars: mechanical strength was slightly reduced for lime and slightly raised for lime metakaolin. The mechanism for the durability improvement was found to be related to the modification of the chemical structure rather than on the alteration of the physical properties of the mortars.

2.2.6 Basalt Fibers

Zych et al. (2012) studied the properties of cement mortars mixed with basalt fibers. Basalt fibers, 5 mm and 12 mm long, with the amount of 0.4 kg/m^3, 1 kg/m^3, 2 kg/m^3 were used as the reinforcement of 3, 7 and 28-day mortars. The results of research concerning flexural strength, work of fracture and compressive strength of basalt fiber reinforced cement mortars as well as basalt fiber resistance in alkaline environment were presented in the paper. lt was found that the addition of fibers caused the increase in flexural strength (up to 20%), the reduction in compressive strength (up to 15%) and the properties tested were determined by the length of fibers whereas the influence of the fiber content was insignificant. The examination of basalt fiber resistance in alkaline environment (10% sodium hydroxide solution at 60°C for 10 days) pointed out the chemical degradation of basalt fibers in the form of reduction of fiber diameter and formation of the deposit on the surface of fiber.

2.2.7 Cellulose Ether

Metalssi et al. (2015) proposed model of the coupled evolution of hydration–moisture transfer processes and their influence on porosity is suggested for polymer-modified-mortars (PMM) with cellulose ether addition. This model was based on mass balance equations of each phase of the material (solid, liquid and gas), and hydration rates of cement compounds. It took into account the effect of the cellulose ether, used as a polymer admixture, on the hydration kinetics. The model allowed describing the time evolution of the water content, the porosity and the amount of anhydrous and hydrated products, which are the main input data characterizing the material properties in most durability predictive models. Simulation results were compared to the experimental ones obtained by thermo gravimetric analysis (TGA) and water porosity measurements. The resolution of macroscopic equations system gives time-evolutions of anhydrous compounds and hydrates and hydration degree of cement. The latter was validated by TGA tests and results show a good agreement between simulated and measured hydration degrees.

The porosity is one of the output parameters of the model. It was determined according to the anhydrous concentrations. Numerical simulations were validated by accessible-to-water porosity measurements. Comparisons showed that experimental values and simulations have quite the same evolution. However, some improvements have to be carried out for a better prediction of this parameter, mainly by studying air entrained mechanisms induced by cellulose ether.

2.2.8 Seaweed

Susilorini et al. (2014) studied the behavior of natural polymer modified mortar with seaweed. In this research, polymer modified mortar used two natural polymer from seaweeds, they were Eucheuma Cottonii (gel) and Gracilaria Sp. The research conducted in two phases, pre-experiment and main-experiment.

Materials used in this research are mortar and seaweed as natural polymer. The species of seaweed used are Eucheuma Cottonii (gel) and Gracilaria Sp. (powder). The Eucheuma Cottonii is extracted from raw boiled seaweed and Gracilaria Sp. is in powder.

This research used mortar mix composition as 1: 1: 0.6 (cement: sand: water) while the composition of seaweed in the mortar is described in Table 2.5.

Table 2.5 Composition of seaweed powder and gel.

Stage of experiment	Seaweed Gel of the cement weight (%)	Seaweed Powder of the cement weight (%)
Pre-experiment	0.1, 0.5, 1 and 5	0.1, 0.5, 1 and 5
Main-Experiment	-	0.1, 0.2, 0.5, 1, 2 and 5

Pre-Experiment The pre-experiment aimed to investigate compressive strength of natural polymer modified mortar with seaweed gel (Eucheuma Cottonii) and seaweed powder

(Gracilaria Sp.) in age of 7 and 14 days. There were 4 (four) compositions of seaweed in the mortar as shown in Table 2.5. The results of pre-experiment will determine which species of seaweed is used for the main experiment.

The results are shown in figure 2.1 and figure 2.2.

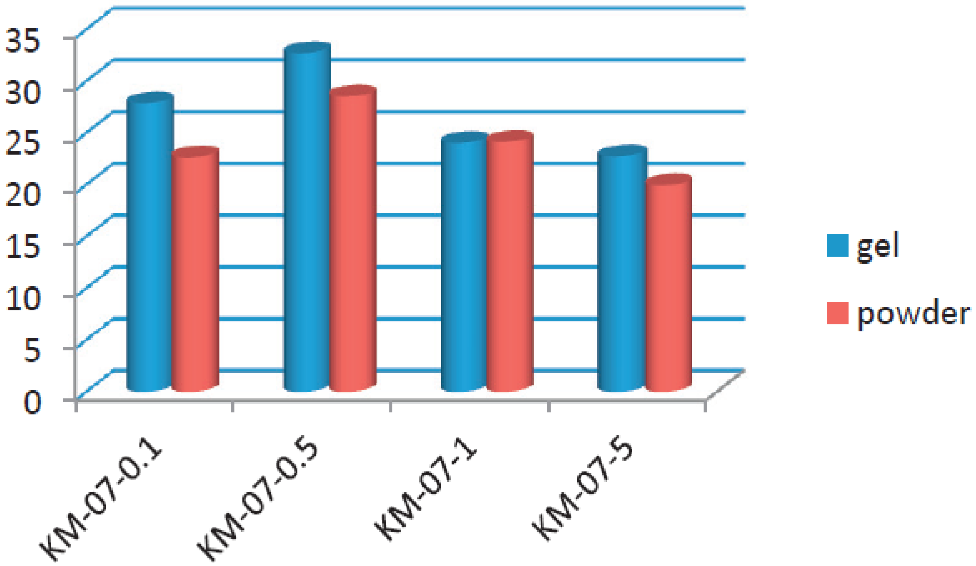


Figure 2.1 Comparison of 7 Day compressive strength of seaweed gel and powder (Susilorini et al. (2014)).

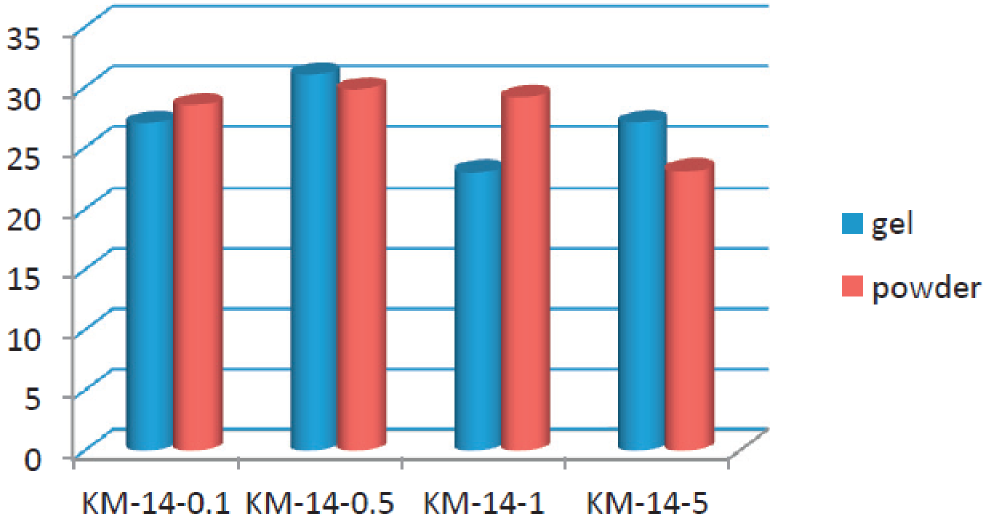


Figure 2.2 Comparison of 14 Day compressive strength of seaweed gel and powder (Susilorini et al. (2014)).

The pre-experiment has shown higher compressive strength on natural polymer modified mortar with seaweed gel at age 7 days for 4 (four) mix compositions. The maximum compressive strength at age 7 days was achieved by KM-07-0.5 gel (32.7 MPa) as shown in Fig. 2.1. It was observed that at the age 14 of days the mix composition KM-14-1 gel (23.03 MPa) was getting lower compared to KM-14-1 powder (29.17 MPa) as described by Fig. 2.2. According to the trend shown by Fig. 2.1 and Fig. 2.2, specimens of KM 07 and 14 powders perform stable performance of compressive strength as there is a gradual increase and then decrease in the strength but in the gel at 1% composition there was a sudden decrease in compressive strength.. As mentioned in the first paragraphs of this paper, natural polymer modified mortar with seaweed gel (Eucheuma Cottonii) and seaweed powder (Gracilaria Sp.) have properties as gelling and thickening agents. Therefore the agarose and agaropectin of Gracilaria Sp. form stronger gel compared to kappa carrageenan of Eucheuma Cottonii that increase the bonding mechanism of mortar. The results of pre-experiment has determined the seaweed powder of Gracilaria Sp. becomes natural polymer for polymer modified mortar specimens of main experiment.

Main-Experiment

The pre-experiment was followed by main-experiment which investigated compressive strength and splitting tensile strength of natural polymer modified mortar with seaweed determined by results of pre-experiment. There were 6 (six) compositions of seaweed in the mortar as shown by Table 2.5. All compressive strength specimens were tested at 7, 14, and 28 days of curing while splitting tensile strength at 28 days of curing. The natural Polymer Modified Mortar with seaweed specimens were then compared to control specimens.

It is shown by Fig.2.3 that mix composition of KM-0.5 has the highest compressive strength (29.28 MPa at 7 days; 29.64 MPa at 14 days; and 30.36 MPa at 28 days) among all mix compositions at all ages (7, 14, and 28 days). It should be noted that compressive strength of KM-0.1, KM-0.2, and KM-0.5 have gradually increased from age 7 days to 14 and 28 days .In the opposite, compressive strength of KM-1, KM-2, and KM-5 have gradually decreased from age 7 days to 14 and 28 days. Control specimens have shown lower compressive strength (18.85 MPa at 7 days; 19 MPa at 14 days; and 25.33 MPa at 28 days) compared to other mix compositions, except of KM-5 at 28 days.

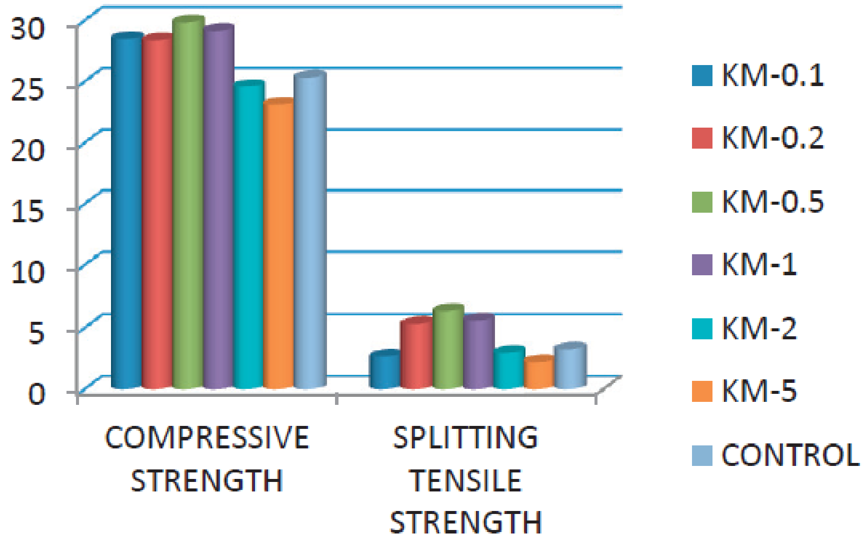


Figure 2.3 28 day compressive strength and tensile strength. (Susilorini et al. (2014)).

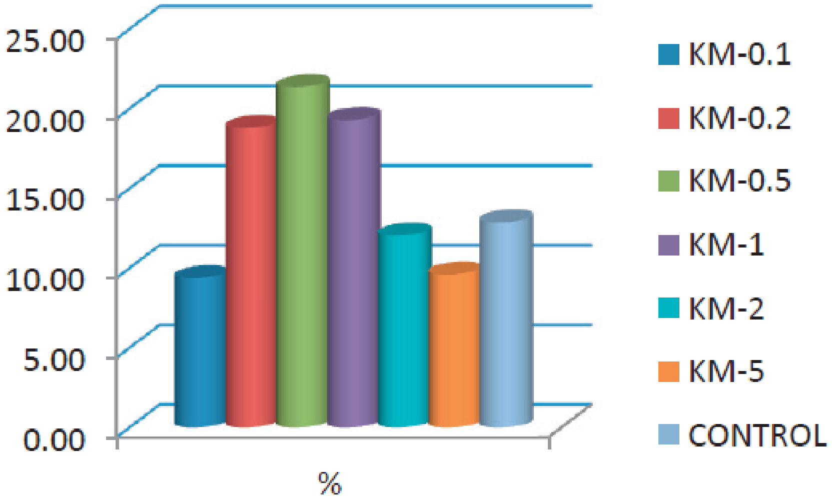


Figure 2.4. Percentage of split tensile strength by compressive strength. (Susilorini et al. (2014)).

The results of main experiment have shown that high dosage of mix compositions (KM-1, KM-2, and KM-5) will not give great improvement of bonding mechanism. It seems that optimum mix composition achieved by KM-0.5.

Since the mortar and concrete are excellent in compressive strength but not very good in tensile strength, the influence of seaweed powder is expected to increase its tensile strength. Fig.2.3 and Fig.2.4 have shown the splitting tensile strength that is achieved by mix composition of KM-0.5.

It is obvious that KM-0.5 has the highest splitting tensile strength (6.27 MPa that is 21.35% of its compressive strength) among the others mix compositions and control specimens (3.26 MPa that is 12.87% of its compressive strength). Unlike the results of compressive strength, KM-1 has high splitting tensile strength (5.63 MPa) that is closed to KM-0.5.

It is emphasized that the agarose and agaropectine have made very strong gel and increased the bonding mechanism that make the performance of natural polymer modified mortar with seaweed powder becoming excellent.

2.3 Need for the Present Study

The major objective of this thesis work is straightforwardly expressed by its title and may be resumed by the following: development, optimization and fully characterization of a PM material with enhanced characteristics according to its foreseen applications.

From the review of literature it is clear that most of the research studies regarding the natural modified mortar have focused on the mechanical properties of the mortar mix like compressive strength, split tensile strength and flexural strength.

Over the last few decades researchers have tries to use different natural polymers to study the properties of mortar and also studied how the environment impact of CO_2 can be reduced.

