DEVELOPMENT OF POLYMER CEMENT COMPOSITES

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Certificate

This is to certify that the thesis entitled *"Development of Polymer Cement Composites"* which is being submitted by ***Ms. Priya Viswanath*** in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, Kochi, Kerala, India, is a record of the bonafide research work carried out by her under my guidance and supervision, at the Department of Polymer Science and Rubber Technology, Kochi, Kerala, India, and no part of the work reported in the thesis has been presented for the award of any degree from any other institution.

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(Supervisor)

Kochi,
20-09-2007

DECLARATION

I hereby declare that the work presented in this thesis entitled "**Development of Polymer Cement Composites**" is based on the original research work carried out by me under the guidance and supervision of Dr. Eby Thomas Thachil, Reader, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, Kerala, India, and, to the best of my knowledge, no part of the work reported in this thesis has been presented for the award of any degree at any other institution.

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PREFACE

Concrete building structures used in refineries, chemical industries and even cattle houses are often exposed to chemically polluted environments due to which their durability is at stake. Permeation of external chemicals into the cement matrix and the interactions between the two phases is the major cause for deterioration under these circumstances. Though, for several years, pure polymeric materials have been known to be used to improve the durability of concrete structures the high cost and incompatibility with cement concrete have restricted their use to areas where their specific properties could prove to be vital. Investigations into the microscopic level properties of such polymer cement composites could uncover and possibly circumvent the interphase incompatibilities and enable the development of tailor made materials for various construction scenarios.

The main objective of this research work was to prepare and evaluate the macroscopic and microstructural properties of polymer cement composites and cement-sand mortars that could possibly yield low-cost indigenous construction materials. It was envisaged to use various thermoplastics, rubbers and thermosets along with Portland cement to prepare polymer cement composites that would help enhance some relevant properties of virgin cement. An endeavour to correlate the structure of the polymers to the property of the polymer cement composites has also been made.

A chapter wise organization of the thesis is given below.

The first chapter gives an account of the discovery, technology, manufacture and the different types of Portland cement together with its admixtures. The deterioration of concrete structures due to exposure to frost and chemically polluted environments has also been discussed. The classification of polymers, followed by a survey of the preparation and properties of polymer cement composites, has also been included. The interactions of polymers and cement in the Portland cement matrix and various theories to explain the microstructural aspects of the polymer cement composites form the latter part of this chapter. The scope and objectives of this research work conclude this section.

The second chapter deals with the preparation and evaluation of cement composites using various thermoplastics and rubbers. The interpretation and discussion of the results obtained from the above experiments and the conclusions form the final part of this chapter.

The synthesis of phenolic thermosetting resins, the preparation of composites with different polymer-cement proportions and the evaluation of properties form the major part of the third chapter. A section on results and discussions throws light on the degree of retention of compressive strength on exposure of the composites to acid, base and kerosene.

The fourth chapter presents the study and analysis of the microstructure of virgin cement composites employing various polymers and the effect of choice of polymer on macroscopic properties. Thermal and chemical analyses of the polymer cement composites carried out to determine the interactions between the polymers and cement concrete phases have been also described and interpreted. The techniques employed viz.

- TGA for thermal properties,
- SEM for microstructure,
- Soxhlet extraction for leachability and
- EDTA titrations for chemical reactions

also constitute a major portion of this chapter. Possible correlations between the structure of the polymers and properties of the polymer cement composites have also been highlighted.

The conclusions, a glossary of some specific terms together with the lists of tables, figures and abbreviations used in this thesis form the last part the report.

ABSTRACT

Research in the field of polymer modified cement has been carried out for the last 70 years or more. Polymers are mostly used to enhance durability and sustainability of cement concrete and in combination with classical construction materials a synergistic effect is obtained. In this work different polymers were added to Portland cement in various proportions and the mechanical and chemical resistance properties of the resultant composites when exposed to chemical environments were studied. Microstructural studies were also carried out to investigate the morphology of the composite and analyse the nature of interactions taking place between the cement and polymer phases. Though most polymers did not improve the compressive strength of the cement paste, it was found that they enhanced the resistance of the virgin cement paste to external chemical environments. The polymers seal the pores in the cement matrix and bridge the microcracks within the composite. Some of the polymers underwent chemical interactions with the cement paste thereby interfering in the hydration of cement. Polymers also decreased the leachability of water soluble components of virgin cement resulting in composites having improved durability. An attempt to correlate the structure of the polymers with the properties of the resultant composites is also presented.

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Chapter 1

INTRODUCTION

1.1 Portland cement

Portland cement is the chief ingredient of cement paste. It is a hydraulic cement that, when combined with water, hardens into a solid mass. Interspersed in an aggregate matrix it forms Portland cement concrete (PCC). As a material, Portland cement has been used for well over 175 years and its behaviour is well-understood from an empirical perspective. Chemically, however, Portland cement is a complex substance whose mechanisms and interactions are yet to be fully comprehended.

1.1.1 History

The technique of firing stone or clay to produce cementing materials for construction is as old as recorded history. The ancient binders - lime, hydraulic lime, gypsum and certain volcanic rocks (Pozzolana) are still in use. The Egyptians, Romans and Indians used different types of cementing materials in the early days in their ancient constructions. Some of the older materials include burnt gypsum, limestone and lime. Certain volcanic ash and sand were used for structures exposed to fresh and salt water. But today they are overtaken by Portland cement, a highly sophisticated relative of hydraulic lime.

Investigations into the development of modern Portland cement were initially carried out by William Aspdin [1] when he found that limestone containing some proportion of clayey soil led to superior hydraulic properties. By this crude method he laid the foundation for an industry, which annually processes literally mountains of limestone, clay, cement rock and other materials into a powder; so fine that it passes through a sieve capable of holding water. This cement is so fine that one pound contains up to 150 billion grains.

1.1.2 Chemical composition

Portland cement concrete is by far the most widely used construction material and its general versatility has been greatly extended by the development of a number of modified forms. It is a basic ingredient of concrete, mortar and most non-specialty grouts. It is a finely-ground powder produced by grinding Portland cement clinker (more than 90%), a maximum of about 5% gypsum which controls the setting time and up to 5% minor constituents (as allowed by various standards). As defined by the European Standard EN197.1, Portland cement clinker is a hydraulic material which consists of at least two-thirds by mass of calcium silicates ($3CaO.SiO_2$ and $2CaO.SiO_2$), the remainder consisting of aluminum and iron containing clinker phases and other compounds. The ratio of CaO to SiO_2 should not be less than 2.0. The magnesium content (MgO) should not exceed 5.0% by mass.

The approximate oxide composition limits for ordinary Portland cement are indicated in Table 1.1 below.

Table 1.1 Composition of ordinary Portland cement [2]

Oxide	%, content by weight
CaO	60-67
SiO_2	17-25
Al_2O_3	3.0-8.0
Fe_2O_3	0.5-6.0
MgO	0.1-4.0
Alkalis (K_2O, Na_2O)	0.4-1.3
SO_3	1.3-3.0

Portland cement clinker is made by heating a homogenous mixture of raw materials in a kiln, to a sintering temperature of about 1450 °C. The aluminium and iron oxides are used as a flux and contribute little to the strength. For special cements, such as Low Heat (LH) and Sulfate Resistant (SR) cements, it is necessary to limit the amount of tricalcium aluminate ($3CaO.Al_2O_3$) formed.

1.1.3 Manufacture of Portland cement

Portland cement is a fine powder, gray or white in color that consists of a mixture of hydraulic cementitious materials comprising primarily of calcium silicates, aluminates and aluminoferrites. The process of manufacture of cement consists of grinding the raw materials, mixing them in appropriate proportions and burning them in a kiln at a very high temperature. The clinker is then cooled, powdered and packed after addition of gypsum.

a. Raw materials

Limestone ($CaCO_3$) constitutes the major raw material for making the clinker. Normally, an impure limestone containing SiO_2 is used. The $CaCO_3$ content can be as low as 80%. Secondary raw materials depend on the purity of the limestone. Some of the secondary raw materials used are clay, shale, sand, iron ore, bauxite, fly ash and slag. These raw materials are subjected to high temperature to form complex compounds. The major compounds formed are called "Bogue's compounds" [3, 4].

The equations suggested by Bogue for calculating the percentages of major compounds are given below.

$$C_3S = 4.07\,(CaO) - 6.72\,Al_2O_3\ --1.43\,(Fe_2O_3) -2.85\,(SO_3)$$

$$C_2S = 2.87\,(SiO_2) -0.754\,(3CaO.SiO_2)$$

$$C_3A = 2.65(Al_2O_3) -1.69\,(Fe_2O_3)$$

$$C_4AF = 3.04\,(Fe_2O_3)$$

C_3S = Tri calcium silicate = $3CaO.SiO_2$ = Alite

C_2S = Di calcium silicate = $2CaO.SiO_2$ = Belite

C_3A = Tri calcium aluminate = $3CaO.Al_2O_3$ = Celite

C_4AF = Tetra calcium aluminoferrite = $4CaO.Fe_2O_3.Al_2O_3$ = Felite

b. Processing

Fig.1.1. Flow chart for the manufacture of Portland cement [5]

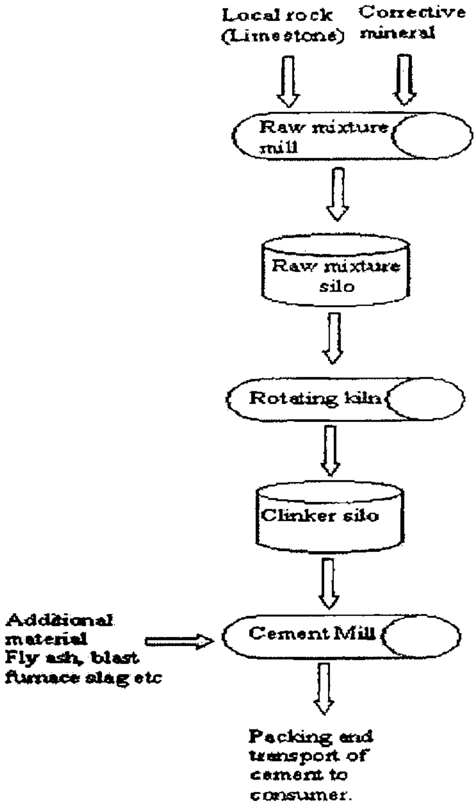


Fig 1.1 shows the flow chart for the manufacture of Portland cement.

The first step in the Portland cement manufacturing process is procuring raw materials. Generally, raw materials consisting of combinations of limestone, shells or chalk and shale, clay, sand or iron ore are mined from a quarry near the plant. At the quarry, the raw materials are reduced by primary and secondary crushers. Stone is first reduced to a size of about 125-mm and then to 19 mm. Once the raw materials arrive at the cement plant, the materials are proportioned to create cement with a specific chemical composition. Two different methods - dry and wet, are used to manufacture Portland cement.

In the dry process, dry raw materials are proportioned, ground to a powder, blended together and fed to the kiln. In the wet process, slurry is formed by adding water to the properly proportioned raw materials. The grinding and blending operations are then completed with the materials in slurry form.

After blending, the mixture of raw materials is fed into the upper end of a tilted rotating, cylindrical kiln. The mixture passes through the kiln at a rate controlled by the slope and rotational speed of the kiln. Burning fuel consisting of powdered coal or natural gas is forced into the lower end of the kiln. Inside the kiln, raw materials reach temperatures of 1430°C to 1650°C. At 1480°C, a series of chemical reactions cause the materials to fuse and create cement clinker-greyish-black pellets. Clinker is discharged red-hot from the lower end of the kiln and transferred to various types of coolers to lower the clinker handling temperatures. Cooled clinker is combined with gypsum and ground into a fine grey powder. The clinker is ground so fine that nearly all of it passes through a 75 micron sieve. This fine grey powder is Portland cement. The final Portland cement product is anhydrous and must be protected from moisture and carbon dioxide if it is to retain its cementing action.

The chemistry and the hydration of Portland cement are summarized below.