This research dissertation focuses on the use of Seaweed Polymer (Eucheuma Cottonii) in different configurations to study the following properties:

i) To develop and optimize a polymer mortar formulation with improved characteristics according to its future end-use;

ii) To study the effect of addition of different dosages of natural polymer of composition of cement mortar on the following mechanical properties:

- Compressive Strength
- Split Tensile Strength

iii) To study the effect of addition of different dosages of natural polymer of composition of cement mortar on the following durability properties:

- Water Sorptivity
- Chloride Penetration

iv) To study the bond strength of the Polymer Modified Mortar with theconventional mortar.

CHAPTER 3

Material, Design and Experimental Setup

3.1 General

The present chapter presents the properties of various materials used for development of polymer modified mortar. The selections of materials have to be ascertained for purpose of achieving the desired properties of mortar. In order to achieve the desired properties for a mortar mix, varying percentages of admixture eucheuma cottonii powder have been used as additive PPC cement and fine aggregates. The later sections of the chapter also present the details of the experimental tests performed on the PMM with the relevant laboratory setup.

3.2 Characteristics of Materials Used

The chemical and physical properties of various materials used for making polymer modified mortar mixes were determined in laboratory as per the relevant IS codes of practice. The materials used in the present experimental study are cement, fine aggregates and water along with natural polymer Eucheuma Cottonii Powder in varying proportions. The various properties of these materials are evaluated to check their acceptance for use in mortar making as per the relevant codal requirements. The description of various materials along with their examined properties which were used in this study is detailed in the succeeding subsections.

3.2.1 Portland Pozzolana Cement

Cement is the most active component of mortar and usually has the greatest unit cost. Its selection and proper use is important in obtaining the most economical balance of properties which are desired for any particular mixture. Cement is a pozzolanic material i.e. when combines with other aggregates it forms a dense matrix which provides strength to the structure. The main purpose of cement is to fill up voids existing between the fine aggregates and make the concrete impermeable. It provides strength to concrete by formulating a bond between the aggregates by forming a solid mass due to its setting and hardening properties when mixed with water. The constitution of cement is only about 30% of the total volume of mix but it significantly affects the strength and durability of the mix formed.

In the present study Porland Pozzolana Cement (PPC) has been used. The cement was obtained from the local sources (Ultra Tech Cement). Cement is manufactured either by intimately inter-grinding Portland cement clinker and fly ash or by intimately and uniformly blending Portland cement and fine fly ash.

The physical properties of the cement as determined from the various tests confirming to Indian Standard IS: 8112:2013 are listed in Table 3.1. The various tests conducted on cement are initial and final setting time, specific gravity, fineness and compressive strength.

Table 3.1: Properties of PPC

Characteristics	**Experimental Values Obtained**	**IS 1489:1991 Specified Values**	**Test Method Referred to IS: 8112:2013**
Specific Gravity	3.12	-	IS 4031 Part 11
Standard Consistency (in %)	28	-	IS 4031 Part 4
Setting Time (min)			IS 4031 Part 5
Initial **Final**	42 367	30 min (Min) 600 min(Max)	
Compressive Strength (MPa)			IS 4031 Part 6
7 Days **28 Days**	23.06 34.19	22 33	

3.2.2 Fine Aggregates

Aggregates occupy the majority of the volume in the mixture and gives dimensional stability to concrete. In mortar, only fine aggregates are used.

Fine aggregates are the aggregates that pass through 4.75mm IS sieve are termed as fine aggregates. The fine aggregates may be of following types:

- Natural sand, i.e. the fine aggregate which results from natural disintegration of rocks;
- Crushed stone sand, i.e. the fine aggregates produced by crushing hard stone; and
- Crushed gravel sand, i.e. the fine aggregates produced by crushing natural gravel.

IS 383 has divided the fine aggregate into four grading zones (Grade I to IV) depending on the particle size distribution. The grading zones become gradually finer from grading zone I to grading zone IV. The fine aggregates were washed to remove silt and clay and were then oven dried for a period of 24 hours. They were then brought down to room temperature and were then used in the mix.

In accordance with IS 383 (Table 4) the fine aggregates were determined to be lying in ZONE II. Specific gravity of fine aggregates was experimentally determined by using the pycnometer and the procedure was carried out by the experimental steps described in IS 2386- part111 (1963). The result of specific gravity was found to be 2.55.

Weight of the fine aggregates used =1000g for the sieve analysis shown in Table 3.2.

Table 3.2 Sieve Analysis of Fine Aggregates

S.No.	**Is_Sieve (mm)**	**Wt. Retained (gm)**	**Percentage Retained**	**Percentage Passing**	**Cumulative Percentage Retained**
1	4.75	24	2.4	97.6	2.4
2	2.36	86	8.6	89	11
3	1.18	191	19.1	69.9	30.1
4	600µ	151	15.1	54.8	45.2
5	300µ	259	25.9	28.9	71.1
6	150µ	247	24.7	4.2	95.8
7	Pan	42	4.2	-	-
TOTAL		**1000**		**SUM**	**255.6**
ZONE II			**FM=2.56**		

3.2.3 Water

Potable water is normally considered satisfactory for mixing and curing of mortar. In the current study accordingly potable water available in the material testing laboratory was used for making mortar mix. It was free from any detrimental contaminants and was of good potable quality.

3.2.4 Natural Polymer: Seaweed Powder

Carrageenans are sulfated linear polysaccharides extracted from certain red seaweed of the Rhodophyceae class. They have been extensively used in the food industry as thickening, gelling agent and more recently used in the food industry as expedient in pill and tablets. Since natural carrageenans are mixtures of different sulfated polysaccharides, their composition differs from batch to batch. Carrageenan from particular seaweed species and geographic district differ considerably in their structure and rheological properties of solutions and gels. The yield and physical properties of carrageenan such as gel strength, gelling and melting temperature as well as chemical properties, determine its values to the industry. The seaweeds are usually extracted with alkali at elevated temperature. Therefore, the quantitative analysis of carrageenan batches is of greatest importance for industry to deliver a standard product and to develop new application based on their unique intrinsic properties.

Kappa carrageenan which can form strong gel is highly valued. A good source of kappa carrageenan is Eucheuma cottonii, which is mainly harvested in the Philippines and Indonesia. The alkaline treatment is an important and well-known reaction of carrageenans, and is used to commercially enhance gel forming behavior.

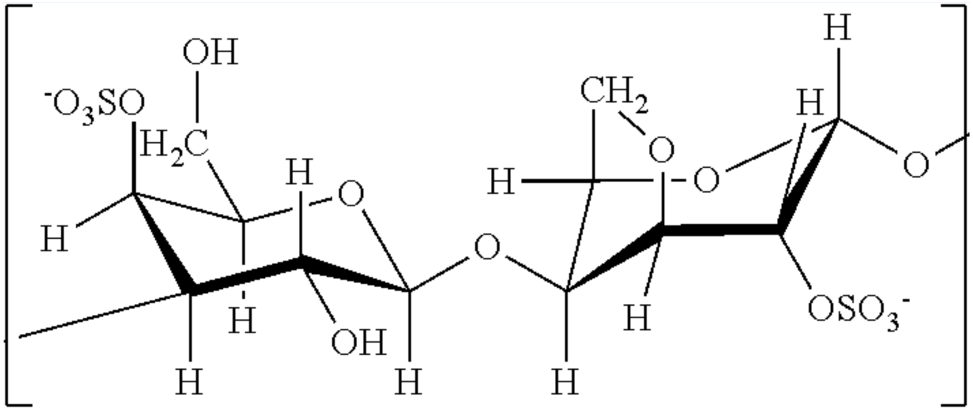


Figure 3.1 Structure of Kappa Carragennan.

Table 3.3: Properties of Seaweed Powder (Provided by Manufacturer**)**

Parameters	**Specification**	**Typical lot**
APPEARANCE	powder	Light yellow
PARTICLE SIZE (MESH)%	60 mesh retention-5 60 mesh passed - 95	Within specification
MOISTURE CONTENT (%)	<= 12	Within specification
PH	7.0 – 10.0	Within specification
VISCOSITY (cps) (1.5% SOLUTION AT 75□C)	>=15.0	Within specification
GEL STRENGTH (g/cm2) (1.5% SOLUTION AT 20□C)	<=80.0	Within specification
KCL GEL STRENGTH (g/cm2) (1.5% SOLUTION + 0.2% KCL AT 20^0C)	>= 250.0	Within specification
KCL BREAKING STRENGTH (g/cm^2)	>=150.0	Within specification
TOTAL PLATE COUNT (cfu/g)	<= 5000	Within specification
MOULDS AND YEAST (cfu/g)	<= 300	Within specification
ESCHERICHIA COLI	Negative	Within specification
PURITY	100%	Within specification

3.3 Experimental Setup

3.3.1 Compressive Strength

The mortar cubes of dimensions 70.6 x 70.6 x 70.6mm were casted under standard laboratory conditions According to procedure laid down in IS: 516-1959 and were tested at a curing period of 7 and 28 days. The specimens prepared were tested on 100 tons capacity Universal Testing Machine (UTM). Eucheuma cottonii powder was directly used in mortar with the composition of 0% (control mix), 0.5%, 1%, 1.5% and 2% of the cement weight. Three cubes of each composition were casted for 7 day test and 28 day test thereby making total of 30 cubes. The cubes were placed in such a way that the load was supplied at the right angle to the faces of cube rotating them at 90^0. Load was applied continuously at the rate of 350 kg/cm^2 /minute until the failure of the specimen takes place.

Figure 3.2 Compressive Strength of Mortar under Universal Testing Machine.

The photograph (Fig. 3.2) shows testing of cube and specimens under Universal Testing Machine.

3.3.2 Split Tensile Strength

The mortar cylinder of dimensions 100mm diameter and 200mm length were casted under standard laboratory conditions according to procedure laid down in IS: 5816-1999 and were tested after a curing period of 28 days. The specimens prepared were tested on 500 tons capacity Automatic Compression Testing Machine (ACTM). With the composition of 0% (control mix), 0.5%, 1%, 1.5% and 2% of the cement weight three cylinders of each composition were casted for 28 day test thereby making total of 15 cylinders. Load was applied continuously at the rate of 5KN/s until the failure of the specimen takes place. The photograph (Fig. 3.3.) shows testing of cube and specimens under Automatic Compression Testing Machine (ACTM).

Figure 3.3 Split Tensile Test under Automated Compression Testing Machine

3.3.3 Water Sorptivity Test

ASTM C1585 is commonly used to determine the absorption (commonly referred to as sorptivity) of water in unsaturated hydraulic cement concretes. This test method consists of preconditioning cylindrical samples 50 mm in thickness and 100 mm in diameter to known moisture content, then exposing the bottom surface of the sample to liquid water and measuring the increase in mass resulting from water absorption. According to the standard conditioning procedure, samples are conditioned for 18 days. This conditioning period begins by first placing the sample in a 50 C and 80% relative humidity (RH) environment for 3 days. The samples are then removed from this environment and placed in individually sealed containers where they remain for a minimum 15 days at 23 C, to allow internal moisture to redistribute throughout the specimens before the test begins. The absorption test involves recording incremental mass change measurements at relatively frequent intervals during the first 6 h after the sample comes in contact with water and subsequently taking one measurement every day for the next 8 days.

Figure 3.4. Sample Testing For Water Sorptivity.

The absorption I is the change in mass divided by the product of the cross sectional area of the test specimen and the density of water. The units of I are mm.

I=m/(a*d)

Where

I= the absorption (mm)

m=the change in specimen mass in grams at time t.

a= exposed area of the specimen in mm^2

d= the density of water in g/cm^3

To estimate the rate of the absorption, the plot of I versus $time^{1/2}$ is plotted.

3.3.4 Rapid Chloride Permeability Test (RCPT)

In this test based on AASHTO T277 (ASTM C1202) test, a water-saturated, 50-mm thick, 100-mm diameter concrete specimen is subjected to a 60 V applied DC voltage for 6 hours using the apparatus shown in Figure 3.6. In one reservoir is a 3.0 % NaCl solution and in the other reservoir is a 0.3 M NaOH solution. The total charge passed is determined and this is used to rate the concrete according to the criteria included in Table 3.4. This test, originally developed by Whiting [1981], is commonly (though inaccurately) referred to as the “Rapid Chloride Permeability Test” (RCPT). This name is inaccurate as it is not the permeability that is being measured but ionic movement. In addition, the movement of all ions, not just chloride ions, affects the test result (the total charge passed).

Lower quality concretes heat more as the temperature rise is related to the product of the current and the voltage. The lower the quality of concrete, the greater the current at a given voltage and thus the greater heat energy produced. This heating leads to a further increase in the charge passed, over what would be experienced if the temperature remained constant. Thus, poor quality concrete looks even worse than it would otherwise i.e. the sample would be porous in nature therefore the charge can easily flow through the sample because of capillarity.

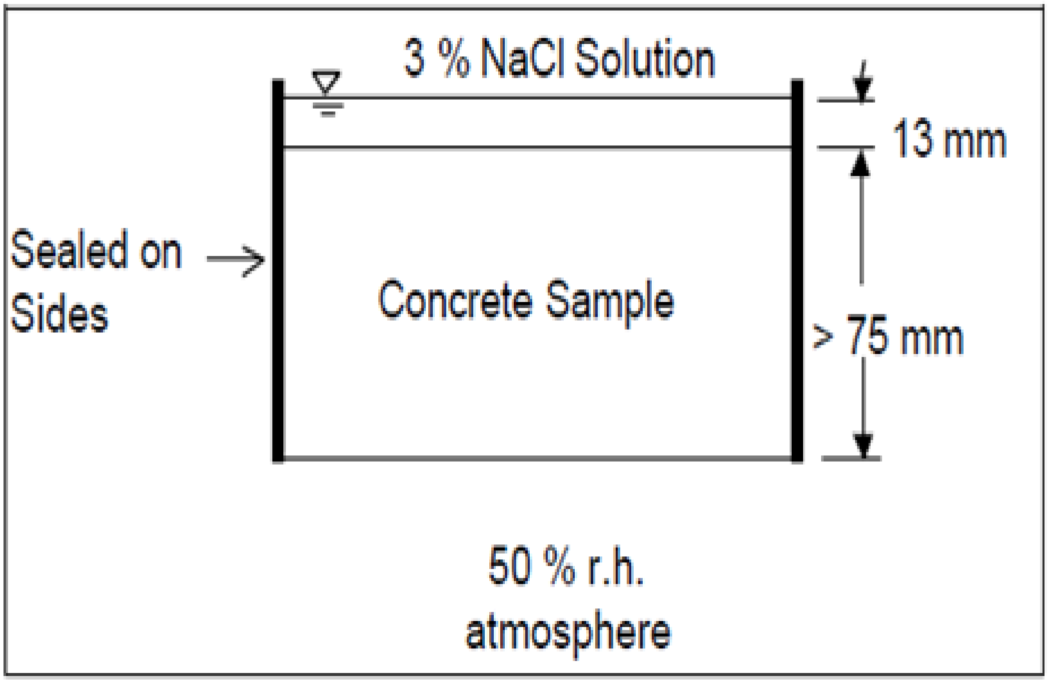


Figure 3.5 AASTHO T259 (salt ponding) Test Setup.

Table 3.4 RCPT Ratings (per ASTM C1202)

Charge passed (coulombs)	**Chloride Ion Penetrability**
>4000	High
2000-4000	Moderate
1000-2000	Low
100-1000	Very Low
<100	Negligible

Figure 3.6 RCPT Apparatus.

3.3.5 Slant Shear Test

The slant shear test (as per ASTM C882), is a test procedure applied to determine the bond strength of retrofitted cement mortar for selection of repair material for strengthening of mortar surfaces.

In this test procedure, the repair material (natural polymer modified mortar) of different compositions was bonded to a substrate (conventional mortar mix) of specimens on a slant elliptical plane inclined at an angle of 30^o with the vertical to form a 76 mm x 152 mm (3-in. x 6-in) composite cylinder. The composite cylinders were prepared as per the following procedure (as shown in Figure 3.7):

i) The conventional mortar cylinders with a given repair material were prepared on the day when the substrate cylinders were 28 days old (28 days moist cured).

ii) Before the repair material was bonded to the substrate mortar, the slant surface of the substrate mortar specimen was cleaned by dry brushing.

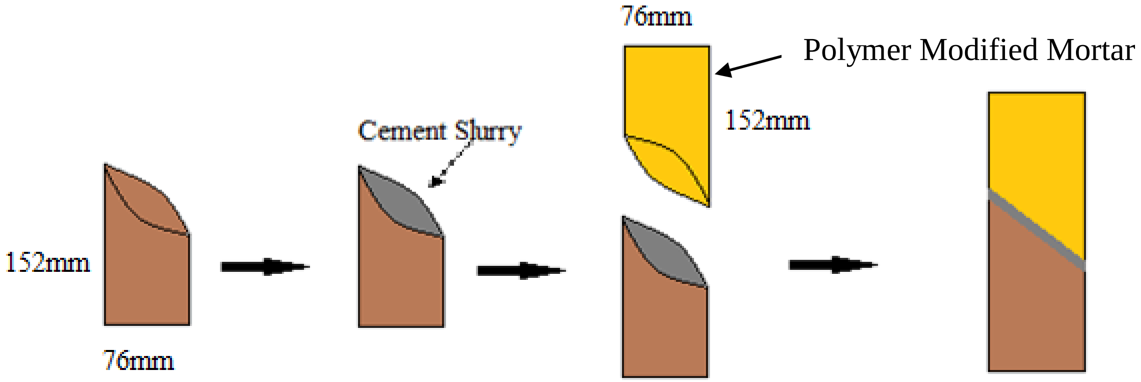
iii) A thick cement slurry was prepared by mixing cement and water in suitable proportions. This slurry was then applied on the cleaned surface of the substrate to act as a bonding agent between the Polymer Modified Mortar and the lower substrate layer.

iv) The Polymer Modified Mortar was then was then joined with the cement slurry treated surface.

v) The composite cylinders were de-molded 24 hours after casting. The composite cylinder so formed was moist cured for 7 days prior to testing.

The composite cylinder was then tested till failure in compressive loading on the 500 ton ACTM. The test assumes that the failure of the composite cylinder occurs preferentially on slant surface to calculate the bond strength.

Figure 3.7 shows the stepwise procedure for the preparation of composite cylinder.



Substrate

Substrate treated with Cement Slurry

Preparation of Composite Cylinder

Figure 3.7 Stepwise Procedure for Preparation of Composite Cylinder

Figure 3.8 shows the slant shear test performed on composite specimen under ACTM.

Figure 3.8 Slant Shear Test in ACTM

The compressive load required to fail the composite cylinder was recorded. The bond strength **S**, was calculated as:

$$S=P/A_L$$

Where

P= Maximum Compressive Load (N)

A_L= Area of Slant Surface (mm^2) (A_L is taken as 9116mm^2 as recommended in ASTM C882)

3.3.6 X-Ray Diffraction

X-Ray Research Method

A crystalline material may be formed of only one crystalline phase or from a mixture of more crystalline phases. A crystalline phase is defined by a certain system (triclinic, monoclinic, rhombic, tetragonal, trigonal, hexagonal, cubic), by a certain elementary cell (simple, with centered bases, with a centered volume, with centered faces) and by the parameters of the elementary cell. In crystallography, the planes and families of atomic planes are noted with the help of Miller's indices (h k l), fielded by the intersection of the atomic planes with axes x, y, z, . We illustrate some atomic planes for a cubic crystalline structure.

X-rays are electromagnetic waves, similar to light, but with a much shorter wave length (λ=0.2-200 A^0). Diffraction is a physical phenomenon that consists of electromagnetic waves avoiding the obstacles when obstacles have a size comparable to the wavelength. This phenomenon can be used to analyze materials as the atomic planes in a material (i.e. obstacles) are at distances comparable to the X-ray wavelength. When a monochromatic pen of X rays falls on a crystal, the spherical waves are emitted due to their reflection of X–rays by the periodically displayed atoms of the crystal; these spherical waves will interfere with one another. A destructive interference will be present in all the space, except for some directions called the Diffraction directions. In a periodic display of atoms (crystalline state), the various parallel planes are situated at a periodic distance "d". The constructive interference of the waves occurs, that is diffraction peaks are reached for a given wavelength "λ" only if Bragg's law is observed :

$$2d \sin\theta = n \lambda$$

where: n is an integer which depends upon the order of reflection;

d is the distance between the atomic planes;

θ - is Bragg's diffraction angle.

X-rays diffraction is produced as a reflection at well defined angles. Each crystalline phase has its own diffraction image. The diffraction image contains a small number of peaks, showing that not all the families of crystallographic planes give peaks; all the crystalline phases with the same elementary cell will exhibit the same succession of Miller Indices for the crystalline families giving peaks. For the X-ray diffraction analysis we used diffraction devices (diffractometers), in general in a Bragg–Brentano arrangement (the specimen is rotated by the diffraction angle "θ" while the detector is turned by the angle "2θ", Figure 3.9). In Fig 3.10, the X-ray diffractometer is shown.

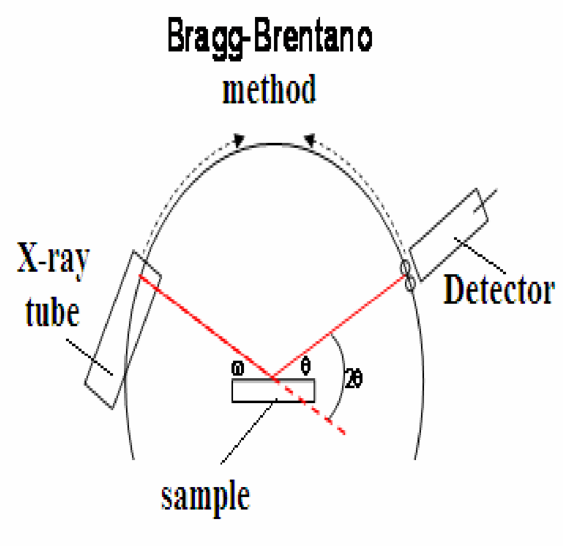


Figure 3.9. Basic Layout of X-Ray Diffractometer

Figure 3.10. X-Ray Diffractometer

The Diffractometer generates a output curve known as Diffractogram. The Diffractogram is formed of a succession of diffraction peaks, i.e. maximum values, which have the diffracted X radiation intensity, measured in pulses/second on the ordinate, and on the abscissa, angle "2θ", where "θ" is the Bragg angle, measured in degrees. The diffraction image depends on the material structure. Diffraction methods enable the performance of the following studies:

i) The determination of the crystalline structures and the qualitative and quantitative analysis of the phases

ii) The study of the transformations of the phases

iii) The study of the crystallographic texture;

iv) The size of the crystallites etc.

3.3.5.1 Identification of Crystalline Phases: The identification of the crystalline phases (or their indexing) can be performed with X-ray diffraction in the case the respective phase covers minimum 3-4% of the weight. The identification can also be performed by calculating using Bragg's law or automatically with Match, XpertScore software, making use of the PDF (Powder Diffraction File) database, which has identification sheets for about 200,000 crystalline phases belonging to metals, alloys, oxides, salts, etc. All the phases in the sample are identified one after another, beginning with the phase in the largest amount. For instance, the identification of the NaCl crystalline phase follows the steps:

i) First, the sample diffraction spectrum is identified by means of the X-ray diffractometer;

ii) The output data: the interplane distances "d" are calculated with the help of Bragg's law. The Miller Indices of the diffraction lines (planes) are also calculated.

iii) With the data as found above (interplane distances "d", relative intensity "I" and Miller indices), the corresponding sheet is searched in the PDF database, finding the full description of the crystalline phase from the crystallographic viewpoint.

The X-ray diffraction analysis were made with a DRON 3 diffractometer, in the angular range of $2\theta = 10 - 70$ degrees, with a $\lambda_{radiation} = 1.54182 A^0$, a 25kV voltage and 25mA intensity, using a Bragg – Brentano arrangement. The diffraction samples were presented as powders (produced by milling) and as cakes.

3.3.5.2 Phase Quantitative Analysis of the Portland Cement Powder: For the direct identification of the phases, we used the Match diffraction software. The software passed throug

-h the stages as mentioned below:

i) The diffraction spectrum is raised with the diffractometer.

ii) The search range is limited in the PDF database to combinations of chemical elements that are present in the sample (About 500 combinations of the elements Ca, Si, S, O, Al, Fe are available).

iii) The phases in the test sample are identified with the help of the PDF sheets by matching sheets with the diffraction lines.

iv) Results are analyzed and checked for the proper nomination of phases.

In our study the X ray diffraction studies were performed on the control mix at 7 days and 28 days of curing and the Polymer Modified Mortar sample which shows the maximum 28 - day compressive strength.

3.4 Polymer Cement Mortar Design

The cement mortar mixture was prepared with using PPC and sand in the ratio of 1:3. The water cement ratio was kept 0.45 and a pilot study was performed using the gel and powder form of natural polymer to determine the form of polymer to be used in experimental study.

Pilot Study

For the purpose of the study of the properties of the state of natural seaweed polymer to be used in the mortar mix following a study was done.

Mix 1

In this first trial, Eucheuma cottonii gel was prepared by adding 10g of seaweed powder in 1 liter of water and heating it up to 70^0C. The mixture was then allowed to cool at the room temperature. A thick gel was formed. Now the gel composition of 0.5%, 1%, 1.5% and 2% of the cement weight was mixed in the mortar. Three cubes of each composition of size 70.6 mm were casted and were cured for 7 days. Compressive strength tests were performed on the samples after 7 days. The results are discussed in Table 3.5.

Mix 2

In this second trial, Eucheuma cottonii powder was directly used in mortar with the composition of 0.5%, 1%, 1.5% and 2% of the cement weight. Three cubes of each composition of size 70.6 mm were casted and were cured for 7 days. Compressive strength tests were performed on the samples after 7 days of curing. The compressive strength results were compared with that of the Trial mix 1 results.

The comparison is shown in Table 3.5

Table 3.5 7 Day compressive strength of Seaweed gel and powder modified mortar

Mix (% By Weight Of Cement)	**7 Day Compressive Strength (MPa)**	
	SEAWEED GEL (Mix 1)	SEAWEED POWDER (Mix 2)
0.50%	12.36	14.35
1%	14.06	16.67
1.5%	10.49	12.39
2%	8.31	9.87

Discussions of the Pilot Study

Natural polymer modified mortar with seaweed gel and seaweed powder have properties as gelling and thickening agents. Hence, the natural powder must form stronger gel that improves the bonding mechanism of mortar.

The pilot study has shown higher compressive strength for the natural polymer modified mortar with seaweed powder at age 7 days for all four mix compositions. The seaweed powder has therefore been adopted as natural polymer for polymer modified mortar specimens of main experiment. The maximum compressive strength at age 7 days is achieved by 1% seaweed powder (16.67 MPa) as described in Table 3.5.

It should be noted that raw boiled seaweed (Eucheuma Cottonii) has been boiled in high temperature (70^0C) to be made into the gel before being applied into mortar and has experienced cement hydration. It means that Eucheuma Cottonii seaweed gel has been boiled twice, which might have reduced its bonding capability.

Figure 3.11 shows the graphical comparison of 7 day compressive strength of Mortar modified with Seaweed Gel and Seaweed Powder.

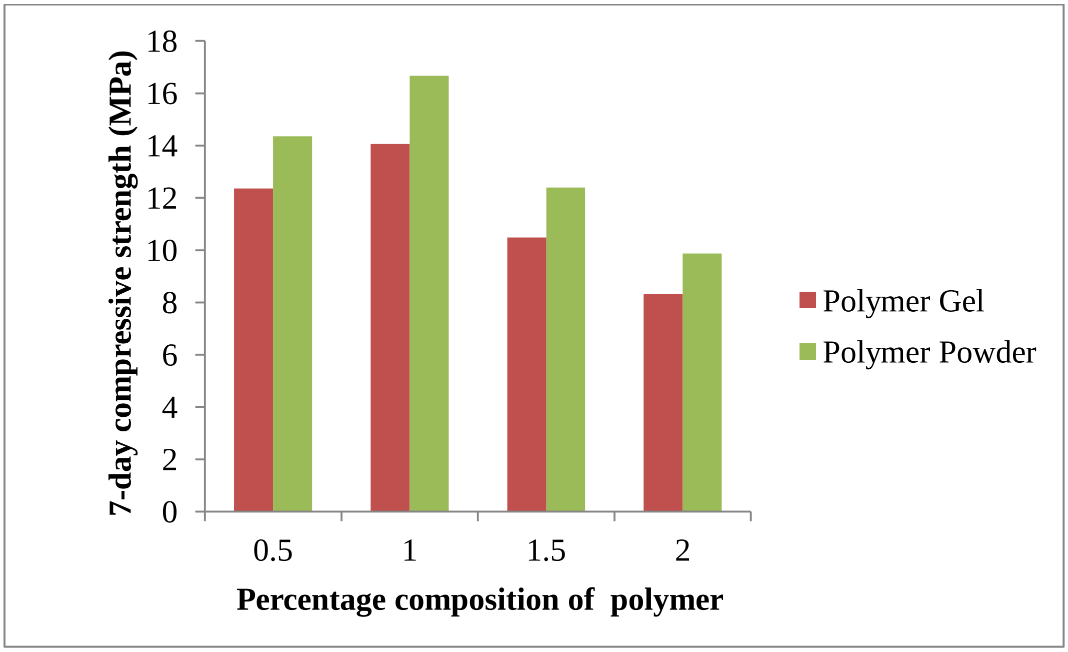


Figure 3.11 Comparison of 7 Day Compressive strength of Seaweed Polymer Gel and Seaweed Polymer Powder mortar.