Raw materials for cement ----Lime stone, clay, shale----

$$\begin{tikzcd}
CaO,\ SiO_2,\ Al_2O_3,\ Fe_2O_3 \arrow[d, "\text{Clinker formed}"] \\
C_3S,\ C_2S,\ C_3A,\ C_4AF \arrow[d, "\text{Hydration}"] \\
\text{C-S-H gel} + Ca(OH)_2
\end{tikzcd}$$

C_3S = Tri calcium silicate = $3CaO.SiO_2$ = Alite

C_2S = Di calcium silicate = $2CaO.SiO_2$ = Belite

C_3A = Tri calcium aluminate = $3CaO.Al_2O_3$ = Celite

C_4AF = Tetra calcium aluminoferrite = $4CaO.Fe_2O_3.Al_2O_3$ = Felite

Tricalcium silicate and dicalcium silicate are the most important of all compounds and constitute 70-80% of cement. The properties of the cement are mainly dependent on the proportion of the oxides added during the manufacture of the cement. For example an excess of lime leads to free lime content and inferior strength for the final cured product. Similarly high alumina and ferric oxide contents in the cement lead to early strength development in cement.

1.1.4 Hydration of cement

Hydration refers to the total changes undergone by anhydrous cement or one of its constituent phases, when mixed with water. Anhydrous cement does not bind the sand and aggregates. Instead it develops the adhesive property after the addition of water. The chemical reactions between the cement and water are generally more complex than simple conversions of anhydrous compounds into the corresponding hydrates. This results in stiffening and significant development of compressive strength. The quality, quantity continuity, stability and the rate of formation of the hydration products significantly contribute to the strength of the cement concrete.

The main cementing and strength-producing compounds formed in Portland cement clinker are the calcium silicates - $3CaO.SiO_2$ and $2CaO.SiO_2$.When mixed with water these anhydrous compounds hydrate, set and slowly harden. Tricalcium aluminate, $3CaO.Al_2O_3$, also present in the clinker forms a hydrate with water and contributes to setting and early hardening properties.

The reaction between cement and water is exothermic. It has been observed that the temperature in the interior of a large mass may reach 50°C above the original temperature of the concrete mass at the time of curing [6]. This temperature that persists for a prolonged period of time is due to the reaction of aluminates and sulphates with water and formation of ettringite. Ettringite is calcium aluminate trisulphate hydrate and is usually the first to crystallize as short prismatic crystals during the first hour of hydration. The hydration reaction is faster in the early period and continues indefinitely at a decreasing rate. Some of the reactions [7] occurring during the hydration are:

$$2C_3S + 6H_2O \rightarrow C_3S_2H_3 + 3Ca(OH)_2$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + Ca(OH)_2$$

C_3S readily reacts with water and produces more heat of hydration than C_2S. It is responsible for the early strength of the concrete. The cement with more C_3S is preferred for cold-weather concreting. The quality and density of $C_3S_2H_3$ formed from C_3S is inferior to the one formed from C_2S. C_2S is responsible for the later strength of the cement. C_3A forms $CaO.Al_2O_3.H_2O$ on hydration and this reaction is very fast. This may lead to flash set which is prevented by the addition of gypsum. This compound does not contribute to the strength of the cement. Depending on the concentration of aluminate and sulphate ions in solution, the precipitating crystalline product is either calcium aluminate trisulphate hydrate ($C_6AS_3H_{32}$) or calcium aluminate monosulphate hydrate (C_4ASH_{18}). As the hydration proceeds there is a gain in the initial compressive strength with increasing temperature [8]. A set-retarding admixture is often used to modify the setting time, especially in hot weather. An accelerator admixture, besides affecting setting time of concrete, is used primarily to the increase rate of strength gain through increased rate of hydration.

1.1.5 Types of Portland cement

The rapid increase in sophistication of design and construction techniques and greater attention to variation in regional and local conditions has created a demand for modification of certain properties of concrete [7]. This has resulted in the development of several "types" of Portland cement and a greater use of concrete admixtures. These types have extensive use in the precast and ready-mix concrete industries.

The production of a different type of Portland cement involves certain adjustments in the manufacturing process, mainly the selection of raw materials, chemical proportions, special additives and the degree of grinding. The inevitable increase in cost of these modified Portland cements over the normal product is due partly to the above adjustments in manufacture and partly to additional handling and storage requirements in the plant.

The following tables (Tables 1.2 and 1.3) show the types of Portland cement and the specifications of the compressive strengths. A brief description of each type follows.

Table 1.2 Portland cement types [9]

Cement Type	Use
I	General purpose cement
II	Moderate resistance to sulphate attack
III	High early strength cement
IV	When a low heat of hydration is desired (in massive structures)
V	When high sulfate resistance is required
I A	A type I cement containing an integral air-entraining agent
II A	A type II cement containing an integral air-entraining agent
III A	A type III cement containing an integral air-entraining agent

Table 1.3 ASTM C 150 Portland Cement Mortar Compressive Strength Specifications in MPa (psi) [10]

Curing Time	Portland Cement Type							
	I	IA	II	IIA	III	IIIA	IV	V
1 day	-	-	-	-	12.4 (1800)	10.0 (1450)	-	-
3 days	12.4 (1800)	10.0 (1450)	10.3 (1500)	8.3 (1200)	24.1 (3500)	19.3 (2800)	-	8.3 (1200)
7 days	19.3 (2800)	15.5 (2250)	17.2 (2500)	13.8 (2000)	-	--	6.9 (1000)	15.2 (2200)
28 days	-	-	-	-	-	-	17.2 (2500)	20.7 (3000)

a. Normal Portland – Type I

This is the standard product that serves most concreting requirements. It is the cheapest and therefore by far the most widely used. Its composition and properties are determined by minimum quality standards such as BIS 269:1989. The typical compositions of this type are:

55% (C_3S), 19% (C_2S), 10% (C_3A), 7% (C_4AF), 2.8% MgO, 2.9% (SO_3), 1.0% Ignition loss and 1.0% free CaO.

b. High Early Strength and Precast Product Cements- Type III

This type of cement achieves a much higher strength than normal Portland at early ages of one, three and seven days. On the 28th day or later there is usually little difference, depending on the modification used in cement manufacture. High early strength cement is frequently used for such special situations as early removal of formwork, early application of load, special precasting procedures and rapid maturing to aid in frost resistance of concrete.

Its typical compound composition is:

57% (C_3S), 19% (C_2S), 10% (C_3A), 7% (C_4AF), 3.0% MgO, 3.1% (SO_3),

0.9% Ignition loss and 1.3% free CaO.

High early strength is achieved today mainly by extra fine grinding of the clinker-gypsum mixture. When the clinker is ground to a fineness intermediate between that of normal Portland and high early strength cement, a product of intermediate cost and intermediate early strength is obtained. On the market, cements of this type are known by various names such as "concrete products cement" and "block-type cement." The main alternative to high early type cements is the use of an accelerator, calcium chloride, with normal Portland.

c. Sulphate-Resistant and Low Heat Cements- Type II and IV

These Portland cement types were developed for reduction of the tricalcium aluminate component. This compound contributes to early strength in both sulphate resistant cement and low heat cement and its presence is highly undesirable.

The typical compound composition of Type II is:

51% (C_3S), 24% (C_2S), 6% (C_3A), 11% (C_4AF), 2.9% MgO, 2.5% (SO_3),

0.8% Ignition loss and 1.0% free CaO.

Tricalcium aluminate combines rapidly with sulphates in the early stages of Portland cement hydration, forming products that result in a net expansion of the hardened cement paste. The hydration of the tricalcium aluminate component of Portland cements produces considerable heat (exothermic reaction).

Low heat cements (Type IV) are manufactured to yield lower tricalcium aluminate contents than normal Portland and are therefore similar in this respect to sulphate-resistant cements. Its typical compound composition is:

28% (C_3S), 49% (C_2S), 4% (C_3A), 12% (C_4AF), 1.8% MgO, 1.9% (SO_3)

0.9% Ignition loss and 0.8% free CaO.

Alternatives to the use of low heat cements for mass concrete or hot weather construction include pre-cooled concrete (usually by means of ice as a part of the mix water) or cold water circulated through pipes incorporated in the concrete mass. When available, pozzolanic materials or fly ash are used to replace a part of the normal Portland cement in mass concrete.

As for high early strength cements, there are intermediate grades of sulphate-resistant and low heat cements, that is, cements in which the tricalcium aluminate component is reduced in manufacture to values between those for normal Portland and sulphate-resistant cement. These are cheaper and are often specified as adequate for moderate sulphate conditions or for moderately massive concrete elements.

d. High sulphate resistant cements Type V

This type is used as a precaution against severe sulphate action - principally where soils or ground waters have high sulphate content. It gains strength at a slower rate than Type I cement. High sulphate resistance is attributable to low C_3A content.

Its typical compound composition is:

38% (C_3S), 43% (C_2S), 4% (C_3A), 9% (C_4AF), 1.9% MgO, 1.8% (SO_3), 0.9% Ignition loss and 0.8% free CaO.

Types Ia, IIa and IIIa have the same composition as types I, II and III. The only difference is that in Ia, IIa and IIIa an air-entraining agent is ground into the mix. The air-entrainment must meet the minimum and maximum optional specification found in the ASTM manual. This is done so that air-entrainment improves resistance of the concrete to freezing under low temperatures.

e. Blended cements

Blended cement, as defined in ASTM C 595, is a mixture of Portland cement and blast furnace slag (BFS) or a "mixture of Portland cement and a Pozzolan (most commonly fly ash)."

Table 1.4 Blended cement types and blended ratios [11]

Type	Blended Ingredients
IP	15-40% by weight of Pozzolan (fly ash)
I(PM)	0-15% by weight of Pozzolan (fly ash) (modified)
P	15-40% by weight of Pozzolan (fly ash)
IS	25-70% by weight of blast furnace slag
I(SM)	0-25% by weight of blast furnace slag (modified)
S	70-100% by weight of blast furnace slag

The use of blended cements in concrete reduces mixing water and bleeding improves finish and workability, enhances sulfate resistance, inhibits the alkali-aggregate reaction and lessens heat evolution during hydration, The last quality reduces chances for thermal cracking on cooling. Blended cement types and blended ratios are presented in Table 1.4.

1.2 Cement concrete

Concrete is a mixture of cement, aggregates and water in appropriate quantities and can be moulded into any shape. The use of concrete in building structures dates back to early civilizations. Apart from the common building structures, cement concrete has found its way into a wide gamut of applications including oil well walls, refractories, sleepers, chemically resistive floorings, launching pads and runways. Over the years numerous kinds of cement concrete have evolved to suit the relevant applications. The basic difference lies in the cementing material used. This section discusses the definition, raw materials and preparation of concrete.

1.2.1 Definition

Cement may be defined as a material with adhesive and cohesive properties which make it capable of bonding mineral fragments into a compact whole [12]. In construction terminology this is referred to as bonding material. It is used with sand, bricks, building blocks etc. Cement concrete, the most widely used construction material, is a combination of Portland cement and water mixed with a wide range of aggregate materials to form a plastic mass. This mass gets eventually cured and converted into a strong durable material of a desired shape on the job site. Since cement is around 10 times more expensive than the aggregate used, it is desirable to use minimum amount of cement. In standard dense concrete it is necessary to have enough cement paste to fill the voids in the aggregate, but using more cement to concrete has an undesirable effect. Though small, these voids undergo minor changes in volume with moisture content, a factor that can affect the load bearing capability. The paste, composed of Portland cement and water, coats the surface of the fine and coarse aggregates. During hydration (the reaction between unhydrous cement and water) the paste hardens and gains strength to form a rock-like mass known as concrete.

1.2.2 Composition

A properly designed concrete mixture possesses the desired workability when fresh and the required durability and strength when hardened. Typically, a mix is about 10 to 15 percent cement, 60 to 75 percent aggregate and 15 to 20 percent water as shown in Fig. 1.2. Entrained air in many concrete mixes may take up another 5 to 8 percent of the total mix.

Fig.1.2 Typical composition of concrete [13]

(Courtesy: Portland cement Association)

The most critical component in cement concrete is the Portland cement itself. This is so because the cement is the one that forms a paste with water, coats each particle of stone and sand and binds them together. The strength of the paste depends to a great extend on the water to cement ratio (W/C) calculated as –

W/C = weight of water / weight of cement

High-quality concrete is produced by lowering the W/C ratio as far as possible without sacrificing the workability of fresh concrete. Lower proportions of water normally produce high quality concrete if the same is properly placed, consolidated and cured.