Table 3.6 denotes the different composition of the polymer used in the mortar mix for the experiment. The samples have been designated as NP- "percentage of polymer". For example, NP-0.5 represents Polymer mortar modified with natural polymer powder of 0.5% composition by weight of cement.

Table 3.6 Mortar Identification and Polymer Composition in Mortar Mix

Mortar Code	**Composition**			
	Cement (Kg/m^3)	**Sand (Kg/m^3)**	**Water/Cement ratio**	**Natural Polymer (Kg/m^3)**
NP	568.35	1705.35	0.45	-

Mortar Code	**Cement (Kg/m^3)**	**Sand (Kg/m^3)**	**Water/Cement ratio**	**Natural Polymer (Kg/m^3)**
NP-0.5	568.35	1705.35	0.45	2.84
NP-1	568.35	1705.35	0.45	5.68
NP-1.5	568.35	1705.35	0.45	8.52
NP-2	568.35	1705.35	0.45	11.36

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 General

This chapter deals with the presentation of the results obtained from the compressive strength, split tensile strength, water sorptivity and rapid chloride permeability tests conducted on the polymer modified mixes of mortar. In order to achieve the objective of study an experimental program was devised in which different percentages of natural polymer seaweed powder were incorporated into the mix to determine the best proportion of materials that can provide the enhanced mechanical properties. The mixes were cast using the proportions as laid down in Chapter 3 (section 3.4). The experimental program consisted of casting, curing and testing of concrete specimen at different curing ages of 7 days and 28 days. The experimental program included the following:

4.2 Main Experiment Study

As discussed in the section 3.4, seaweed powder was selected for the further studies of mechanical and durability properties of polymer modified mortars.

In the following sections, the results of the compressive strength test, split tensile strength, water sorptivity and Rapid Chloride Permeability Test performed on the five different compositions of seaweed powder as per standard codes are discussed in the following sections.

To study the phase formation in the cement hydration reaction of seaweed polymer, XRD analysis was performed on the sample of Polymer Modified Mortar with seaweed polymer as a natural polymer. Therefore XRD analysis shows the formation of different compounds during the cement hydration reaction. The compounds of the phase formations were used to study the mechanical and durability properties of polymer modified mortar.

4.3.1 XRD Analysis

XRD analysis was performed to check the effect of seaweed polymer in the mortar mix on the cement hydration reaction. XRD analysis was performed on the sample to study the ongoing phase formation in the modified sample and study its properties and compare them with the controlled mix.

4.3.1.1 7 Day Analysis of NP Sample.

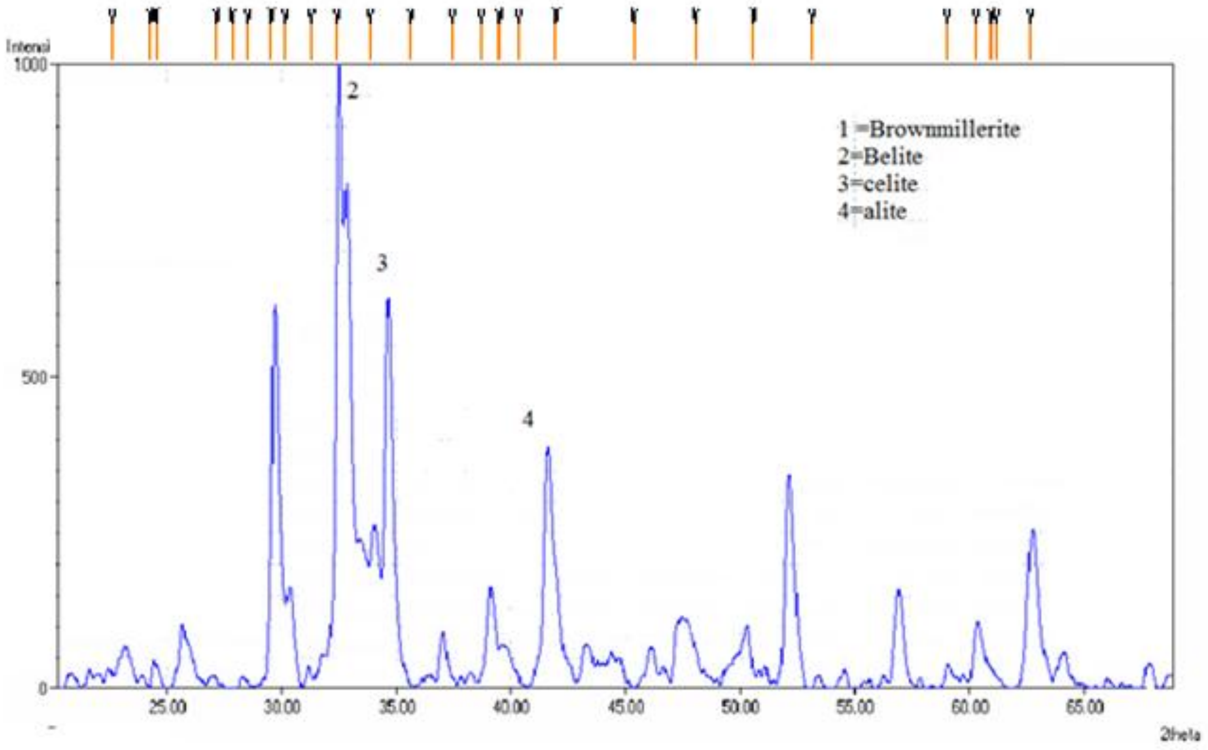


Figure 4.1 XRD graph of 7 day NP

Discussions

Fig. 4.1 shows the XRD graph between the angle (2Θ) and the intensity of the 7 day control mix.

In fig 4.1, there were four major peaks observed.

- **Alite** was found to be in abundance in the mortar. As the formula of alite is Ca_3SiO_5, sometimes formulated as $3CaO\cdot SiO_2$.The chemical name of the compound is tricalcium silicate which is responsible for the development of the early mortar strength and also early setting. Alite is more reactive because of its higher Ca content, and the presence of an oxide ion in the lattice. During clinker grinding, first step of partial dissolution of C_3S involves hydration of superficial oxide ions and leads to a hydroxylated C_3S surface. The hydrate is referred to as the calcium silicate hydrate – "C-S-H" – phase. It grows as a mass of interlocking needles that provide the strength of the hydrated cement system. High alite reactivity is desirable in Portland cement manufacture, and this is achieved by retaining, as far as possible, high temperature polymorphs, in crystals that are small, distorted and highly defective. Defects provide sites for initial water attack.

- **Belite** is an industrial mineral important in Portland cement manufacture. Its main constituent is dicalcium silicate, Ca_2SiO_4, sometimes formulated as $2\ CaO \cdot SiO_2$ (C_2S in cement chemist notation). Belite is the mineral in Portland cement responsible for development of "late" strength. The other silicate, alite contributes "early" strength, due to its higher reactivity. Belite reacts with water (roughly) to form calcium silicate hydrates (C-S-H) and portlandite ($Ca(OH)_2$).
- **Celite** Tricalcium aluminate $Ca_3Al_2O_6$, often formulated as $3CaO \cdot Al_2O_3$ to highlight the proportions of the oxides from which it is made, is the most basic of the calcium aluminates. It does not occur in nature, but is an important mineral phase in Portland cement keeping with its high basicity, tricalcium aluminate reacts most strongly with water of all the calcium aluminates, and it is also the most reactive of the Portland clinker phases. Its hydration phases leads to the formation of $Ca_2AlO_3(OH) \cdot nH_2O$ which leads to the phenomenon of "flash set" (instantaneous set), and a large amount of heat is generated.
- **Brownmillerite** ($Ca_2(Al,Fe)_2O_5$) is a dark brown crystalline phase commonly found in cements. Calcium aluminoferrite has little effect upon the physical properties of cement. On hydration it forms $4CaO.Al_2O_3.nH_2O$ and hydrated iron oxide gel. In principle, this is a fast and energetic reaction, but precipitation of an insoluble layer of hydrated iron oxide upon the calcium aluminoferrite crystal surface forms a barrier to further reaction.

The products formed above are responsible for providing the initial strength to the mortar and also for the setting of the mortar.

4.3.1.2 7 Day Analysis of NP-1 Seaweed Polymer Mortar

Fig. 4.2 shows the XRD graph between the angle (2ϴ) and the intensity of the 7 day cured sample of NP- 1.

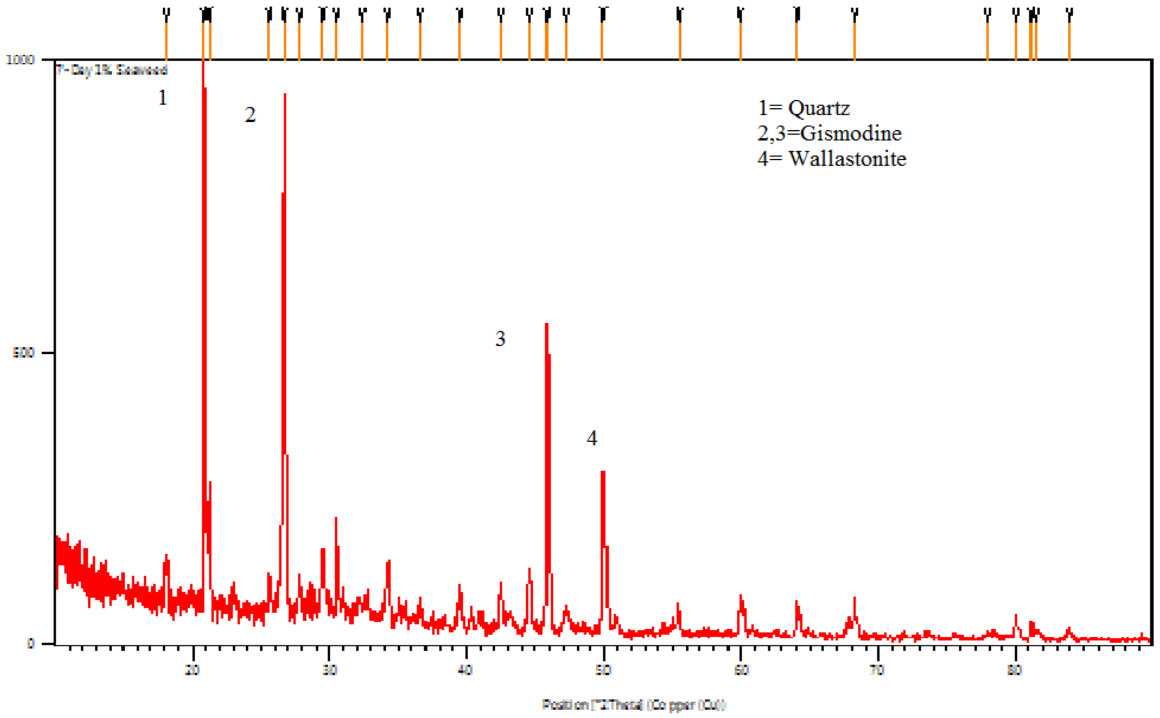


Figure 4.2 XRD Graph of 7 Day NP-1 Sample

Discussions

Four peaks were discovered corresponding to the following compounds:

- **Quartz** SiO_2. It is the compound formed in majority in the sample. During the curing stage inactive SiO_2 can be activated, and therefore can quickly react with $Ca(OH)_2$. Since in the early stage quartz is reacting with calcium hydroxide quickly more of the CSH gel is obtained thus increasing the initial strength of the sample as less hydroxide is left.
- **Gismodine.** $CaAl_2Si_2O_8H$. It is the aluminate hydrate which is formed due to the presence of the seaweed powder. As vacant hydroxyl groups present in the structure of Kappa Carragennan, they react with the calcium silicates to form aluminate gel. It has better cementing behavior. The aluminate hydrate formed is a good route to reduce the

environmental impact as these hydrates produces less CO_2 emissions, therefore there is less amount of the heat generated. Further with increase in degree of hydration, the strength is increased.

- **Wollastonite** (Calcium meta Silicate) is a white mineral which is formed in the hydration process of the seaweed powder with the cement. Wollastonite inclusion can affect rate and extent of hydration of cement in addition to CH formation and matrix permeability.CH reduction in the matrix due to its deposition at interfaces can reduce the permeability of the body and access to cement grains by water because due to its deposition vacant pores are filled thus reducing the capillary action of water.

4.3.1.3 28 Day Analysis of NP Sample.

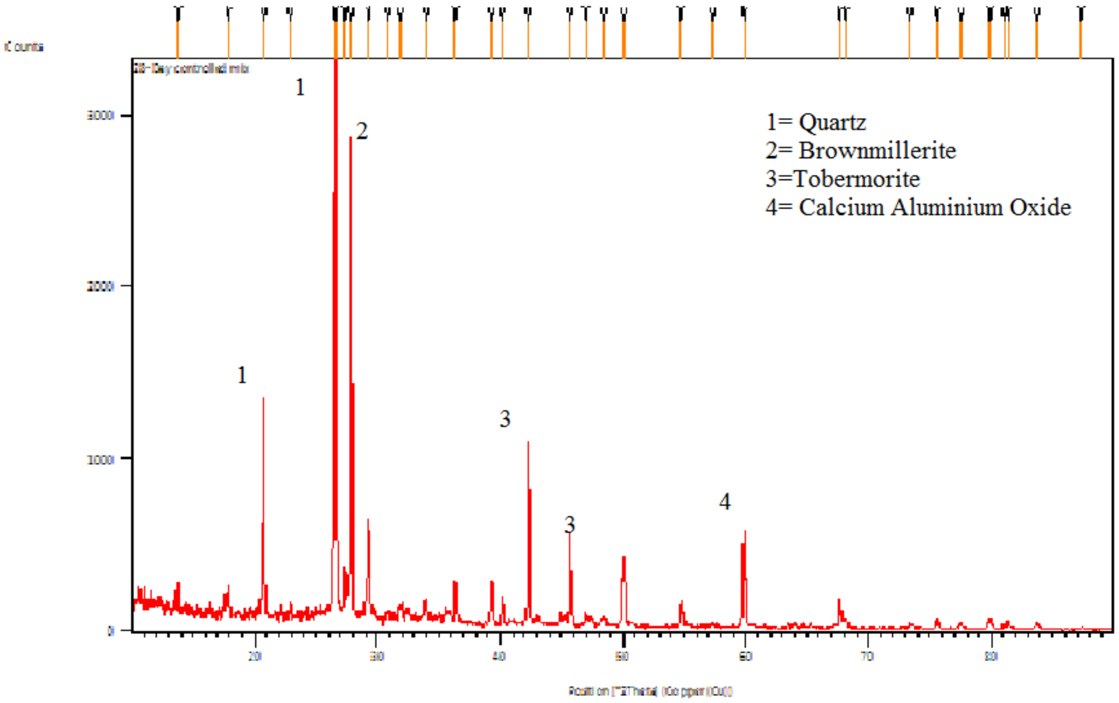


Figure 4.3 XRD Graph of 28 Days cured NP

Discussions

- **Quartz** SiO_2. It is the compound formed in majority in the sample. It is responsible for the strength during the late stages of the cement hydration reaction as it forms CSH gel with the calcium carbonate.