Concrete is produced in four basic forms, each with unique applications and properties.

1. Ready mixed concrete, by far the most common form, accounts for nearly three-fourths of all concrete. It is batched at local plants and delivered in the familiar trucks with revolving drums.
2. Precast concrete products are cast in a factory. These products benefit from tight quality control achievable at the production plant. Precast products range from concrete bricks and paving stones to bridge girders, structural components and panels for cladding.

3. Concrete masonry, another type of manufactured concrete, is best known for its conventional 8 x 8 x 16-inch block though it is now fabricated into various shapes and sizes to suit different building applications and architectural needs. The materials in this category include mortar, grout and terrazzo.
4. Soil-cement and roller-compacted concrete are used for pavements and dams.

A new generation of advanced products incorporates fibres and special aggregates to create roofing tiles, shake shingles, lap siding and countertops.

1.2.3 Components

Apart from the basic cement, wide variety materials have been used to prepare cement concrete. The major components of cement concrete are described below.

a. Aggregates

Aggregates which form an essential ingredient of concrete are inert granular materials such as sand, gravel or crushed stone. They account for 60 to 75 percent of the total volume of concrete and are divided into two categories viz. fine and coarse. The former generally consists of natural sand or crushed stone passing through a 9.5-mm sieve. Coarse aggregates are particles greater than 4.75 mm. The particle diameter generally ranges from 9.5 mm to 37.5 mm. Gravels constitute the majority of coarse aggregates used in concrete with crushed stone making up most of the remainder.

Natural gravel and sand are usually dug or dredged from a pit, river, lake or seabed. Crushed aggregate is produced by crushing quarry rock, boulders, cobbles or large-size gravel. Recycled concrete is a viable source of aggregate and has been satisfactorily used in granular sub bases and in new concrete. Aggregate processing consists of crushing, screening and washing the aggregate to obtain proper cleanliness and gradation.

Some characteristics considered when selecting an aggregate include [7]:

1. Grading: This refers to the determination of the particle-size distribution for the aggregate. Grading limits and maximum aggregate size are specified because they affect the amount of aggregate, cement and water required, workability, pumpability and durability of concrete.
2. Shape and size: Particle shape and surface texture influence the properties of freshly mixed concrete more than the properties of hardened concrete [14]. Rough-textured, angular and elongated particles require more water to produce workable concrete than smooth, rounded compact aggregate. Consequently, the cement content must also be increased to maintain the W/C ratio. Generally, flat and elongated particles are avoided or are limited to about 15 percent by weight of the total aggregate.
3. Bulk density: This depends on the particle size distribution and shape of the particles. This gives an idea of the voids between the particles m in concrete. The void content between particles affects the amount of cement paste required for the mix. Angular aggregates increase the void content. Larger sizes of well-graded aggregates and their improved grading can decrease the void content.
4. Absorption and surface moisture of aggregate: These factors are measured while selecting aggregate because the internal structure of aggregate is made up of solid material and voids that may or may not contain water. The amount of water in the concrete mixture must be adjusted to include the moisture conditions of the aggregate.
5. Abrasion and skid resistance: These properties are essential when the aggregate is to be used in concrete that is constantly subject to abrasion as in heavy-duty floors or pavements. Different minerals in the aggregate wear and polish at different rates. Harder aggregates are selected in highly abrasive conditions to minimize wear.

b. Water

This is the most important component of concrete since it participates in the chemical reactions with cement and helps to give strength to the structure [15]. The quality and composition of water is thus a very important factor. Generally, the pH of the water used for mixing should be between 6 and 8 and free from organic matter [7]. Another method to determine the suitability of water for mixing is to compare it with compressive strengths of 7 and 28 days old concrete prepared using distilled water. The water is acceptable if the strengths are up to 90%. This test is usually done in coastal areas or marshy areas where the water is brackish in nature and of doubtful quality.

Carbonates and bicarbonates of sodium and potassium affect the setting time of cement. At higher concentrations these salts reduce the strength of the concrete [16]. Brackish water contains chlorides and sulphates which influence the hydration reaction at higher concentrations [17]. Salts of manganese, tin zinc, copper and lead also cause a reduction in the strength of concrete. Sodium iodate, sodium phosphate and sodium borate reduce the initial strength of concrete [7]. Sodium sulphide is detrimental even at 100ppm. Silts and suspended particles are undesirable since they interfere with the setting, hardening and bond characteristics. Algae in the water used for mixing can also cause a marked reduction in the strength of the concrete [8]. They either combine with cement to reduce the strength of the bond or cause a large amount of air entrainment. Algae present on the surface of the aggregate too have the same effect.

Seawater accelerates the early strength of concrete but is not generally used as it reduces the 28-day strength of the concrete by about 10-15%. It also causes efflorescence and persistent dampness. Even in prestressed concrete work, seawater is avoided as it can cause stress corrosion and undue loss of cross section of small diameter wires used within [19].

c. Sand

These are fine aggregates obtained from riverbanks, sea beds or lakes. Sand has already been dealt with in the section on aggregates (1.2.3. a.).

d. Portland cement

This is dealt in detail in Section 1.1.

1.3 Cement concrete durability

Concrete is a versatile and widely used construction material. Its record of durability is remarkable when one considers the variety of severe exposures it is subjected to [20, 21]. There are, however, phenomena that can produce considerable damage if well-known precautions are not taken. The service conditions of concrete structures have altered in past two decades due to the advent of industrialization. This has led to early deterioration due to corrosion of embedded reinforcement and spalling of concrete cover exposing the reinforcement bars to further corrosion resulting in structural instability of the concrete structures [22, 23]. The quality of the hardened cement is more important than the choice of aggregate in determining the durability of concrete under aggressive or severe environmental conditions. When the paste is dense and occupies all possible voids around the aggregate, water enters the interstices very slowly if at all. This helps in achieving durability since both cement and aggregate will thus be protected from contact with chemical agents in the environment.

Durability is defined as the ability of the cement concrete to resist weathering action, chemical attack, abrasion or any other process of deterioration. Causes for deterioration of a concrete structure may be physical, mechanical or chemical. Mechanical damage is caused by impact, abrasion, erosion or cavitation [24-26] and physical causes include the effects of high temperature or of the differences in thermal expansion of aggregate and of the hardened cement paste. External chemical attack takes place through the action of aggressive ions such as chlorides, sulphates or of carbon dioxide, as well as many natural or industrial liquids [27] and gases [28]. Most processes that can cause deterioration in concrete produce an ultimate excessive expansion resulting in cracking. This is true of sulphate attack and alkali-aggregate reaction. The causes of concrete damage can be both physical and chemical in nature. Some of the main factors causing deterioration are carbonation, alkali-aggregate reactions and attacks by sulphates, de-icing salts and other chemicals.

The following sections discuss various agents which attack cement concrete.

1.3.1 Frost

The critical factor in frost damage, as in most potentially destructive processes involving concrete, is the moisture condition of the material [29]. The concrete elements subjected to continuous or frequent wetting are susceptible to damage by freeze-thaw cycling. In recent years the frost damage problem has been aggravated by the wide use of de-icing salts. The severest exposures are horizontal areas or any surfaces on or near ground level subjected to both freeze-thaw cycling and de-icing salts while wet.

The maximum resistance to freeze –thaw damage depends upon the size and distribution of pores and capillaries and the degree of saturation in hardened cement paste [30]. During the hydration of the cement the products formed are greater in volume than initial cement grains. Therefore, the voids in the cement matrix are reduced. When the W/C ratio is too high the water left after the hydration reaction is adsorbed on the surface of the voids and this water converts to ice at very low temperature. Since the total surface area in matured cement paste is very high, the proportion of such water is quite large.

In cold countries, sea water exposures are severe because of the combination of freezing conditions and high moisture content at and near the waterline. Durability requires high density air- entrainment and low porosity. In hydraulic structures those sections that are subject to freezing and thawing require similar precautions. Air entraining agents and certain light weight aggregate concretes are usually used for high resistance to frost action and even to de-icing salts [31].

1.3.2 Corrosion

Corrosion in concrete structures can originate from metal reinforcements [32]. These metals can be grouped into four general categories:

a. Those used on exterior as cladding, roofing and flashings,

b. Those incorporated in construction as structural and reinforcing steel, masonry etc.

c. Those used in the services to a building such as piping, storage tanks for hot water, drains and heating ducts,

d. Those buried in the ground.

Corrosion refers to any process involving the deterioration or degradation of metal components. In building structures, the corrosion is due to a single metal with water containing some salts in the solution. Corrosion takes place in the presence of pure water also. The other agents that promote the corrosion reaction are certain bacteria, which are capable of removing hydrogen and act as depolarizing agents.

Metals used in the exterior of buildings are frequently exposed to atmospheric conditions though they may be modified by adequate design. The principal atmospheric factors affecting the corrosion of metals are temperature, extent of pollution by sulphur dioxide and chlorides and the length of time during which metal remains wet by water. Some design features could be modified to protect the metal from normal corrosion. Traps and recesses in roofs, gutters and spouts that collect and store water for long periods should be avoided since corrosion will proceed as long as the metal is wet. This is significant in case of bridges, towers and other exposed structures made of metal.

1.3.3 Sulphate attack

Sulphates present in soil, groundwater, seawater, decaying organic matter and industrial effluent surrounding a concrete structure pose a major threat to the long-term durability of the concrete [33]. Sulphate attack of concrete may lead to cracking, spalling, increased permeability and loss of strength. Essentially, two forms of sulphate attacks are known to exist:

1. Reaction of sulphates with alumina-bearing hydration products and/or unhydrated tricalcium aluminate (C_3A) to produce ettringite and
2. Reaction with calcium hydroxide to produce gypsum.

In hardened concrete, the formation of ettringite by sulphate attack can, though not always, result in expansion. Because of the concrete's low tensile strength, expansive strains resulting from ettringite formation during a sulphate attack can lead to cracking and reduced performance. To limit the ettringite form of sulphate attack, cements low in C_3A, such as ASTM Type II or Type V Portland cement, are recommended [34].

1.3.4 Seawater attack

In marine environments, the penetration of water, chloride and other aggressive ions into concrete is the most important factor in the physical and chemical process of deterioration. It is the microstructure of concrete that mainly controls the physical/chemical phenomena associated with water movements and the transport of ions in concrete. Chlorides from seawater penetrate the concrete, reach the reinforcement and after a certain time, when the chloride content exceeds a critical level (i.e. the chloride threshold level), corrosion is initiated. However, there are some other requirements that also must be fulfilled to achieve an ongoing corrosion process, e.g. sufficient supply of oxygen, to enable the oxidation and presence of electrolyte to enable formation of an electrical circuit.

The concomitant presence of sulphate and chloride ions in marine environments causes deterioration of reinforced concrete structures and reinforcement corrosion [17]. The reaction of the concrete with the sulphate ions in marine environments is similar to that of sulphate ions in non-marine environments, but the effects are different due to the presence of chloride ions in the former [35,36]. The effect of the conjoint presence of chlorides and sulphates on the sulphate resistance of hydrated Portland cements is inconclusive and highly debated. The sulphate attack in marine environment gives rise to expansive ettringite, gypsum and brucite and sometimes is associated with calcite formation [37-39].

The sulphate resistance of concrete structures in marine environments can be improved by using sulphate-resisting construction materials and by controlling sulphate permeation into concrete. Some of the methods available to prevent sulphate attack are by using sulphate-resisting construction materials such as Type II and Type V cement and introducing Pozzolana such as fly ash, blast furnace slag in concrete [40-43]. Typically, Type I cement contains between 8% and 12% C_3A, as defined by ASTM C 150, whereas Type II cement contains less than 8% C_3A and Type V cement less than 5% C_3A. The sulphate permeation may be controlled by increasing compactness, low W/C ratio, appropriately designed and constructed joints, proper curing, surface treatment and use of precast concrete in place of cast-in-situ concrete [44-46].

1.4 Admixtures of cement concrete

Chemical admixtures are the ingredients in concrete other than Portland cement, water and aggregates added to the mix immediately before or during mixing. Producers use admixtures for the following reasons:

a. to reduce the cost of concrete construction;

b. to modify the properties of hardened concrete;

c. to ensure the quality of concrete during mixing, transporting, placing and curing; and

d. to overcome certain emergencies during concrete operations. Admixtures are classified according to the function they perform. There are five distinct classes of chemical admixtures [47]

   (i) air-entraining,
   (ii) water-reducing,
   (iii) retarding, accelerating and
   (iv) plasticizers (superplasticizers)
   (v) all other varieties of admixtures fall into the specialty category whose functions include corrosion inhibition, shrinkage reduction, alkali-silica reactivity reduction, workability enhancement, bonding, damp proofing and colouring.

1.4.1 Water reducing agents

These admixtures produce a concrete of given workability at lower W/C ratio than that of a control concrete containing no admixture [48]. These help in producing a concrete of similar workability and strength development with lower water content without adversely affecting the durability or engineering properties of the concrete.

Some of the water reducing admixtures which also serve other functions is:

a. Accelerating water-reducing admixtures: These not only help in reducing the water but also give higher strengths during the initial stages of hydration. This is very useful at lower temperatures; eg. calcium chloride or calcium formate with lignosulphates.

b. Retarding water-reducing mixtures: These help in extending the period of time when the concrete is in the workable state. This is useful during the transportation, handling and placing of the concrete; eg. hydroxylated polymers like corn starch.

c. Air entraining water reducing agents: These possess the ability to entrain microscopic air bubbles into the cement paste and also reduce the W/C ratio; eg. sodium dodecyl benzene sulphonate.

d. Superplasticizers: These are formulated from materials which allow much greater additions to be made (up to 10 times more than normal water reducing admixtures) to the concrete mix without producing adverse side effects such as air entrainment and excessive retardation; eg. salts of naphathalene formaldehyde sulphonate acids.

Though a variety of admixtures are available only five of the following chemicals form the basis of all water reducing admixtures,

(i) lignosulphonate [49-51],

(ii) hydroxy carboxylic acid,

(iii) hydroxylated polymers,

(iv) formaldehyde naphthalene sulphonate [52] and

(v) formaldehyde melamine sulphonate salts.

1.4.2 Air entraining agents

These are organic materials usually in solution form, which when added entrain a controlled quantity of air in uniformly dispersed microscopic bubbles. The bubbles act as ball bearings and modify the properties of fresh concrete namely workability, segregation and finished quality. Air entraining agents influence the following properties:

a. Durability: These agents help to withstand the effects of freeze-thaw conditions and presence of de-icing agents especially on roads that are exposed to low temperature [53].

b. Cohesion: Concretes that are produced using fine aggregates exhibit a tendency to bleed and segregate. The presence of a small amount of entrained air (2-4% by volume) leads to an improvement in cohesion or mix stability.

c. Density: These admixtures are used to enhance the thermal insulation properties and also to produce lightweight concrete with lightweight aggregates.

The side effects to be considered while using air entraining agents are

(i) Reduction in the water to cement ratio since the air bubbles act as "lubricants",

(ii) Decrease in the compressive and tensile strengths with increasing air content and

(iii) Increase in the yield of the concrete for a given weight of mix ingredients.

Some of the raw materials used as air entraining agents are abietic and pimeric acid salts, fatty acid salts, alkyl-aryl sulphonates, alkyl suphates and phenol ethoxylates.

Air entraining admixtures produce concrete which is more durable in conditions of freezing and thawing especially in the presence of de-icing salts. Such concrete is also more resistant to sulphate attack, provides better protection to embedded reinforcement [54] and is more tolerant to poor curing conditions. Further, there appears to be no change in the development of compressive strength [55] and volume deformations [56, 57].

1.4.3 Accelerators and retarders

Concrete accelerators increase the rate of hardening of cement and concrete mixes. The major material used is calcium chloride and is mainly employed in cold weather [58]. It is effective in maintaining satisfactory gain in strength of the concrete above and below freezing temperatures. In normal dosages of 1 to 2 per cent by weight of the cement, calcium chloride shortens the time of set of fresh concrete and increases the rate of strength-gain. In practice, a decrease in time of set is required for early finishing of floors or quick-setting in spray-type processes. As an accelerator of strength-gain calcium chloride can provide for early application of load.

Unfortunately, calcium chloride has a number of side effects that are generally detrimental. These effects are not substantial and can often be overcome. They are associated mainly with corrosion of reinforcing steel, drying shrinkage [59], creep [60], heat evolution and resistance to sulphate attack. Triethanolamine, an organic accelerator is used in formulations to compensate for set-retarding properties of other admixtures. In this connection it is used with some air-entraining and water-reducing admixtures.

Premature stiffening and hardening can create difficulties in discharging, placing and compacting fresh concrete. Set-retarding admixtures are now used extensively in such situations, particularly in ready-mix concrete where long hauls in hot weather are involved. They extend the plastic period without significantly affecting subsequent strength gain.

A set-retarder [61] may be useful in preventing unsightly "construction joints" by ensuring that the concrete in one "lift" remains plastic long enough for the next lift to be intermixed with it. It may help to reduce maximum temperatures by extending the time over which the heat of reaction within the concrete mass is given off. It also finds use in grouts, pumped concrete and other processes. Set-retarders used are derived mainly from two sources - salts of lignosulphonic and hydroxy carboxylic acids. Other retarders used are detergents, sugars and more recently, silicones. Dosages range from 0.2 to 1 per cent by weight of the cement. Over dosages are be an obvious hazard.

1.4.4 Plasticizers

Plasticizers are water-reducing admixtures which increase the workability of plastic or fresh concrete and allow it to be placed more easily, with less consolidating effort. Organic substances or combinations of organic and inorganic substances, which give a higher workability with the same or lower water content, are termed as plasticizing admixtures. Most of the plasticizers are surfactants and are classified as [7]:

a. Anionic surfactants such as lignosulphonates and derivatives

b. Non ionic surfactants such as polyglycol esters, acid of hydroxylated carboxylic acids and derivatives

c. Others such as carbohydrates etc.

Plasticizers are used in the amount of 0.1% to 0.4% by weight of cement. Superplasticizers or high-range water-reducing admixtures are also a class of plasticizers, used to significantly increase workability but are more powerful as dispersing agents. These produce a homogenous, cohesive concrete without segregation and bleeding. They are used for the production of flowing, self leveling self compacting, high strength and high performance concretes. This improves the strength and durability characteristics. Some of the superplasticisers used are sulphonated melamine formaldehyde condensates and modified lignosulphonates.

1.4.5 Other chemical admixtures

Some of the other admixtures include -

- Damp-proofing and waterproofing admixtures intended to reduce water penetration of the larger pores in concrete. They include soaps, butyl stearate, mineral oil and asphalt emulsions.
- Corrosion-inhibiting admixtures sparingly used in the precast industry. Examples are sodium benzoate, stannous and ferric chlorides and

sodium nitrite. These are used mainly in the case of corrosion caused by the addition of calcium chloride as accelerator.

- Modified mortars made with bonding admixtures such as polyvinyl chlorides and acetate, acrylics and butadiene-styrene co-polymers used in bonding the old concrete to the new one.

1.5 Polymers

This section deals with the classification and properties of polymers.

1.5.1 Introduction

About 30% of all polymers produced each year are used in the civil engineering and building industries. Polymers offer many advantages over conventional materials including lightness, resilience to corrosion and ease of processing [62]. They can be combined with fibres to form composites which have enhanced properties, enabling them to be used as structural members and units and their properties are very different from those of traditional ones such as concrete and metal.

The term *polymer* originates from Greek words *poly* and *mer* meaning many parts. These materials contain long molecular chains, made from many units of monomers [63] as shown in Fig. 1.3. Polymers made of a single type of monomer are called homopolymers while those made of different monomers constitute a copolymer. In the latter, the ratio and configuration of the individual monomers influence its properties. The important parameters influencing the properties of polymers are the rate of polymerisation, the length of polymer chains, crystallinity and crosslinking and presence of additives.

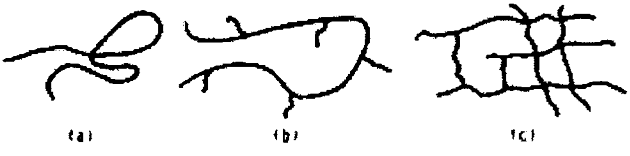


Fig.1.3. Schematic Representation of Polymer Molecules:
(a) Linear (b) Branched (c) Cross-linked

When heat is applied to a polymer having linear or branched molecules, the material softens at a certain temperature and then starts to flow as the molecules are free to slide over one another. Polymers having highly cross-linked molecules do not soften with heat or show any significant flow because the individual chain segments are chemically attached to each other and form a rigid structure. As organic materials, polymers decompose with excessive heat, producing smoke and leaving charred residues.

Two important characteristic temperatures associated with polymers are glass-transition temperature (Tg) and melt temperature (Tm). The glass-transition temperature is the temperature below which a polymer has properties of an inorganic glass, including hardness, stiffness and transparency. Above this temperature the material has plastic or elastic properties and is in a rubbery state. The position of the glass-transition temperature with respect to room temperature will determine the type of application or the usefulness of the polymeric material. For example, polymers such as polystyrene and poly(methyl methacrylate), with glass-transition well above room temperature (100 and 110°C, respectively), are normally used in the glassy state as plastics. Polymers having glass-transitions below room temperature, for example, polyisoprene (-83°C) and polyisobutylene (-65°C), are used in rubbers. The melt temperature (Tm) is also called flow temperature for amorphous polymers and crystalline melting point for crystalline polymers. At the melt temperature (usually a range) solid elements of the polymers are in equilibrium with the molten state and thus the polymer mass is practically a viscous liquid. Highly cross-linked polymers have neither glass-transition nor melting temperature.

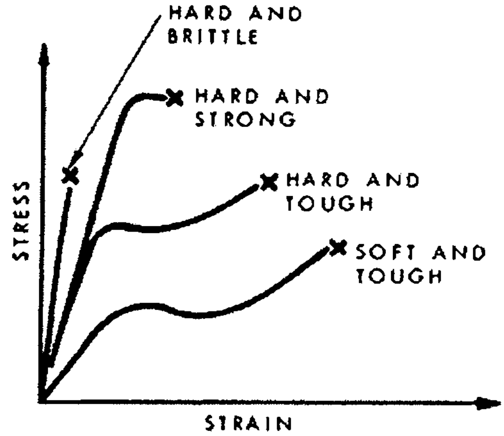
1.5.2 Properties and behaviour of polymers

The properties of polymers are very different from conventional materials used for construction such as metals and concrete. This may be attributed to their structure and high molecular weight. Some properties of polymers may be summarized thus:

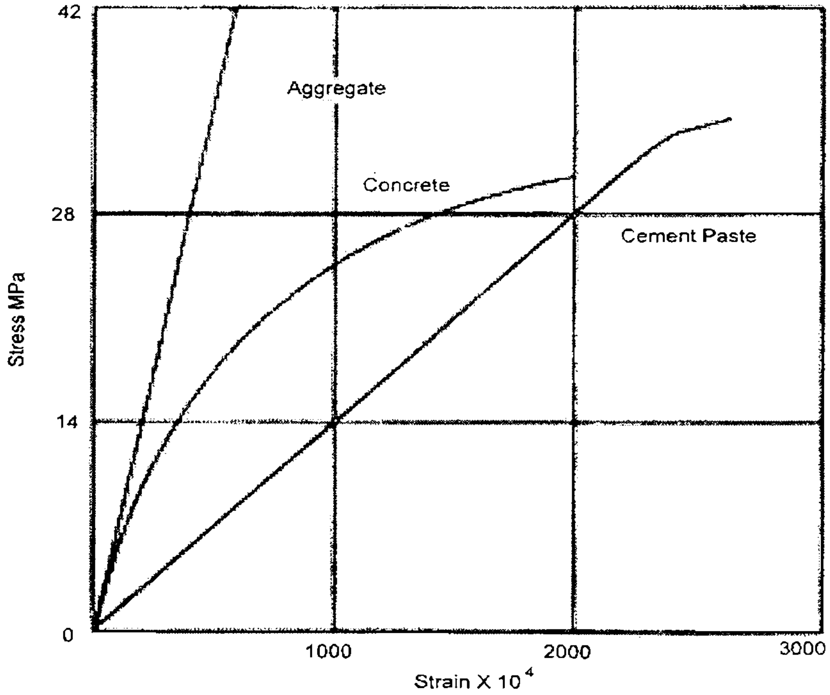
a. They have a lower density than metals which is an attribute useful in applications where reduction in weight is important. Polymers and plastics generally have densities in the range 0.83 to 2.5 g/cm^3, although some, such as foamed plastics, have densities as low as 0.01 g/cm^3 and filled plastics have densities as high as 3.5 g/cm^3.

b. Most of them are transparent, some translucent and a few are opaque. This mostly depends on the degree of crystallinity in the polymer and the compounding ingredients added to them. Some virgin polymers like PMMA when free from impurities are isotropic to visible light and have high clarity approaching that of glass. Fillers are incorporated in polymers to make them translucent or opaque.

c. Polymers have good mechanical properties such as low modulii and high strength to weight ratios compared to metals as depicted in Fig. 1.4 and 1.5. The deformation behaviour depends not only on the magnitude of stress applied but also the period of time for which it is applied. The properties of the polymer depend mainly on temperature and the rate of application of stress. Polymers exhibit viscoelastic behaviour i.e. the deformational response of amorphous polymeric materials to non-destructive (relatively small) stresses.