- **Brownmillerite** .($Ca_2(Al,Fe)_2O_5$) is a dark brown crystalline phase commonly found in cements. Calcium aluminoferrite has little effect upon the physical properties of cement. On hydration it forms $4CaO{\cdot}Al_2O_3{\cdot}nH_2O$ and hydrated iron oxide gel. It is responsible for the final setting of the mortar.
- **Tobermorite** is a calcium silicate hydrate mineral with chemical formula: $Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$ or $Ca_5Si_6(O,OH)_{18}{\cdot}5H_2O$. This compound is responsible for the strength in the cement mortar as it is a binding agent which holds together the matrix of the cement mortar and helps it to form a hardened hydrate paste.
- **Calcium Aluminium Oxide** ($Ca_3Al_2O_6$). The oxide of the aluminum is also formed in the later stage of the cement hydration reaction. The oxide function is to act as a flux and allowing the calcium silicates to form at a lower temperature and contribute little to the strength.

4.2.1.4 28 Day Analysis Of NP-1 Sample

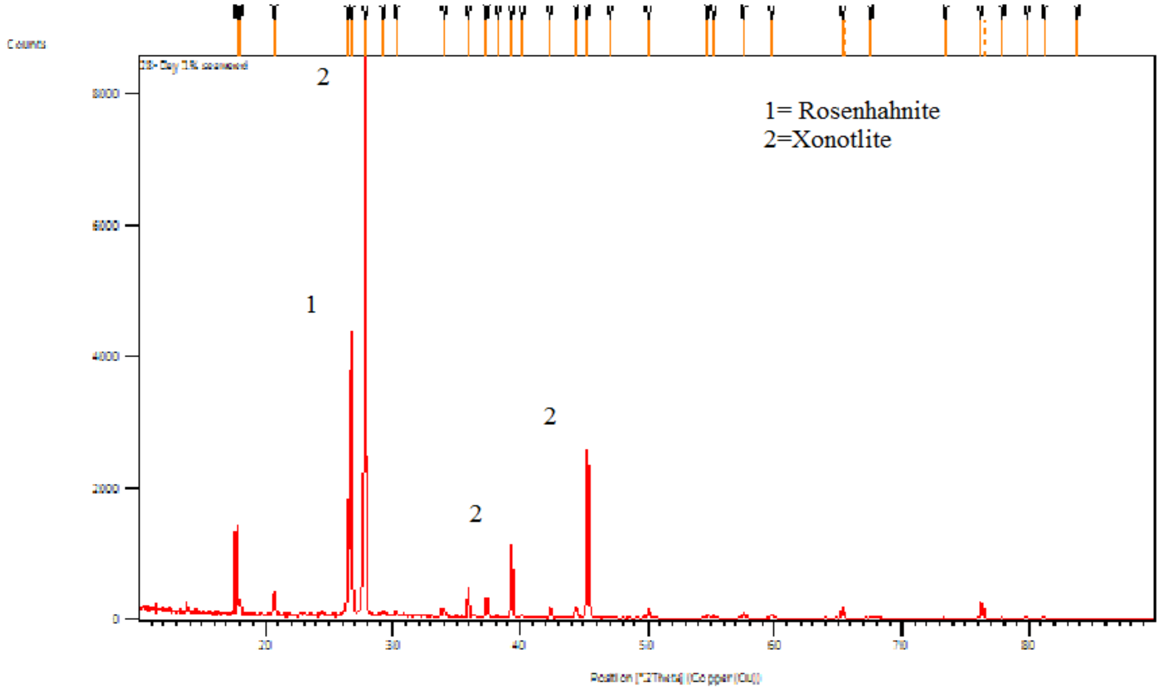


Figure 4.4 XRD Graph of 28 days cured NP-1.

Discussions

- **Rosenhahnite** ($Ca_3H_2O_{10}Si_3$). This mineral compound is formed in the hydration reaction due to the presence of nanosilica particles present in the seaweed powder. In the structure of kappa carraggenan there are vacant hydroxyl groups which in the process of hydration reaction react with CSH gel to form Calcium Silicate Hydroxide. Calcium silicate Hydroxide is a strong emulsifier and improves the degree of hydration. It also refines the pore structure due to accelerated hydration mechanism and leads to denser microstructure.
- **Xonotlite** ($Ca_6Si_6O_{17}(OH)_2$) is a calcium silicate hydrate. They are small microfiber which are formed during the hydration process. It is a fine compound phase which fills all the pores in the microstructure. Further, being a microfiber it also incorporates ductility into the structure.

4.3.2 Compressive Strength

Three cubes of each composition of seaweed powder were prepared and cured for 7 days and 28 days for the compressive strength analysis. The procedure has been discussed in section 3.4.1
The samples were tested in axial compressive loading in 100 ton UTM. Table 4.1 presents the results of 7 day compressive strength of seaweed powder mortar.

Table 4.1. 7 Day Compressive Strength of Seaweed Powder Mortar

Mixes	Compressive Strength (MPa) 7 Days	Increase in Strength (%)
NP	11.05	0
NP-0.5	14.35	29.86
NP-1	16.67	50.85
NP-1.5	12.39	12.12
NP-2	9.87	-10.67

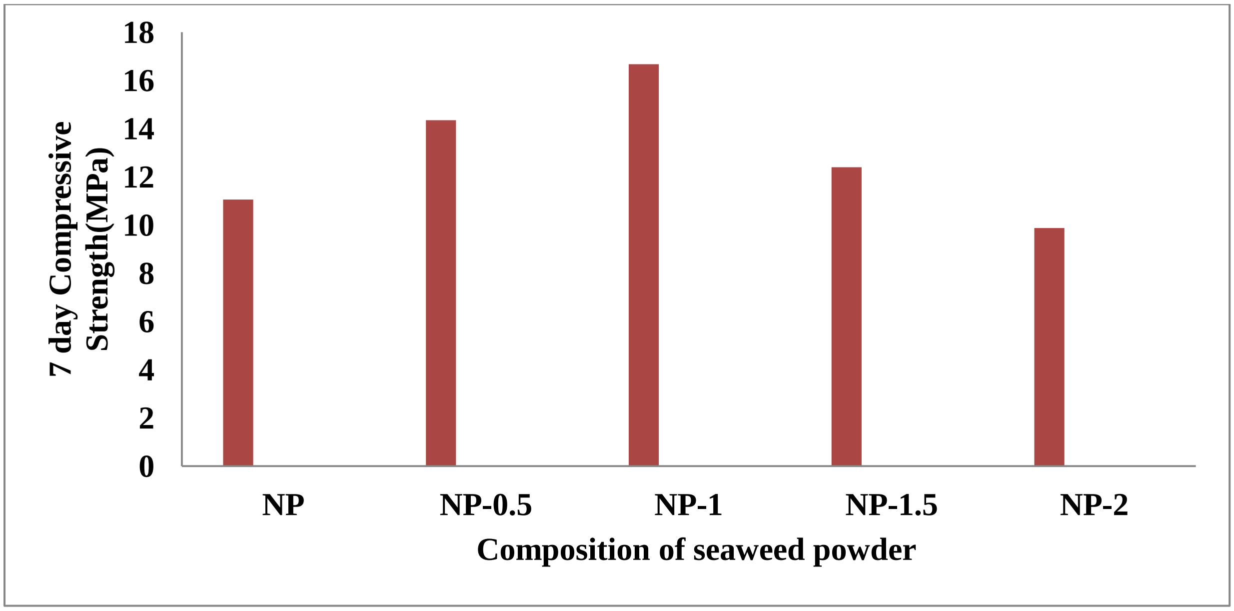


Figure 4.5 7 Day Compressive Strength of Seaweed Powder in Mortar

Table 4.2 28 Day Compressive Strength of Seaweed Powder in Mortar

Mixes	**Compressive Strength(MPa) 28 Days**	**Increase in Strength (%)**
NP	29.10	0
NP-0.5	32.33	11.08
NP-1	35.83	23.10
NP-1.5	31.06	6.70
NP-2	26.83	-7.90

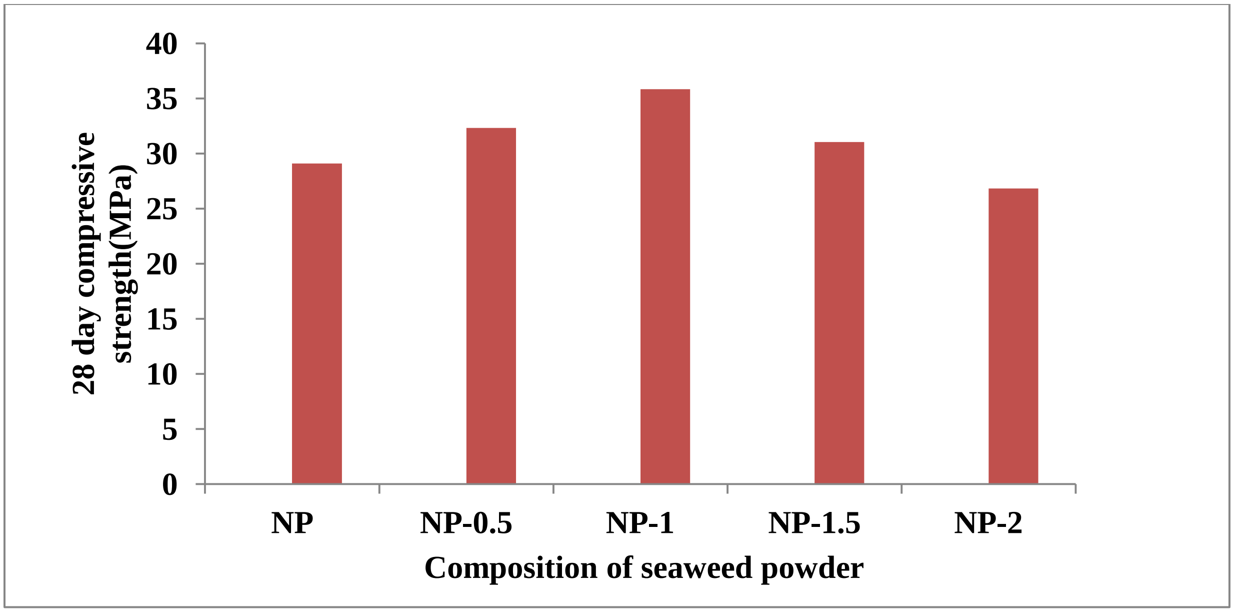


Figure 4.6 28 Day Compressive Strength of Seaweed Powder in Mortar

Discussions

The experimental results show:

i) There is an increase in the 7 day compressive strength for the samples NP-0.5, NP-1 and NP-1.5 by 29.86%, 50.85% and 12.12% respectively as compared to NP but the compressive strength decreases by 10.67% strength for NP-2.

ii) There is increase in the 28 day compressive strength for the samples NP-0.5, NP-1 and NP-1.5 by 11.08%, 23.10% and 6.70% respectively as compared to NP but the compressive strength decreases by 7.9% strength for NP-2.

The 23.10% increase in 28 days compressive strength on addition of 1% of seaweed polymer is higher than the percentage increase 7.96 % reported on the addition of 15% of SBR. (Ghai et al.,2016))

From the test results it can be observed that the percentage increase in compressive strength after 7 days is higher than the 28 days compressive strength. This can be attributed to higher amount of **Quartz (SiO_2)** formation on addition of seaweed polymer (as observed from XRD analysis shown in Figure 4.3). During the curing stage inactive SiO_2 is activated, and therefore quickly reacts with $Ca(OH)_2$. Since in the early stage quartz is reacting with calcium hydroxide quickly, more amount of the C-S-H gel is obtained thus increasing the initial strength of the sample as less hydroxide is left.

The increase in the 28 days compressive strength can be explained due to the formation of mineral compound **Rosenhahnite ($Ca_3H_2O_{10}Si_3$)** formed in the hydration reaction due to the presence of nanosilica particles present in the seaweed powder. In the structure of kappa carrageenan there are vacant hydroxyl groups which in the process of hydration reaction react with C-S-H gel to form Calcium Silicate Hydroxide which is a strong emulsifier and improves the degree of hydration. It also refines the pore structure due to accelerated hydration mechanism and leads to denser microstructure.