(a)



(b)

Fig. 1.4 Tensile stress-strain curves for (a) Four types of polymeric material. (b) Concrete, cement paste and aggregates

Table 1.5 Tensile properties of polymers [64]

Material	Density (kg/m^3)	Tensile strength (GN/m^2)	Flexural modulus (GN/m^2)	% elongation at break
ABS (high impact)	1040	38	2.2	8
Acetal (homopolymer)	1420	68	2.8	40
Acetal (copolymer)	1410	70	2.6	65
Acrlic	1180	70	2.9	2
Cellulose acetate	1280	30	1.7	30
CAB	1190	25	1.3	60
Epoxy	1200	70	3.0	3
Modified PPO	1060	45	2.3	70
Nylon 66	1140	70	2.8	60
PEEK	1300	62	3.8	4
PET	1360	75	3	70
Phenolic (mineral filled)	1690	55	8	0.8
Polyamide-imide	1400	185	4.5	12
Polycarbonate	1150	65	2.8	100
Polyetherimide	1270	105	3.3	60
Polyethersulphone	1370	84	2.6	60
Polyimide	1420	72	2.5	8
Polypropylene	905	33	1.5	150
Polysulphone	1240	70	2.6	80
Polystyrene	1050	40	3.0	1.5
Polythene (LD)	920	10	0.2	400
Polythene (HD)	950	32	1.2	150
PTFE	2100	25	0.5	200
PVC (rigid)	1400	50	3.0	80
PVC (flexible)	1300	14	0.007	300
SAN	1080	72	3.6	2
DMC (polyester)	1800	40	9	2
SMC (polyester)	1800	70	11	3

d. Impact strength is a measure of toughness or resistance to breakage under high velocity impact conditions. Polymeric materials are either brittle or tough, depending on the temperature and the rate of impact, i.e., rate of deformation. Impact strength of polymers and derived plastics depends upon the position of the glass transition temperature (Tg) with respect to room temperature and ease of crystallization. Far below the glass-transition, amorphous polymers break with a brittle fracture, but they become tougher as the service temperature approaches Tg. Above Tg, amorphous polymers are in a rubbery state so that the term impact ceases to have any significance.

e. Polymers, generally, have lower thermal resistance than metals especially in the presence of oxygen. Among the common polymers, poly tetrafluoroethylene has the highest thermal stablility due to the presence of strong C—C and C—F bonds. Thermoplastic polymers are those which when heated through a range of temperature change from rigid solids to highly viscous liquids as shown in Fig. 1.5. Thermosetting polymers on the contrary, do not soften but undergo contraction and charring at high temperatures.

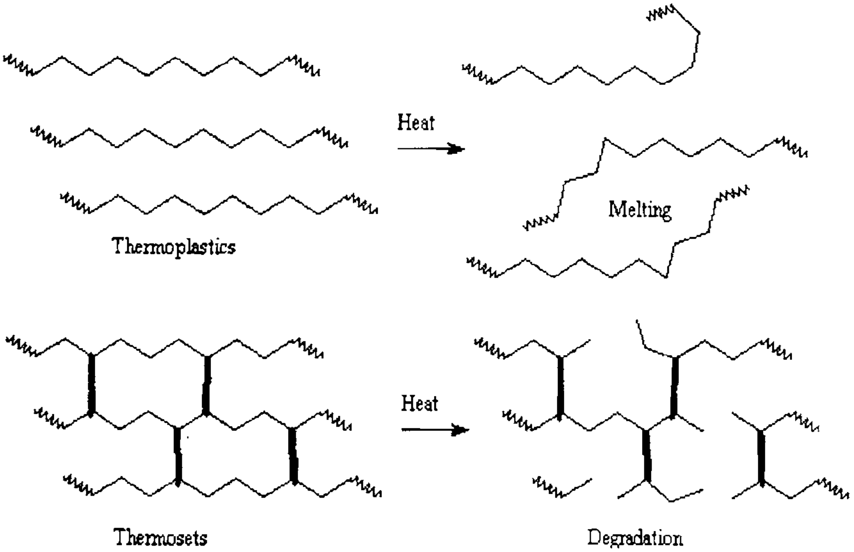


Fig.1.5. Thermal behaviour of polymers

Plastics have coefficients of thermal expansion considerably higher than those of common metals (1.0 to 2.5 x 10^{-5}/°C). The thermal properties of some polymers are given in Table 1.6.

Table 1.6 Thermal characteristics of polymers [64]

Material	Density (kg/m^3)	Thermal conductivity (W/m/K)	Glass transition temperature Tg (°C)	Max. service temperature (°C)
ABS	1040	0.25	115	70
Acetal (homopolymer)	1420	0.2	-85	85
Acetal (copolymer)	1410	0.2	-85	90
Acrylic	1180	0.2	105	50
Cellulose acetate	1280	0.15	--	60
CAB	1190	0.14	--	60
Epoxy	1200	0.23	--	130
Modified PPO	1060	0.22	--	120
Nylon 66	1140	0.24	56	90
PEEK	1300	--	143	204
PET	1360	0.2	75	110
Phenolic (glass filled)	1700	0.5	--	185
Polyamide-imide	1400	0.25	260	210
Polycarbonate	1150	0.2	149	125
Polyester	1200	0.2	--	--
Polyetherimide	1270	0.22	200	170
Polyethersulphone	1370	1.18	230	180
Polyimide	1420	---	400	260
Polyphenylene sulphide	1340	---	85	150
Polypropylene	905	0.2	-10	100
Polysulphone	1240	--	180	170
Polystyrene	1050	0.15	100	50
Polythene (LD)	920	0.24	-120	50
Polythene (HD)	950	0.25	-120	55
PTFE	2100	0.25	-113	250
PVC (rigid)	1400	0.16	80	50
PVC (flexible)	1300	0.14	80	50
SAN	1080	0.17	115	60
DMC (polyester)	1800	0.2	--	130
SMC (polyester)	1800	0.2	--	130
Polystyrene foam	32	0.032	--	--
PU foam	32	0.032	--	--

Halogen containing polymers such as PTFE, PVC and chlorinated PVC are flame retardant since they liberate halogens that inhibit the free radical oxidation chain reaction. Special additives are generally added to polymers to make them fire resistant.

f. Though the chemical resistance of the polymers depends on the nature and formulation of the polymer they are generally resistant to weak acids, alkalis and water. Some polymers like polyesters and polyamides hydrolyse in the presence of acid and alkali. Organic solvents such as toluene and benzene affect plastics and strong acids and sometimes cause discolouration and embrittlement. Weathering resistance depends on the polymer and compounding ingredients added to them.

1.5.3 Classification of polymers

Based on the properties of the polymers, they are classified into rubbers, thermoplastics and thermosets.

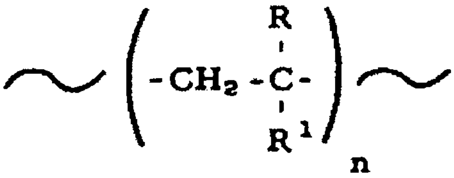
a. Thermoplastics [65]

Thermoplastics constitute an important class of synthetic material used increasingly in a variety of applications. For example, in building and construction they perform various functions as light structural and decorative components or as auxiliaries to other materials and components.

Thermoplastics are linear or highly branched polymers which become plastic on heating and under load. These can be easily processed under heat and pressure and can be remoulded if reheated. Therefore, these materials can be recycled. During heating the thermal energy in the molecule increases with the Brownian motion and the intermolecular bonds are overcome. The intermolecular bonds are very few as in the case of small polymer chains and polymers with small side groups and little or no crosslinking. The crystallinity of the polymer depends on the arrangement of polymer chains in the molecule.

(i) Polyethylene plastics

The major families of commercially available thermoplastics are polyethylene, polypropylene, poly (vinyl chloride), polystyrene, acrylics, nylons and cellulosics. With the exception of nylons and cellulosics, the principal member of each family is based on polymers that have an entirely carbon-carbon backbone chain. This can be represented by the general formula of Fig. 1.6; groups designated R and R^1 are given in Table 1.7. Nylons and cellulosics are based on polymers that also have atoms other than carbon in the main chain.



$$\sim\left(-CH_2-\overset{R}{\underset{R^1}{C}}-\right)_n\sim$$

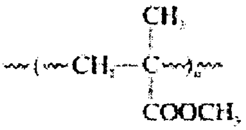
Fig.1.6 General formula of thermoplastic polymers having a C-C backbone chain

Table 1.7 Thermoplastic polymers with a C-C backbone chain

R	R^1	Name of Polymer	Abbreviation
H	H	Polyethylene	PE
H	CH_3	Polypropylene	PP
H	Cl	Poly(vinyl chloride)	PVC
H	OH	Poly(vinyl alcohol)	PVAL
H	C_6H_5	Polystyrene	PS
H	COOCH	Poly(methyl acrylate)	PMA
CH	COOCH	Poly(methyl methacrylate)	PMMA
H	$COOCH_3$	Poly(vinyl acetate)	PVAC

(ii) Acrylic Plastics

This family of plastics includes a range of polyacrylates, poly(methyl methacrylate) (PMMA) (Fig.1.7) and the important fibre-forming polymer, polyacrylonitrile. The most important acrylic plastics are based on PMMA, which is amorphous. Outstanding properties of PMMA are optical clarity, lack of colour and unusually good resistance to outdoor weathering. The three basic types available are cast sheet (used in glazing), standard moulding powder (used for making lenses and dials) and high-impact powder, which gives less transparency but will take higher shock loads.



$$\sim(\sim CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\sim)_n\sim$$

Fig.1.7 Structure of PMMA

(iii) Nylons

Nylons are formed from reactions between molecules possessing amino (-NH_2) and carboxylic acid (-COOH) groups. They have nitrogen atoms in their backbone chain (Fig.1.8). Nylons are characterized by high strength, outstanding toughness, wear-resistance, good chemical resistance and very low coefficient of friction. Parts made from nylon, however, have poor dimensional stability owing to moisture sensitivity and because they undergo cold flow. Nylons were first used in the form of fibre and films, but recent improvements in materials and processing techniques have made them suitable for various light engineering applications for gears, bearings, bushes, cams and other mechanical parts, in rollers and tracks for cabinets, domestic appliance housings, slides, wire coverings and car components.

$$\sim\sim NH-(CH_2)_x-CO-NH-(CH_2)_y-CO \sim\sim$$

Fig.1.8 Structure of polyamide molecule

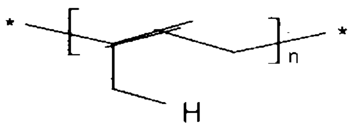
(iv) Cellulosics

These plastics are produced by chemical modification of cellulose, a natural polymer found in wood, cotton, etc. The best known plastic of this class is cellulose acetate. Its outstanding properties are toughness, high impact strength, electrical properties and light weight. Its greatest disadvantages are low heat distortion temperature and high water absorption characteristics. Cellulose acetate is used to make tool handles, housings, toys, light fixtures, shades and in protective coatings and lacquers for wood and metals.

b. Important elastomers or rubbers

The term elastomer is often used interchangeably with the term rubber and is preferred when referring to vulcanisates. Elastomer comes from two terms, *elastic* (describing the ability of a material to return to its original shape when a load is removed) and *mer*. They are amorphous polymers existing above their glass transition temperature, so that segmental motion is possible. At ambient temperatures rubbers are thus relatively soft (E~3MPa) and deformable. On application of an external force the chains uncoil and slip past each other but regain the original shape and dimensions after the force is removed. The important types of elastomers are given below.

i. Unsaturated rubbers: These are mostly general purpose rubbers and are vulcanised using sulphur as crosslinking agent. They are generally employed in the manufacture of tires and hoses. Natural rubber and butyl rubber have isoprene monomer units in addition to the isobutylene units in case of butyl rubber. The isoprene units in the butyl rubber facilitate the vulcanisation of the ubber with sulphur. The stereo-regularity makes it possible for butyl rubber to crystallise on stretching resulting in very high gum strength.