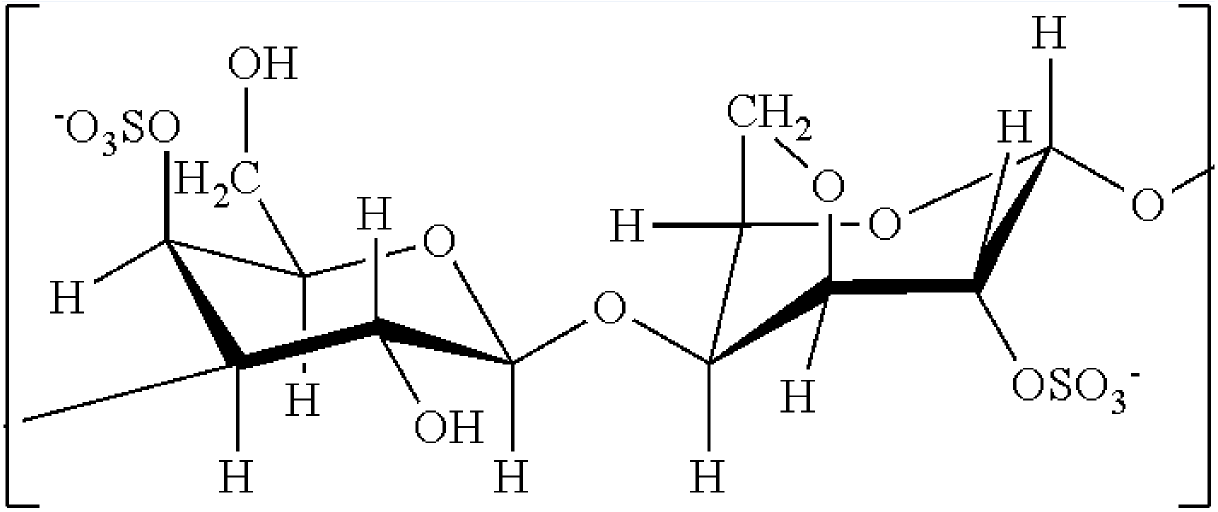


Figure 4.7 Structure of Seaweed Powder

The structure of the carrageenan contain OH^- group (Figure 4.7) which bonds with the cement to form emulsifier, which is a thick gel that holds cement and the aggregates together strongly and the also the voids of the structure are also filled, so an overall strong matrix is formed thus the increase in the compressive strength is observed.

4.2.3 Split Tensile Strength

The cylindrical samples of 100 mm diameter and 200 mm length were prepared. The curing of the samples was done for 28 days. The test was performed under ACTM according to procedure discussed in section 3.4.2.

The results of the 28-day split tensile strength test are shown in Table 4.3.

Table 4.3 Split Tensile Strength of Seaweed Powder Mortar

Mixes	Split Tensile Strength (MPa)	Increase in Split Tensile Strength (%)	Percentage of compressive strength
NP	3.11	0	10.67
NP-0.5	4.26	36.97	13.2
NP-1	5.89	89.38	16.43
NP-1.5	3.08	-0.96	9.91
NP-2	2.20	-29.26	8.2

Figure 4.8 shows the Split Tensile Strength of different compositions of seaweed powder in cement mortar

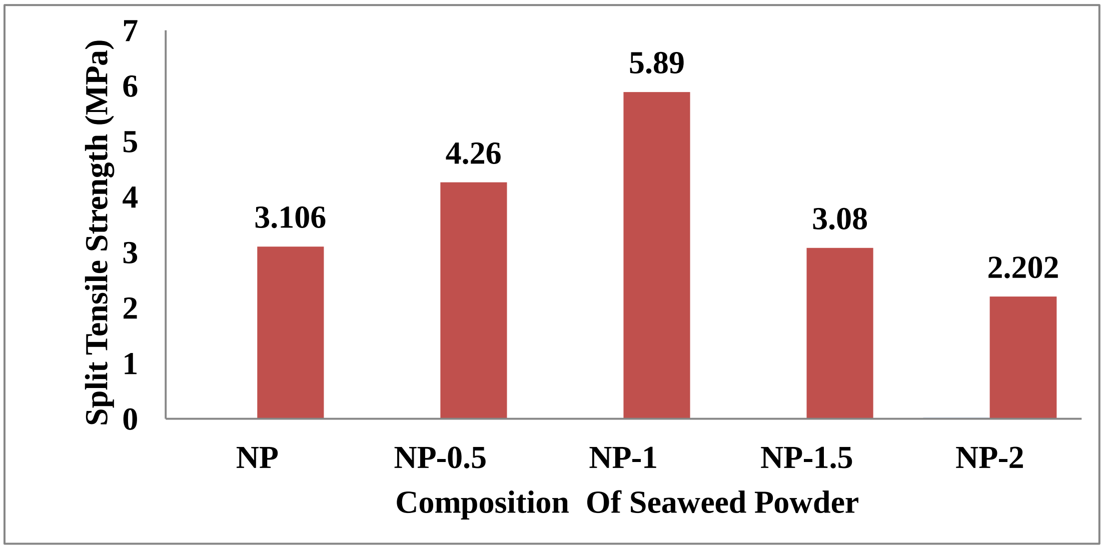


Figure 4.8 Split Tensile Strength of Seaweed Powder in Cement Mortar

Discussions

From Table 4.3, it can be observed that there is an increase in the Split Tensile Strength of the mortar when seaweed polymer powder at 0.5% and 1% by the weight of cement is mixed with it. The maximum strength of 5.89 MPa was observed for the specimen NP-1 at the composition of

1% seaweed powder; this strength was approximately 90% higher than the Split Tensile Strength of the control specimen. Further, this strength is 16.43% of the corresponding compressive strength, as illustrated in Table 4.3.

The increase in Tensile strength due to addition of Seaweed powder in specimen NP-1 can be understood from the XRD analysis. It was observed that the additional compound **Xonotlite** ($Ca_6Si_6O_{17}(OH)_2$) was formed in the NP-1 seaweed polymer modified mortar; this compound was absent in the control mix mortar. **Xonotlite** is a calcium silicate hydrate which consists of small microfibers formed in the hydration process. It is a fine compound phase in which all the pores are filled with these fibers which provide the ductility to the sample. Hence an increase in the tensile strength is observed.

4.2.4 Water Sorptivity

This test method consists of preconditioning cylindrical samples 50 mm in thickness and 100 mm in diameter, then exposing the bottom surface of the sample to liquid water according to section 3.3.3.

The test was performed according to ASTM C1585.The observations were observed regarding each sample and then compared with NP. Table 4.4 shows the example of distinctive characteristics of NP and NP-0.5.

Table 4.4 Characteristics of the NP and NP-0.5

Characteristics	NP	NP-0.5
Average Weight of sample	776g	745g
Average Diameter	100.4mm	100.7mm
Specific Gravity of Water	$1 g/cm^3$	

.

Table 4.5 shows the absorption values, I (mm) of control mix (NP) corresponding to the increase in mass calculated at the time interval as per ASTM C1585.

Table 4.5 Absorption values of NP at 28 day curing

√Time ($s^{1/2}$)	Δm (g)	I (mm)
0	0	0
8	5	0.157969386
17	8	0.252751018
24	10	0.315938772
35	12	0.379126527
42	15	0.473908159
60	19	0.600283668
85	27	0.853034685
104	29	0.91622244
120	32	1.011004072
134	33	1.042597949
147	35	1.105785703
304	39	1.232161212
440	40	1.26375509
518	40	1.26375509
657	41	1.295348967
726	42	1.326942844
789	42	1.326942844
831	43	1.358536721

Table 4.6 shows the absorption values, I (mm) of NP-0.5 corresponding to the increase in mass calculated at the time interval as per ASTM C1585.

Table 4.6 Absorption values of NP-0.5 at 28 day curing

√Time ($s^{1/2}$)	Δm (g)	I (mm)
0	0	0
8	4	0.126124141
17	8	0.252248281
24	10	0.315310351
35	12	0.378372422
42	15	0.472965527
60	17	0.536027597
85	23	0.725213808
104	26	0.819806913
120	29	0.914400019
134	31	0.977462089
147	33	1.040524159
304	36	1.135117265
440	37	1.1666483
518	38	1.198179335
657	39	1.22971037
726	39	1.22971037
789	40	1.261241405
831	40	1.261241405

From the data shown above in Table 4.5 and Table 4.6, the curve shown in Figure 4.9 has been plotted between the absorption and the square root of time for the control mix and 0.5% seaweed powder modified mortar. On the same lines, Figures 4.10 through 4.12 shows the comparison of water absorption behavior of control mix with mortar modified with different proportions of seaweed powder.

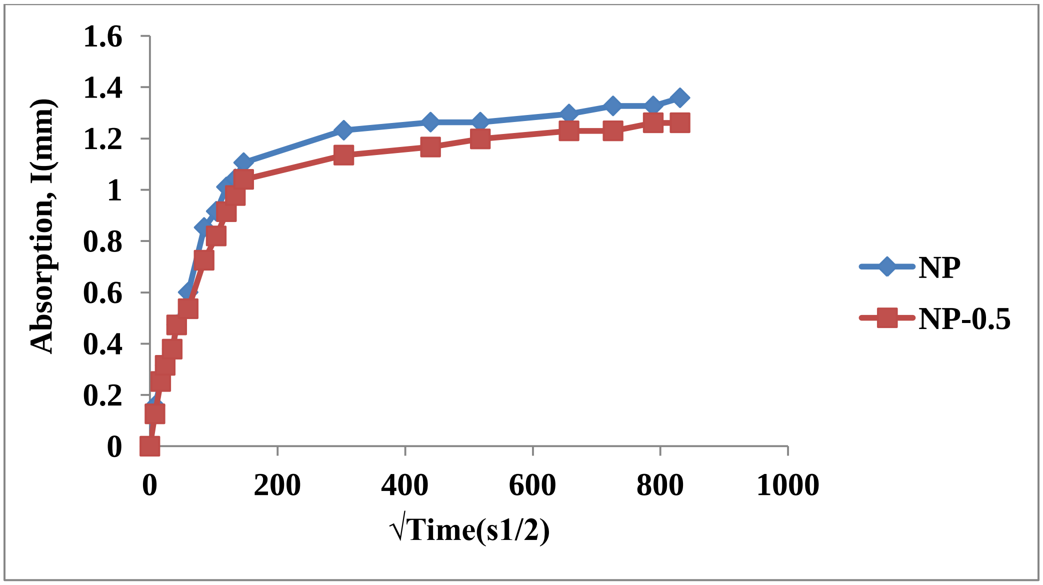


Figure 4.9 Absorption vs Square Root of Time Graph between NP and NP-0.5

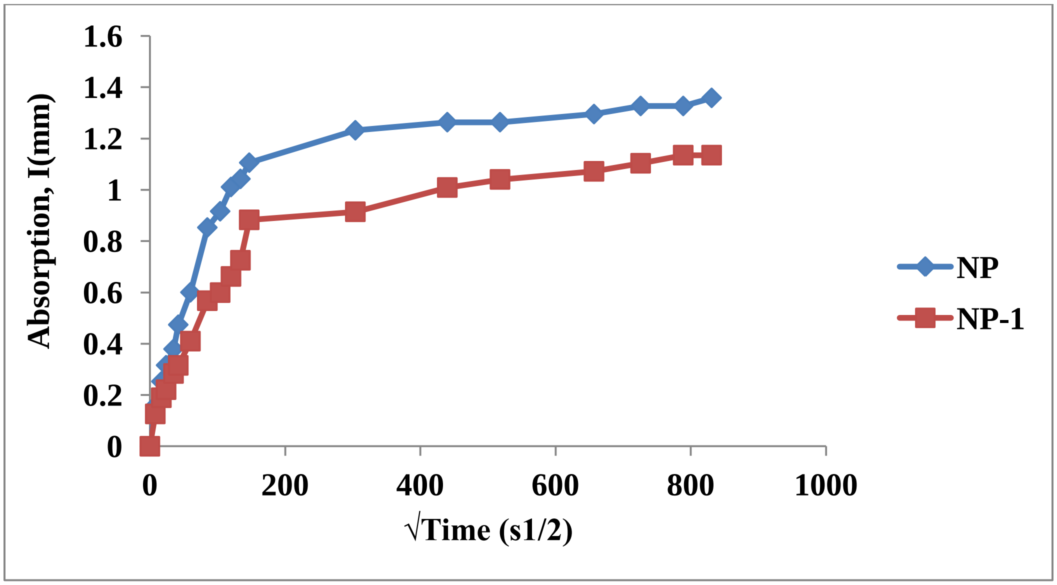


Figure 4.10 Absorption vs Square Root of Time Graph between NP and NP-1

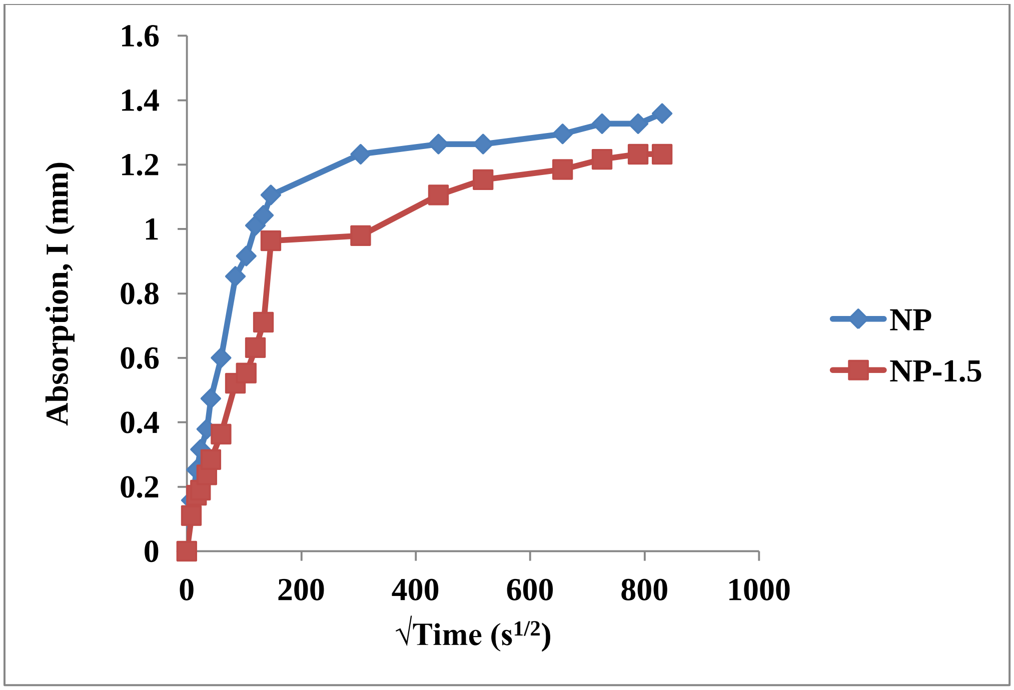


Figure 4.11 Absorption vs Square Root of Time Graph between NP and NP-1.5

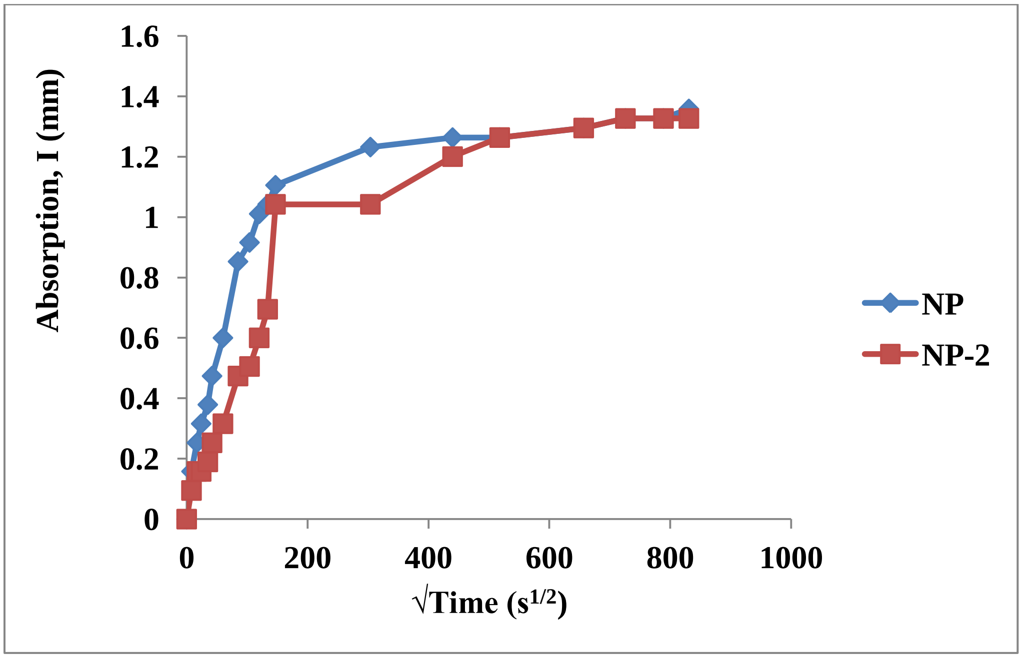


Figure 4.12 Absorption vs Square Root of Time Graph between NP and NP-2

Figure 4.13 presents the combined comparison of water absorption behavior for all Polymer modified mortars with respect to the control mix.