1. Natural Rubber (NR) (Fig.1.9): Most important commercial source of natural rubber is the tree *Hevea brasiliensis.* Natural rubber is essentially a polymer of isoprene units, a hydrocarbon diene monomer and monomer units are arranged in cis arrangement and it is this spatial configuration that gives rubber its highly elastic character.

2. Polyisoprene (IR): Butyl rubber (copolymer of isobutylene and isoprene, IIR)

   Halogenated butyl rubbers (Chloro Butyl Rubber CIIR; Bromo Butyl Rubber BIIR)

3. Polybutadiene (BR): These rubbers have butadiene units as the backbone unit as in Fig.1.10 with acrylonitrile (in Nitrile rubber) and styrene (in SBR) as co monomers). These are also vulcanised using sulphur as crosslinking agents.

Fig.1.10. Structure of butadiene repeating unit

Some of the important rubbers in this category are given below.

I. Styrene-butadiene Rubber (copolymer of polystyrene and polybutadiene, SBR) R= styrene. These are general purpose rubbers and used in tyres.

II. Nitrile Rubber (copolymer of polybutadiene and acrylonitrile, NBR), also called buna N rubbers. R= acrylonitrile. Nitrile rubber is highly oil resistant than other rubbers and is mostly employed in the manufacture of oil hoses and seals.Hydrated Nitrile Rubbers (HNBR) Therban® and Zetpol® .

III. Chloroprene Rubber (CR), polychloroprene, Neoprene, R= Cl.

ii) Saturated rubbers: Most of these rubbers are special purpose rubbers due to their unique properties. These contain no unsaturation in their repeat unit and therefore cannot be vulcanised by sulphur. The crosslinking agents used for vulcanisation are zinc oxide in case of polysulphide rubbers, peroxides for silicone rubbers, diisocynates for polyurethanes and carbamate of hexamethylene diamine for halogen rubbers. The main rubbers in this category are:

1) EPM (ethylene propylene rubber, a copolymer of polyethylene and polypropylene) (Fig. 1.11) and EPDM rubber (ethylene propylene diene rubber, a terpolymer of polyethylene, polypropylene and a diene-component)

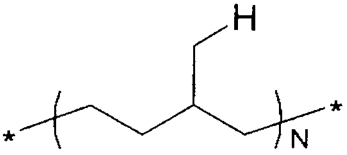


Fig.1.11. Structure of EPM rubber

2) Epichlorohydrin rubber (ECO)

3) Polyacrylic rubber (ACM, ABR)

4) Silicone rubber (SI, Q, VMQ) (Fig. 1.12) - Silicone rubber is a polymer that has a "backbone" of silicon-oxygen linkages, the same bond that is found in quartz, glass and sand. Silicone rubber offers excellent resistance to extreme temperatures, being able to operate normally from -127°C to +300°C. In such conditions the tensile strength, elongation, tear strength and compression set can be far superior to conventional rubbers.

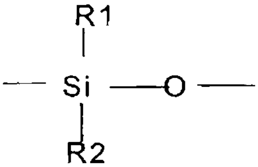


Fig.1.12. Structure of Silicone rubber

5) Fluorosilicone Rubber (FVMQ)
6) Fluoroelastomers (FKM, FPM)
7) Perfluoroelastomers (FFKM)
8) Tetrafluoro ethylene/propylene rubbers (FEPM)
9) Chlorosulfonated Polyethylene (CSM), (Hypalon®)
10) Ethylene-vinyl acetate (EVA)

iii) Various other types of elastomers: Thermoplastic elastomers are a unique class of polymers in which end use properties of vulcanised elastomers are combined with processing advantages of thermoplastics. E.g. thermoplastic elastomers (TPE), (Hytrel), Thermoplastic Vulcanizates (TPV) (Santoprene), Polyurethane rubber, Polysulfide rubber.

c. Thermosetting polymers

Thermosetting polymers are ones that initially flow on heating and then become crosslinked to form a hard, infusible product. They are cured or crosslinked by catalysts, heat or radiation. They form permanent crosslinks between the polymer chains and form dense and rigid three-dimensional networks. This dense network makes them hard and contributes to the strength at high temperature and resistance to chemicals. These polymers are used in a variety of applications, including construction, where they are generally preferred because of their greater strength and higher resistance to *creep*. Thermosetting materials do not dissolve and only swell if they interact with solvents.

Thermosets include epoxies, unsaturated polyesters, phenolics, amino resins (urea- and melamine-formaldehyde), polyurethanes (used in foams and coatings), allyls and furane resins and alkyds.

(i) Epoxy resins (Fig. 1.13): These are the reaction products of bis phenol A and epichlorohydrin.

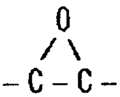
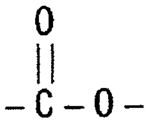


Fig.1.13. Repeating unit of epoxy resins

This is one of the thermosetting resins widely used in the fields of surface coatings adhesives, encapsulation of electronic components, road surfacing and floorings. These are chemically resistant and can be blended with other resins such as alkyds, phenolics and amino-resins. They are highly resistant to wear and have low shrinkage on cure and low creep.

Epoxy glass-fibre-reinforced materials are mainly used in printed electrical circuits and in wing and fuselage structural members of jet aircrafts where they must maintain their strength over a wide range of temperatures. Other structures fabricated from reinforced epoxy thermosets are pipes, tanks, pressure vessels and tooling jigs and fixtures. Epoxy resins are used in a number of heavy-duty applications in civil construction; for wear-resistant terrazzo, industrial flooring and for filling potholes and repairing cracks on highways and bridges.

(ii) Unsaturated polyesters: These resins are important as laminating resins, moulding compositions, fibres, foams, films and surface coating materials. They contain a number of ester linkages in the main chain (Fig. 1.14).



$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-$$

Fig.1.14. Repeating unit of unsaturated polyester resins

Polyester resins, available as very highly viscous liquid to brittle solid are crosslinked via an addition mechanism across the double bonds in the polyesters and the reactive diluent. They have good dimensional stability and good physical and electrical properties. In building construction, corrugated and flat sheets made from glass-fibre-reinforced polyester (GRP) are used for roofs, awnings, skylight domes, partitions, wall siding, decorative fixtures, fences, bathroom accessories and surfacing of concrete floors.

(iii) Phenolic resins: These are normally used as insulators and for heat resistant applications. They are condensation products of phenolic compounds such as phenol, m-cresol, resorcinol and formaldehyde. These are produced as novolacs and resols depending on the catalyst used and the ratio of the phenolic compound and the formaldehyde (Fig. 1.15).

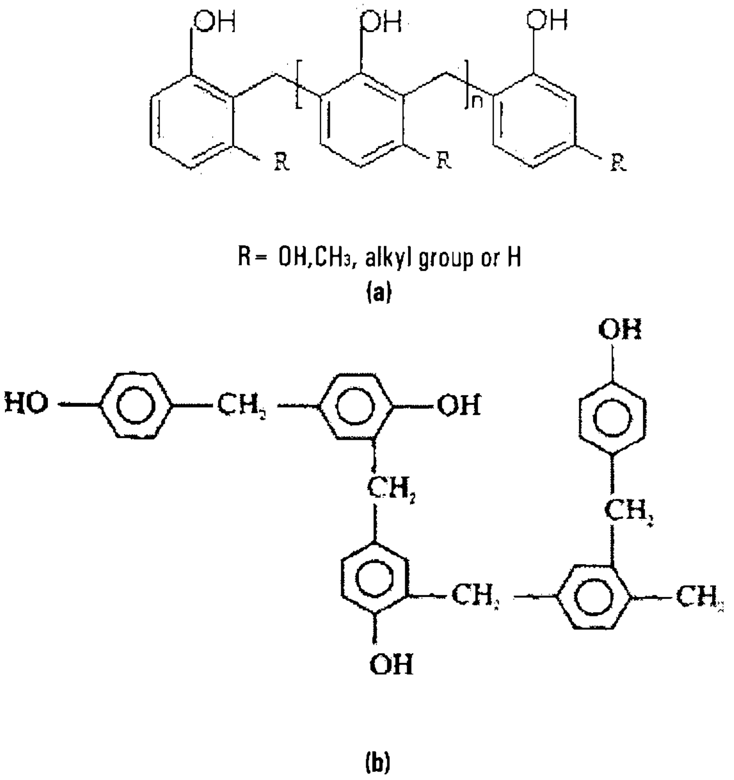


Fig.1.15. Repeating unit of phenolic resins (a) resols (b) novolacs

There may be different side groups (indicated as R in Fig.1.15 (a)) in the meta position of the phenolic molecule. In the case of phenol the side group is H, CH_3 for m-cresol and OH for resorcinol.

The general-purpose grades of these resins are usually filled with wood flour and other low-priced fillers to reduce cost and provide a balance of good insulation and strength. Heat-resistant phenolic compounds contain mineral fillers such as diatomaceous earth, mica and asbestos and can withstand temperatures up to 260°C (500°F) without impairment of the finish or physical properties. Typical applications include handles of kitchen utensils, parts for appliances and ovens and electrical switch gear. Impact-resistant compounds contain fibrous reinforcing materials such as cotton, glass and special grades of asbestos. A number of industrial applications, including heat setting adhesives, abrasive wheels and sandpaper, are possible owing to their good adhesive properties and bonding strength. Phenolics are also used in varnishes and protective coatings.

(iv) Amino resins: Melamine formaldehyde and urea formaldehyde resins fall under this category and are called so because they are produced by the reaction of amines or compounds bearing the amino group ($-NH_2$), with formaldehyde.

- Urea formaldehyde resin (Fig. 1.16)

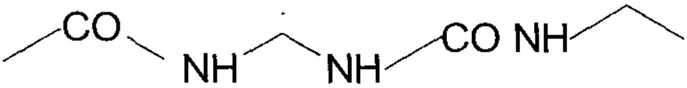


Fig.1.16. Repeating unit of UF resins

- Melamine formaldehyde resin (Fig. 1.17)

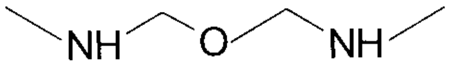


Fig.1.17. Repeating unit of MF resins

Amino resins are clear and colourless, a distinct advantage over the phenolics. They also have better hardness than phenolics, but their impact strength and moisture resistance are lower. Ureas have lower hardness, heat resistance and moisture resistance than melamines.

Amino resins are used in the fabrication of industrial and decorative laminates, adhesives, protective coatings, paper manufacture and moulding compounds. Since these resins are colourless to light coloured their products can be made in many colours.

(v) Alkyd resins (Fig. 1.18): These resins are made by reacting polyhydric alcohol usually glycerol and polybasic acid, usually phthalic acid and fatty acids of various oils such as linseed oil, soyabean oil and tung oil.

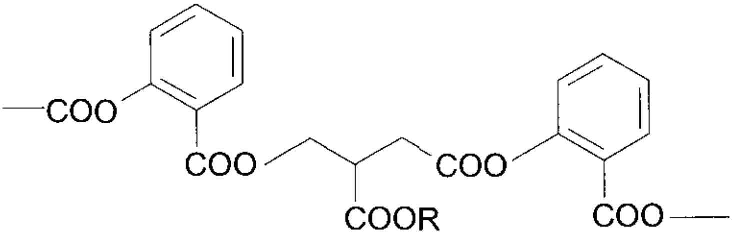


Fig.1.18. Repeating unit of alkyd resins

Many commercial alkyd resins are modified with epoxy resin, phenolic resin, rosin and have good durability, flexibility, gloss retention, reasonable heat resistance, good colourability, dimensional stability and good electrical properties.

1.6 Polymer composites

Composite materials are macroscopic combinations of two or more distinct materials having a discrete and recognisable interface separating them. Polymers offer many advantages over conventional materials including lightness, resilience to corrosion and ease of processing. Polymer composites are mainly used for their high strength to weight ratios; corrosion resistance flexibility and ability to tailor make the materials according to the application. There are essentially two types of polymer composites - reinforced composites and filled composites. The reinforced composites are used in applications where superior mechanical properties are required. Fibre reinforced plastics are important examples of this type of composites. The fibres used are glass, Kevlar, carbon and boron. The important resins used as matrix in fibre reinforced plastics are epoxy and polyesters. In filled composites, the fillers are added to the polymer matrix to improve properties other than mechanical such as resistance to chemicals and environment.

About 30% of all polymers produced each year are used in civil engineering and building industries. They can be combined with fibres to form composites which have enhanced properties, enabling them to be used as structural members and units. Polymer composites can be used in many different forms ranging from structural composites in the construction industry to high technology composites used in aerospace and space satellite applications.

These properties are influenced by manufacturing techniques, environmental exposure and loading histories. Designing with composites is thus an interactive process between the constituent materials used, the composite material and an understanding of the manufacturing technique for the composite component.

1.7 Use of polymers in concrete

Although the physical properties and relatively low cost make Portland cement concrete the most viable construction material, it is not without limitations. Some of the major ones have been listed below [31].

a Low flexural strength

b Low failure strain

c Susceptibility to frost damage and

d Low resistance to chemicals.

These drawbacks are well recognized and can usually be accommodated in most applications. In certain situations, these problems can be solved by using materials which contain an organic polymer or resin instead of or in conjunction with Portland cement. These relatively new materials offer the advantages of higher strength, improved durability and good resistance to corrosion, reduced water permeability and greater resistance to damage from freeze-thaw cycles.

The use of polymers in cement concrete and mortar is not entirely new. Naturally available polymers such as bitumen; glutinous rice paste, molasses etc. have been used to enhance the properties of the existing building materials. The first patent on the use of natural rubber as an additive for paving material was issued to Cresson in 1923 [66]. Ever since, considerable research in this field, has been conducted. Moreover, durability of the building structure has been reduced due to ever increasing chemical pollution in the environment [67]. In 1930s rubber latexes like natural rubber, poly(styrene-butadiene) (SBR), poly(acrylonitrile–butadiene), polychloroprene (CR) were used for the preparation of polymer cement concrete. Thermoplastics such as polyvinyl acetate, acrylics and vinylidine chlorides introduced in 1960s had greater strengthening effects on the mortars than elastomers.

Polymer concrete [68], made by blending various polymers with cement, enhances workability, durability and strength of the cement concrete structures.

Some of the polymeric admixtures now used extensively in civil engineering are in the form of adhesives, modifiers and matrix materials. Among the various types of composites of polymers and cement, polymer concrete is increasingly used in construction and repair of highways and bridges and in the manufacture of various kinds of precast articles. The cement mortars or concrete that are modified by polymers are called Polymer modified mortar (PMM) or Polymer modified concrete (PMC). The properties of the composite (Table 1.8) depend mainly on the ratio and the nature of interactions between the polymer and cement.

Table 1.8 Typical properties of polymer-containing concrete composites and Portland cement concrete [68, 69]

Material	Tensile Strength MPa	Modulus Of Elasticity GPa	Compressive strength MPa	Shear Bond Strength KPa	Water Absorption	Acid Resistance†	Freeze thaw resistance No. of cycles/% Wt loss
PIC	10.5	42	140	-	0.6	10	3500/2
PMC	14.7	49	273	-	<_0.6	>_10	-
PCC	5.6	14	38	>_4550	-	4	-
Portland cement concrete	2.5	24.5	35	875	5.5	-	700/25

The values given represent average values; the properties of commercial products may vary over a wide range, depending on formulation and production process.

† Improvement factor in relation to Portland cement concrete

1.7.1 Polymers as cement admixtures

Polymers as admixtures to cement may be classified into four categories depending on the particle size and form. These may be added to the cement as

a latexes,
b redispersible powders or emulsions,
c water-soluble polymers or
d liquid polymers.

a) Polymer latexes or dispersions

These polymers are in the form of particles of 0.05-5 μm diameter dispersed in water. Polymer latexes are classified into cationic, anionic and non-ionic depending on the charges borne by the polymer particles. Apart from the polymer particles they consist of emulsifiers, different monomers and stabilizers. The total solids content is about 40- 50% by mass. Some of the requirements for the polymer latexes to be used as admixtures are:

i. They should have high stability in the presence of calcium and aluminium ions present in the cement during its hydration. They must also have good mechanical stability during the mixing and processing of the cement concrete and mortar.

ii. They must not have adverse influence on the hydration. The polymer latexes must form polymer films in the concrete or mortar and must adhere on the cement hydrates and aggregates.

iii. They must possess good water and alkali resistance in the presence of the alkaline cement environment. They must also have high thermal stability.

iv. Some of the latexes used in the present study are SBR, NBR, PVAC, polyacrylic and polyacrylic styrene.

b) Redispersible polymer powders

These are manufactured in a two step process - firstly the polymer latexes are made by emulsion polymerization and then spray dried to obtain polymer powders with particle sizes of the order of 1-10μm. These are dry blended with cement followed by wet mixing with water.

c) Water soluble powders

These are mostly water soluble powdered polymers. Cellulose derivatives, polyvinyl alcohol and polyacrylamide form some of the typical examples. These are added to the cement concrete or mortar in the form of powders or aqueous solutions during mixing. When added as a powder they are blended with the cement-aggregate mix before adding water.

In the work reported herein, polymer cement composites have been prepared using polyvinyl alcohol and polyethylene glycol both of which are water-soluble polymers.

d) Liquid polymers

Liquid polymers are viscous polymeric substances such as epoxy resin and unsaturated polyester resin mixed with an accelerator and a hardener or a catalyst. The above mixture is added to the cement mortar or concrete during mixing. These are sparingly used compared to the other types.

In this study preliminary experiments on a set of liquid phenolic resin polymers were carried out. Based on the viability, a detailed study on two specific phenolic resins viz. phenol formaldehyde resin and m-cresol formaldehyde resin was carried out using different ratios of the monomers.

1.7.2 Cement concrete- polymer composites

Cement concrete-polymer composites are classified into three types depending on their process technology.

a) Polymer modified cement concrete (PMC) and Polymer modified mortar (PMM)

Portland cement mortar (often known as cement mortar) is made by mixing Portland cement with sand and water. PMM and PMC are composite materials made by partially replacing and strengthening the cement hydrate binders of conventional mortar and concrete with polymeric modifiers or admixtures such as polymeric latexes or dispersions, redispersible powders, water soluble powders, liquid resins and monomers. This type has a monolithic co-matrix in which the organic polymer matrix and cement gel matrix are homogenized. The properties of PMM and PMC are characterized by such a co-matrix. When the modification is due to polymer latexes, water-soluble polymers or redispersible powders, the water in the admixture is used for cement hydration and a polymer film is formed. When liquid resins or monomers are used the water added is taken up for the cement hydration and polymerization of the liquid resins and monomers takes place in situ.

i) Process technology

The process technology of PMC and PMM are the same as that of conventional cement mortar and concrete. The polymeric modifiers are added to the cement concrete while mixing and cured under optimum conditions. The types of cement employed for the manufacture of these composites depend on the application.

The mix designs of this type, though similar to the conventional ones, depend on the workability, strength, adhesion, waterproofness and chemical resistance requirements. The above properties are mostly dependent on the polymer cement ratio rather than the W/C ratio. The polymer cement ratio (P/C) is defined as –

P/C = {(weight of polymer) / (weight of cement used in the PMM /PMC)}

In the case of polymer latexes the numerator is the weight of the total solids content of the latex whereas for redispersible polymer powders, water-soluble powder, liquid resins and monomers the the actual weight of the polymer is used. Normally the P/C ratio is 5-15% and W/C ratio is in the range 30-50%.

The latex is diluted by blending it with water and then it is added to the cement. The mix time is so selected as to avoid entrapment of air. The redispersible powders and water-soluble powders are dry mixed with the cement before the addition of water.

ii) Principles of polymer modification

1) *Latex modification:* In latex modified mortar and concrete both cement hydration and polymer film formation take place yielding a monolithic

matrix phase with a network structure in which the cement hydrate and polymer phase interpenetrate each other. Some chemical reactions may take place between the cement and the polymer phases.

Ohama's theory [70] that explains the co-matrix formation is illustrated in Fig.1.19 as a three-step model.

In the first stage, the polymer latexes are mixed with fresh cement mortar and concrete to form a uniformly dispersed cement paste phase. In this paste the cement gradually undergoes hydration and the polymer particles deposit partially on the surfaces of unhydrated and hydrated cement particle mixtures.

In the second stage, the cement hydration takes place using the water present in the capillary pores as a result of which the polymer particles flocculate to form a continuous, close packed layer on the surfaces of unhydrated cement and hydrated cement gel.

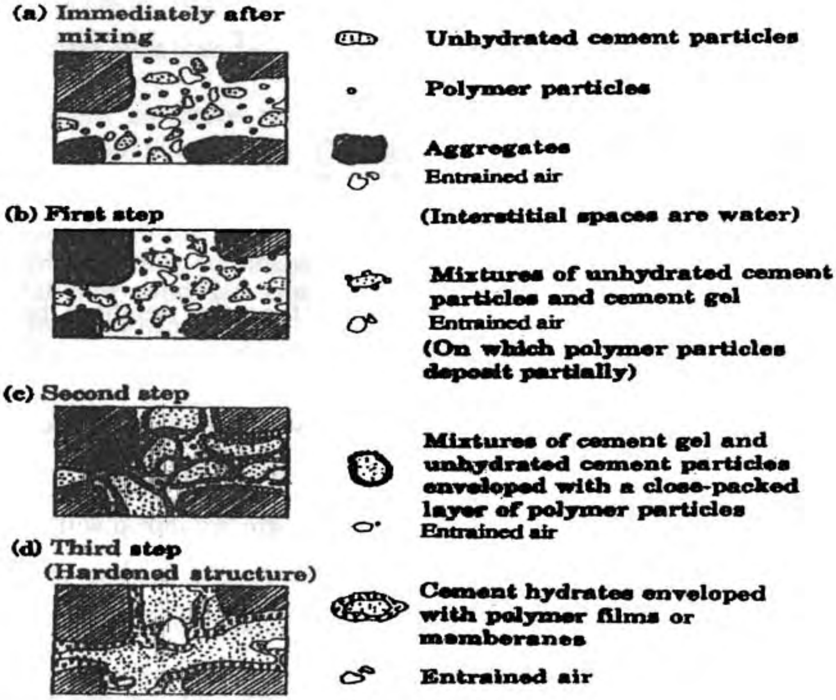


Fig.1.19. Steps involved in polymer modified concrete

Some chemical reactions may take place between the particle surfaces of the reactive polymers such as poly acrylic esters (PAE) and poly (vinylidene chloride –vinyl chloride) and Ca^{2+} ions from $Ca(OH)_2$ or silicate ions on surfaces of the aggregates. Such reactions (Fig. 1.20) improve the properties of hardened latex-modified mortar and concrete [71-74].