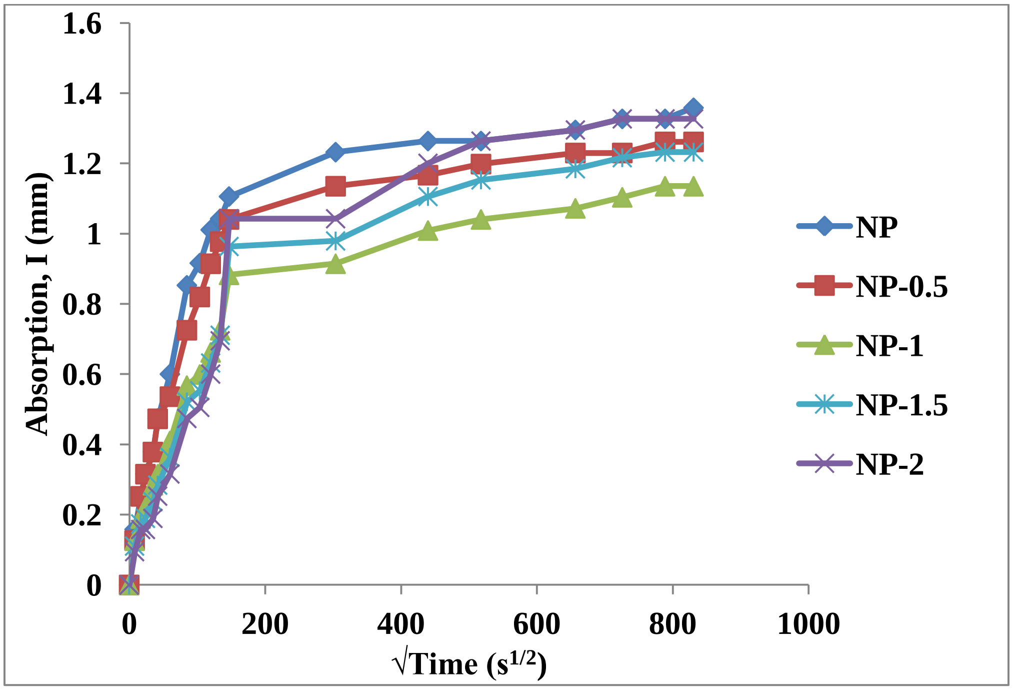


Figure 4.13 Absorption vs Square Root of Time Graph between Control Mix and Different Seaweed Compositions in Mortar

Discussions

In the above figures, a specific trend is observed in the water absorption behavior of the mortars modified with seaweed powder. For each composition of seaweed polymer powder, i.e. 0.5%, 1%, 1.5% and 2%, there is a decrease in the water absorption capacity of the polymer modified mortar. The maximum decrease in the water absorption is recorded in the case of the 1% seaweed powder polymer mortar.

The reduction in the water absorption due to addition of Seaweed powder can be understood from the XRD analysis. In the phase formation of the polymer matrix, it was observed from the XRD analysis that the **Rosenhahnite** ($Ca_3H_2O_{10}Si_3$) and **Xonotlite** ($Ca_6Si_6O_{17}(OH)_2$) were the additional compounds formed in the NP-1 seaweed polymer modified mortar; (these compounds were absent in the control mix mortar):

Rosenhahnite is formed in the hydration reaction due to the presence of nanosilica particles present in the seaweed powder. In the structure of kappa carraggenan there are vacant hydroxyl groups which in the process of hydration reaction react with C-S-H gel to form Calcium Silicate Hydroxide which is a strong emulsifier and improves the degree of hydration. It also refines the pore structure due to accelerated hydration mechanism and leads to denser microstructure.

Xonotlite ($Ca_6Si_6O_{17}(OH)_2$) is a calcium silicate hydrate. They are small microfiber which is formed in the hydration process. It is a fine compound phase in which all the pores are filled and being a microfiber there is also ductility incorporated in the structure.

These phase products are responsible for the refining of the pores of the mortar because of the emulsification of the seaweed powder. The smaller pores thus lead to a reduction in the water absorption of the polymer modified mortars.

4.2.5 Rapid Chloride Permeability Test

A water-saturated, 50-mm thick, 100-mm diameter concrete specimen is subjected to a 60 V DC voltage applied for 6 hours as per the procedure discussed in section 3.3.4. The apparatus for the test has been shown in Figure 3.6.

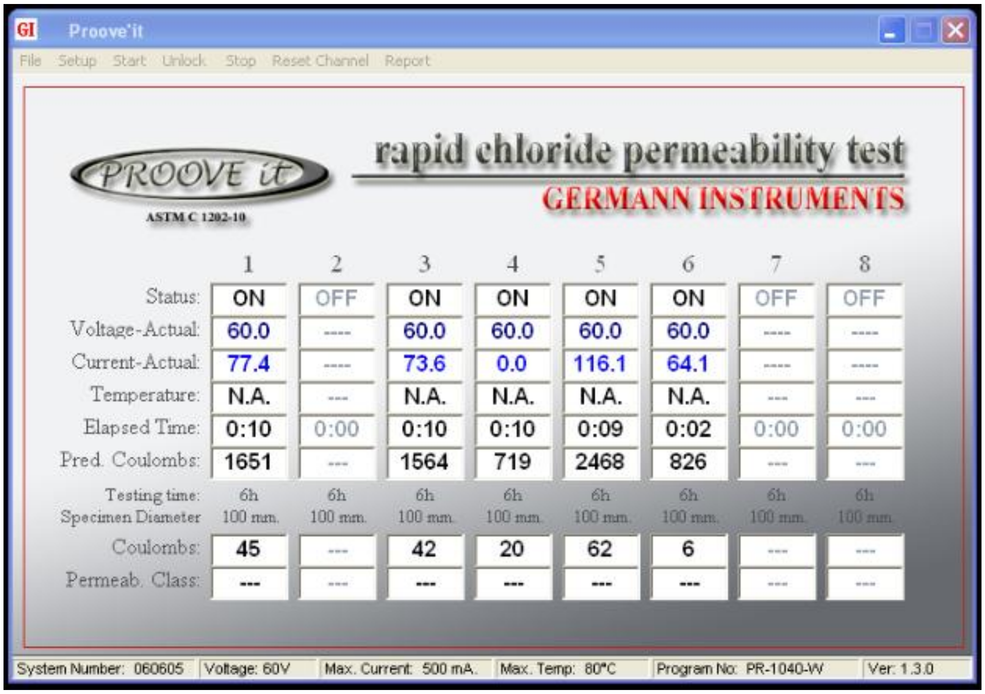
The samples were tested at 28 days and 56 days for 6 hours each. Readings were taken at periodic intervals of one hour and the apparatus was regularly checked to ensure the continuous movement of the charge through the sample.

1st Hour (At 28 Days)

Figure 4.14 shows the screenshot of test output for the RCPT specimens (cured for 28 days) at the end of first hour of testing. The values 1, 2 etc. (and so on) at the top show the sample number. The value of the charge generated, i.e. for example, 45 coulombs for the specimen 1, is noted for each sample. A tentative idea of the permeability of each sample i.e. low, moderate etc can be made manually, by comparison with the corresponding ranges in the Table 3.4.

Final Hour Reading (At 28 Days)

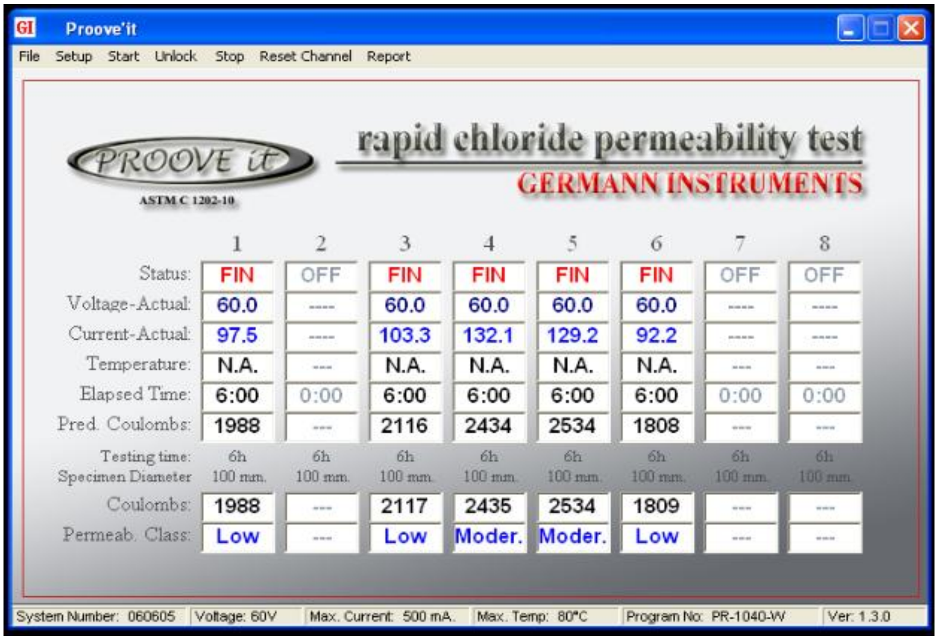
Figure 4.15 shows the final test output for the RCPT specimens (cured for 28 days) at the end of the testing, i.e. after 6 hours. The value of the charge generated, i.e. for example, 1988 coulombs for the specimen 1, is noted for each sample. As seen from the Figure, the test apparatus automatically gives the final classification of the permeability of the specimen as low, moderate or high, in accordance with the calibration Table 3.4, which is already built into the system.



	1	2	3	4	5	6	7	8
Status:	ON	OFF	ON	ON	ON	ON	OFF	OFF
Voltage-Actual:	60.0	----	60.0	60.0	60.0	60.0	----	----
Current-Actual:	77.4	----	73.6	0.0	116.1	64.1	----	----
Temperature:	N.A.	---	N.A.	N.A.	N.A.	N.A.	---	---
Elapsed Time:	0:10	0:00	0:10	0:10	0:09	0:02	0:00	0:00
Pred. Coulombs:	1651	---	1564	719	2468	826	---	---
Testing time:	6h	6h	6h	6h	6h	6h	6h	6h
Specimen Diameter	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.
Coulombs:	45	---	42	20	62	6	---	---
Permeab. Class:	---	---	---	---	---	---	---	---

System Number: 060605 | Voltage: 60V | Max. Current: 500 mA. | Max. Temp: 80°C | Program No: PR-1040-W | Ver: 1.3.0

Figure 4.14 Readings of 28 days curing of RCPT samples of Seaweed Mortar and Control Mix at the End of One Hour



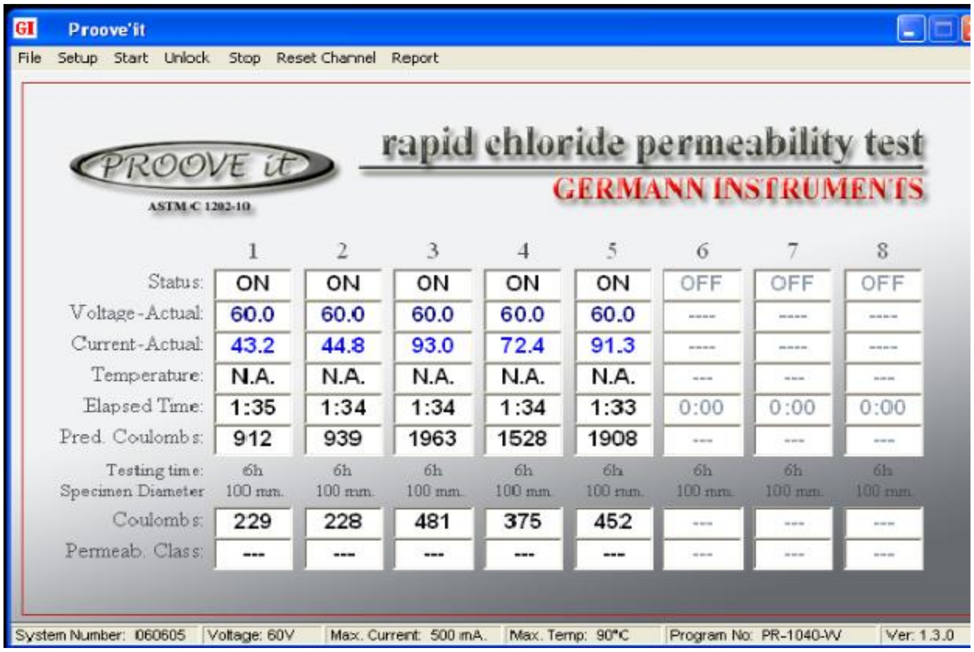
	1	2	3	4	5	6	7	8
Status:	FIN	OFF	FIN	FIN	FIN	FIN	OFF	OFF
Voltage-Actual:	60.0	----	60.0	60.0	60.0	60.0	----	----
Current-Actual:	97.5	----	103.3	132.1	129.2	92.2	----	----
Temperature:	N.A.	---	N.A.	N.A.	N.A.	N.A.	---	---
Elapsed Time:	6:00	0:00	6:00	6:00	6:00	6:00	0:00	0:00
Pred. Coulombs:	1988	---	2116	2434	2534	1808	---	---
Testing time:	6h	6h	6h	6h	6h	6h	6h	6h
Specimen Diameter	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.
Coulombs:	1988	---	2117	2435	2534	1809	---	---
Permeab. Class:	Low	---	Low	Moder.	Moder.	Low	---	---

System Number: 060605 | Voltage: 60V | Max. Current: 500 mA. | Max. Temp: 80°C | Program No: PR-1040-W | Ver: 1.3.0

Figure 4.15 Final Readings of 28 days Curing of RCPT samples of Seaweed Mortar and Control Mix

1^{st} Hour (At 56 Days)

Figure 4.16 shows the screenshot of test output for the RCPT specimens (cured for 56 days) at the end of first hour of testing. The value of the charge generated, i.e. for example, 45 coulombs for the specimen 1, is noted for each sample and manually compared with the corresponding ranges in the Table 3.4. This gives the user a tentative idea of the permeability of each sample i.e. low, moderate etc.



	1	2	3	4	5	6	7	8
Status:	ON	ON	ON	ON	ON	OFF	OFF	OFF
Voltage-Actual:	60.0	60.0	60.0	60.0	60.0	----	----	----
Current-Actual:	43.2	44.8	93.0	72.4	91.3	----	----	----
Temperature:	N.A.	N.A.	N.A.	N.A.	N.A.	---	---	---
Elapsed Time:	1:35	1:34	1:34	1:34	1:33	0:00	0:00	0:00
Pred. Coulombs:	912	939	1963	1528	1908	---	---	---
Testing time:	6h	6h	6h	6h	6h	6h	6h	6h
Specimen Diameter	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.
Coulombs:	229	228	481	375	452	---	---	---
Permeab. Class:	---	---	---	---	---	---	---	---

System Number: 060605 | Voltage: 60V | Max. Current: 500 mA. | Max. Temp: 90°C | Program No: PR-1040-W | Ver: 1.3.0

Figure 4.16 Readings of 56 days Curing of RCPT samples of Seaweed Mortar and Control Mix at the End of One Hour

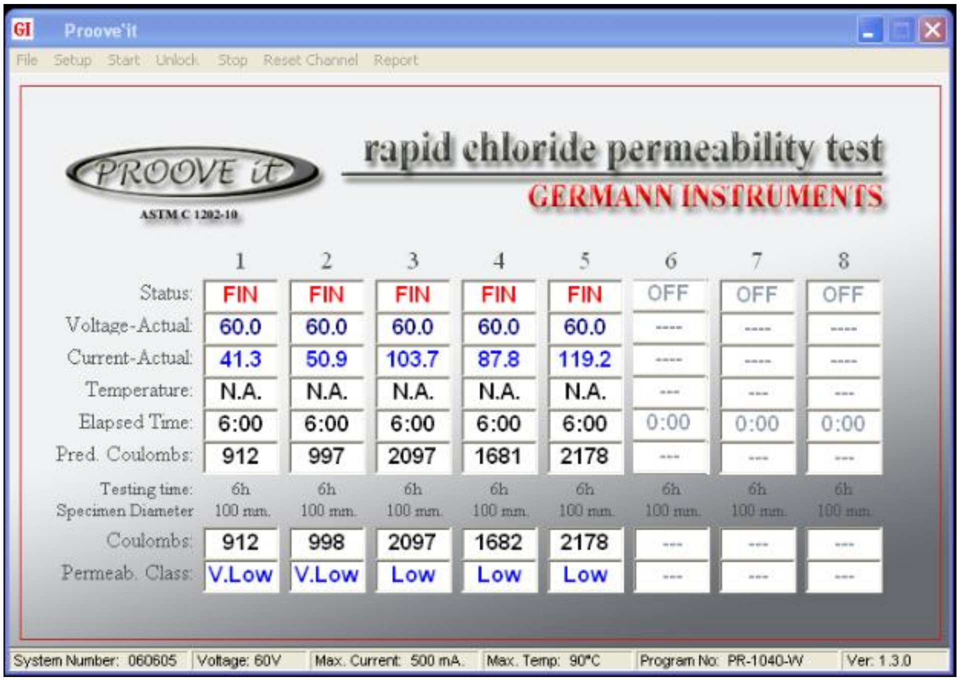
Final Hour Reading (At 56 Days)

Figure 4.17 shows the final test output for the RCPT specimens (cured for 56 days) at the end of the testing, i.e. after 6 hours. As discussed earlier, the test apparatus automatically gives the final classification of the permeability of the specimen based on the value of the charge generated (in coulombs), in accordance with the calibration Table 3.4.

Discussions

In the Rapid Chloride Permeability Test, the charge passed through the samples is used to determine the permeability.

Table 3.4 is used to determine the permeability of the sample.



	1	2	3	4	5	6	7	8
Status:	FIN	FIN	FIN	FIN	FIN	OFF	OFF	OFF
Voltage-Actual:	60.0	60.0	60.0	60.0	60.0	----	----	----
Current-Actual:	41.3	50.9	103.7	87.8	119.2	----	----	----
Temperature:	N.A.	N.A.	N.A.	N.A.	N.A.	---	---	---
Elapsed Time:	6:00	6:00	6:00	6:00	6:00	0:00	0:00	0:00
Pred. Coulombs:	912	997	2097	1681	2178	---	---	---
Testing time:	6h	6h	6h	6h	6h	6h	6h	6h
Specimen Diameter	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.	100 mm.
Coulombs:	912	998	2097	1682	2178	---	---	---
Permeab. Class:	V.Low	V.Low	Low	Low	Low	---	---	---

System Number: 060605 | Voltage: 60V | Max. Current: 500 mA. | Max. Temp: 90°C | Program No: PR-1040-W | Ver: 1.3.0

Figure 4.17 Final readings of 56 days curing of RCPT samples of seaweed mortar and control mix

Table 4.7 shows the permeability of different compositions of seaweed modified mortar at 28 days of curing

Table 4.7 Permeability values at 28 days curing of various compositions of seaweed mortar and control mix.

Mix Composition	Charge(Coulombs)	Permeability
NP	2534	Moderate
NP-0.5	1988	Low
NP-1	1809	Low
NP-1.5	2117	Low
NP-2	2435	Moderate

Table 4.8 shows the permeability of different compositions of seaweed modified mortar at 56 days of curing

Table 4.8 Permeability values at 56 days curing of various compositions of seaweed mortar and control mix.

Mix Composition	Charge(Coulombs)	Permeability
NP	2097	Low
NP-0.5	998	Very Low
NP-1	912	Very Low
NP-1.5	1682	Low
NP-2	2178	Low

It can be seen from Table 4.7 and Table 4.8 that the permeability of the control mix is moderate at 28 days of curing and low for 56 days of curing. The permeability of the samples reduces up to addition of 1% of seaweed powder at both 28 and 56 days of curing. For the 1% composition of the seaweed polymer mortar the charge passing through is the least; therefore the permeability of the 1% seaweed modified mortar is the lowest among all tested specimens at 28 and 56 days of curing. Thus, 1% seaweed powder may be regarded as the optimum percentage of natural polymer additive to achieve the best durability performance in a mortar mix.

Beyond 1% polymer addition, the permeability increases with the addition of seaweed powder; the charge generated increases for 1.5% and 2% addition of seaweed powder into the mortar. However, the charge generated is still lower than the charge for the control mix, signifying a improved durability response for the Seaweed Powder modified mortar in general as compared to the ordinary mortar mix.

The reduction in the permeability due to addition of Seaweed powder can be understood from the XRD analysis. In the phase formation of the polymer matrix, it was observed from the XRD analysis that the **Wollastonite** (Calcium meta Silicate), **Xonotlite** ($Ca_6Si_6O_{17}(OH)_2$) were the additional compounds formed in the NP-1 seaweed polymer modified mortar; (these compounds were absent in the control mix mortar):

Wollastonite ($CaSiO_3$) is a white mineral which is formed in the hydration process of the seaweed powder with the cement. Wollastonite inclusion can affect rate and extent of hydration of cement in addition to CH formation and matrix permeability.CH reduction in the matrix due to its deposition at interfaces can reduce the permeability of the body and access to cement grains by water.

Xonotlite ($Ca_6Si_6O_{17}(OH)_2$) is a calcium silicate hydrate. They are small microfiber which is formed in the hydration process. It is a fine compound phase in which all the pores are refined.

These phase products are responsible for the refining of the pores of the mortar because of the emulsification of the seaweed powder. The compounds are negatively charged as they contain the hydroxyl group. Therefore, when the negatively charged chloride ion attacks the mixture, both being negatively charged ions repel each other. Hence, the movement of the chloride ion is hindered, which in combination with the smaller pore size, leads to lower permeability

4.2.6 Slant Shear Bond Strength

The evaluation of the bond strength of PMM with the old conventional mortar mix Slant Shear test is performed as per ASTM C882.
The results of the slant shear test are summarized in Table 4.9.

Table 4.9 Slant Shear Strength Results and Failure Modes

Mixes	Test results at 7 day		
	Load (KN)	**Bond strength (MPa)**	**Failure Mode**
NP	19.2	2.106	Type 1
NP-0.5	28.4	3.115	Type 2
NP-1	36.7	4.025	Type 3
NP-1.5	23.7	2.598	Type 1
NP-2	16.4	1.799	Type 1

Discussions
The experimental results shown in Table 4.9 show that the interfacial bonding between substrate and PMM was generally better up to 1.5% addition of the seaweed powder as compared to conventional mortar mix. The results show an increase in bond strength of NP-0.5, NP-1 and

NP-1.5 with a relative increase of 47.91%, 91.12% and 23.36% respectively over the control mix. However, the bond strength for NP-2 decreased by 14.57% as compared to the control mix.

Figure 4.18 shows various Failure Modes of different composite samples during slant shear test. Generally, the failure modes could be grouped into three distinct forms, namely:

i) Type 1: Interfacial failure combined with minor substrate cracking or damage.
ii) Type 2: Interfacial failure combined with substrate fracture.
iii) Type 3: Substratum failure.

TYPE 1 FAILURE **(Control Mix)**

TYPE 2 FAILURE **(0.5%, 1.5% and 2% Seaweed Powder)**

TYPE 3 FAILURE **(1% Seaweed Powder)**

Figure 4.18 Failure Modes for different percentages of Seaweed Addition

From the test results shown in Table 4.9 and the failure modes shown in Figure 4.18 following observations were made:

When the repair material and the substrate were cast of the Conventional Mortar Mix (CMM), the compressive failure occurred between the interfacial surfaces (Type 1) of the composite cylinder. As the shear failure is brittle in nature therefore Tpre 1 failure should be avoided.

The interfacial failure along with the substrate failure (Type 2) is observed when the substrate is repaired with NP-0.5, NP-1.5 and NP-2. As the compressive strength of these repair materials is slightly higher than the CMM, therefore at compression interfacial failure along with the substrate failure is observed with a slight damage to the repair material.

The substratum failure (Type 3) is only observed for the NP-1 repair material. As the compressive strength of the repair material is relatively higher than that of CMM, therefore with a little damage to the repair material compressive failure is observed in the substrate witout any interfacial material.

Based on the percentage change observed from Table 4.9, it is evident that 1% seaweed powder is the optimal addition percentage which provides the highest increase in the bond strength with Type 3 failure, hence can be used as a retrofitting material.

The enhancement in shear bond strength can be related to greater adhesion between natural PMM and rough conventional mortar. Due to presence of seaweed in mortar, Rosnhahnite ($Ca_3H_2OSi_3$) is formed during the cement hydration reaction, which refines the pore structure of mortar due to accelerated hydration mechanism and leads to denser microstructure thus enhancing bond strength.

CHAPTER 5

SUMMARY AND CONCLUSIONS

5.1 Conclusions

The present study was undertaken to develop Natural Polymer Modified Mortar and to investigate the compressive strength, split tensile strength, durability properties and the slant shear bond strength of mortar specimens at w/c of 0.45, with the addition of 4 percentages of Natural polymer Seaweed (Eucheuma Cottonii) powder.

- The addition of seaweed natural polymer whether in gel form or in powder form results in the increase in the compressive strength of the mortar as compared to conventional mortar.
- There was an increase in the compressive strength of mortar samples modified by adding 0.5%, 1% and 1.5% of seaweed powder of (by the weight of cement) as compared to the control mix. However, the compressive strength of the 2% Seaweed powder mortar was lower than the control mix. The maximum strength was observed at 1% composition with 7 day strength of 16.67 MPa (50.85% more than control mix) and 28 day strength of 35.83 MPa (23.1% higher than the control mix).
- There was an increase in the split tensile strength for all compositions up to 1% as compared to the control mix. The maximum strength was observed for the sample with 1% composition i.e. 5.89 MPa which is 16.43% of its compressive strength.
- In the Water Sorptivity test there was a decrease in the water absorption of the samples of every composition as compared to the control mix. From the graphs, the minimum water absorption was observed in the samples of 1% Seaweed addition.
- The evaluation of durability by Rapid Chloride Permeability Test exhibited a low permeability for each mortar sample with Seaweed powder as an additive. The lowest permeability was observed for the sample of 1% seaweed composition.
- In slant shear test, maximum bond strength was observed for 1% seaweed PMM, 3.115 MPa (91.12% more than control mix). There was only compressive failure

observed in the conventional mortar mix with minimal damage to the repair material in the composite cylinder and no interfacial failure was observed.

Based on the conclusions above, addition of Seaweed powder by 1% of weight of cement is the optimum mix composition to enhance the mechanical and durability properties of the conventional cement mortar.

5.2 Scope for Further Studies

The followings are some of the possible areas of future study for Natural Polymer Modified Mortar:

- The behavior of Polymer Modified Mortar in cyclic fatigue type durability studies i.e. freezing and thawing may be evaluated.
- The research work can be extended to study the effect of corrosive environments by immersing Polymer Modified Mortar in salt water to try and simulate the actual physical condition of corrosion that affects the durability.
- The abrasion and toughness properties of the Polymer Modified Mortar may be evaluated.

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