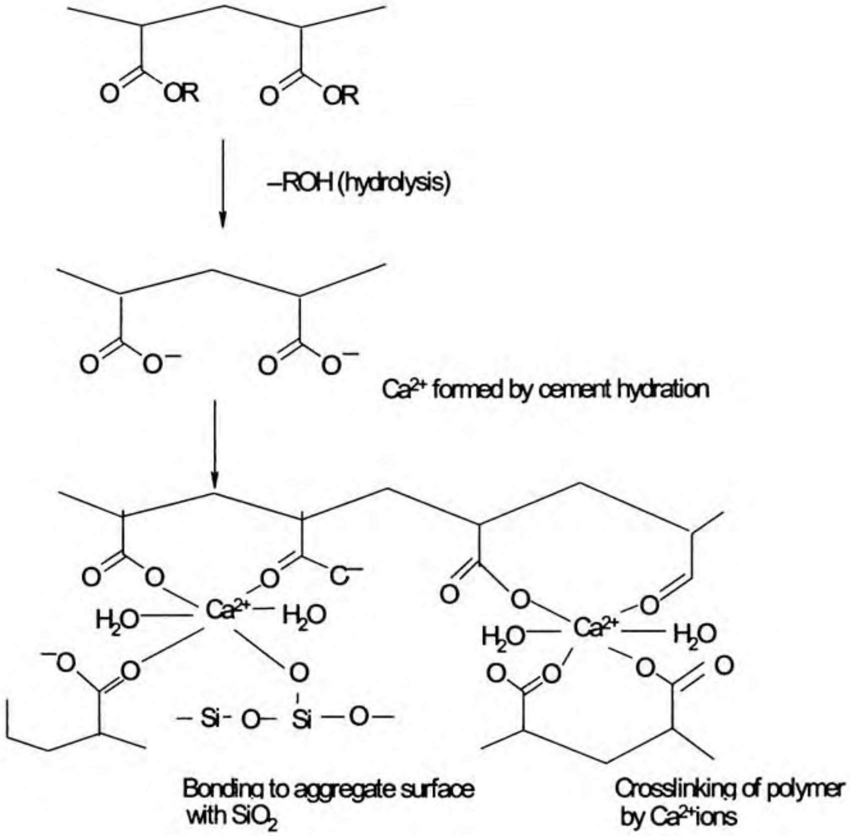


Fig.1.20 Schematic illustration of reaction between polymers with carboxylate group (ester linkage) and ordinary Portland cement aggregate

In the third step, the closely packed polymer particles coalesce to form a continuous film or membrane due to the withdrawal of water by cement hydration. This film forms a monolithic network in the polymer phase interpenetrating throughout the cement hydrate phase.

The film formed by the latex acts as a bridge over the micro-cracks thereby preventing crack formation and improves the cement hydrate and aggregate bond. This effect decreases the water wettability, resistance to moisture or air penetration, chemical resistance and improves with increasing P/C ratio.

2) *Modification by redispersible powders*: The principle of polymer modification by redispersible powders is almost similar to that by latexes. These redispersible powders are added to the cement in the dry state. They re-emulsify and behave similar to their respective latexes when water is added.

3) *Modification by water-soluble polymers*: Water-soluble polymers are added to the cement after dissolving them in water. This results in an increase in the viscosity of the water. The surface activity thus improves workability and prevents the "dry out" phenomenon. They form a thin film and contribute very little to the strength parameters of the composite.

4) *Modification with liquid resins or monomers*: The resins are added to the cement during the mixing at higher percentages than the latexes. Since the resins are of lower molecular weights or are prepolymers further polymerization and cement hydration take place simultaneously. This results in an interpenetrating network of both the polymer and cement phases.

iii) Properties of PMC

Mortar is a mixture of sand, cement and water.

1) The polymer particles in the fresh mortar modified with polymer latexes exhibit a ball bearing action thereby improving its consistency.

2) The W/C ratio is reduced with increase in the P/C ratio which contributes to strength development. Air entrainment is more than in conventional cement concrete. Therefore, the freeze-thaw durability and consistency are improved.
3) The setting process is dependent on the polymer type and P/C ratio and is generally delayed compared to the conventional mortars and concrete.

The strength of these composites is influenced by various factors that tend to interact with each other. The main factors are -

a. The nature of the materials used i.e. the polymers, cements and aggregates,
b. The control factors for mix proportions such as P/C ratio, W/C ratio, binder–void ratio, air content etc. and
c. Curing and testing methods.

Most of the PMCs and PMMs provide a larger ductility than ordinary cement concrete and mortar. PMC and PMM have a coefficient of thermal expansion equal to or slightly greater than ordinary cement concrete.

The resistance to chloride ion penetration and carbonation is improved with increasing P/C ratio. The effects of filling and sealing by polymers are reflected in the reduced transmission of such gases as CO_2, O_2 and H_2O (vapour) as well as water impermeability. These also have excellent adhesion properties, high abrasion resistance and good chemical resistance superior to those of ordinary cement mortar and concrete.

iv) Applications

PMC and PMM are being widely used as construction materials throughout the world due to the above cited advantages. In Japan research on polymer mortar and cement has been carried out for more than 40 years. Of late polymer modified paste and slurry with high P/C ratios have been used as a liquid applied compound for waterproof membrane coatings for apartment houses, silos and underground tanks in Japan and Germany [75, 76]. Ethylene vinyl acetate is employed to improve workability and adhesion of fresh cement mortar. Water-soluble polymers such as methylcellulose, hydroxy methylcellulose, polyvinyl alcohol and poly acrylates are used for plastering and underwater concreting work.

Studies on the carbonation, chloride ion penetration and oxygen diffusion characteristics reveal PMC as a low cost promising material to prevent corrosion of building structures. Some polymers like poly (vinylidene chloride-vinyl chloride) release chloride ions, which cause corrosion of structural steel supports [77].

Ethylene-vinyl acetate (EVA) is usually used to improve workability and adhesion of fresh cement mortars. Commercially available epoxy resin (EP), unsaturated polyester (UP) resin (polyester-styrene system), vinyl ester resin (VE) and acrylic resin have been used to prepare PMCs [78]. The cure temperatures of poly methylmethacrylate mortars and concrete have been found to be far lower than that of ordinary cement concrete. Rods of fiber-reinforced plastics have been used to reinforce the structures with polymer mortars and concrete.

Ohama et al have recently developed an epoxy-modified mortar without any hardener that exhibits considerable strength below 20% [79]. In Germany, developments in epoxy modified mortars and concrete include a one-component epoxy resin for the cement modifier and a dry mortar using epoxy resin. The former does not require hardeners to be added at the construction site while the latter is produced as a dry mixture of epoxy resin with a hardener, cement and aggregates. The dry mixture can be applied by the addition of water in the field [80, 81].

Research on SBR-modified and unmodified lightweight aggregate concrete (LWAC) in Brazil revealed that the polymer increased the workability and cohesive nature of the mix in the fresh state. SBR- modified LWAC exhibited high structural efficiency compared to the unmodified one though its compressive strength is lower [82]. Hydroxyethyl cellulose (HEC) and EVA are added to anhydrous cement and aggregates. HEC has a major effect on the fresh mortar properties such as water retention capacity and rheology. EVA influences the behaviour of hardened mortars.

Polyvinyl alcohol based polymer modified concrete and mortars showed that the polymer caused several changes in the microstructure and increased the voids in the composite thereby decreasing its compressive strength [83]. Some work done to overcome the problems due to re-emulsification of some copolymers like styrene butadiene, vinyl acetate–ethylene, styrene–acrylic and acrylics revealed that a newly developed epoxy emulsion based polymer exhibited better chemical and mechanical properties [84].

Liu and Chen [85] studied the effect of lightweight expanded polystyrene (EPS) on SBR latex modified concrete and compared it with the EPS concrete. The SBR latex improves the bond between the cement matrix and EPS particles at certain polymer cement ratio and increases the flexural strength.

b) Polymer concrete

This was used as early as 1958 in USA [86], Japan [87] and Soviet Union [86] to produce building cladding and consisted of aggregates with a polymer binder without Portland cement or water. Polyester-styrene, acrylics, epoxies, vinyl and furan ester and urethanes are widely used. Since the polymeric binders replace the conventional mortars and concrete the polymer matrix binds the aggregates. Properties such as strength, chemical resistance, freeze-thaw resistance and abrasion resistance are better than that of conventional concrete or mortar. The poor resistance to high temperature and the dependence of the mechanical properties on temperature are the major undesirable properties of this group of polymer cement composites. Thermoplastics are serviceable till their glass transition temperature above which they lose their mechanical properties.

This could possibly be improved by employing crosslinking agents and thereby increasing the glass transition temperature. Thermosetting resins retain their properties till their decomposition temperature. Since the cost of various polymers is high compared to Portland cement and other cements the mix design must ensure minimal percentage of polymeric binders to disperse aggregates under closely packed conditions in the polymer matrix.

i) Processing

Polymer concrete is prepared by using forced mixing type mixers. The proportions of the polymer binder range from 9-25% of the total mass. The mix proportions usually used are - Polymers:Fillers:Aggregates ≡ 1:0-1.5:3-7.0. Fine aggregates used for PC are river gravels and sands and for coarse aggregates, crushed stones such as limestone, granite and silica sand etc. Fillers most often used are ground $CaCO_3$, powder or fumed silica and fly ash. After mixing, the PC mixtures can be cast or moulded in a manner similar to conventional cement concrete and then subjected to ambient temperature or heat cure. Trowels are often used for surface finishing.

PC is very difficult to work on compared to conventional concrete with the exception of PMMA or acrylic mortars and mortars using low viscosity MMA monomer. These harden faster than cement concrete thereby reducing the labour costs.

ii) Properties

Since polymeric binders have poor thermal stability the properties are dependent on temperature [88]. PC has a large hardening shrinkage and reaches about 5-10 times the drying shrinkage of ordinary concrete. They have good abrasion resistance, impact resistance and electrical insulating properties though they are mostly temperature dependent.

PCs are completely monolithic and have a watertight microstructure with a chemical binder and filler. They are thus impermeable to chemicals, moisture and gas. Since they absorb no moisture they are superior in terms of freeze-thaw resistance in most cases except for polyester resins [89].

iii) Applications

PC overlays have been in use as bridge surfaces and floors in sports arenas and stadia, laboratories, hospitals, factories and entrances. They are also used to manufacture drain pipes, underground boxes, man-hole covers, building cladding, floor tiles, architectural mouldings and machine tool bases.

Though a considerable amount of research has been carried out on polymer concrete in the past three decades, its engineering properties have not been explored in depth. Vipulanandan et al [90] have reportedly used organic polymers such as polyesters, epoxies and polymethylmethacrylates (PMMA) as binders for cement. Their studies on polyesters and epoxies revealed that the strength, failure mode, failure strain and stress-strain rate are dependent on the curing method, strain rate and temperature. Fowler [91] et al have studied methylmethacrylate PC and concluded that the initiator to promoter ratios, testing temperature and aggregate type have varying effects on the strength of the composite. These effects may be possibly due to the thermoplastic nature of the polymer used. Vaidya and Nadkarni [92] have reported that recycled polyethylene terephthalate (PET) does not adversely affect the properties of the PC and therefore could decrease its cost. Wang Xin-You [93] studied the fracture behaviour of the bonding interface between carboxylic styrene butadiene (SB) latex modified cement mortar and old cement and found that the bonding strength increased with increasing amount of the polymer. The freezing resistance was found to be the best at P/C=0.08 and is lower than for ordinary cement mortar. Gorninski et al [94] assessed the storage modulus of PC using orthophthalic and isophthalic polyester binders and compared the results with Portland cement concrete. The results revealed that the type of the resin and concentration of fly ash used as filler had an effect on the modulus of elasticity of the composite. Pratap [95] has studied on the electrical applications of PC based on silica fillers (silica sand, desert sand, quartz powder, etc.) with vinyl ester resin and acrylic resin respectively as binders and concluded that acrylic based PC is economical and has better electrical properties than vinyl ester based PM.

c) Polymer impregnated concrete (PIC)

Polymer impregnated concrete and mortar are composite materials made by impregnating the hardened cement mortar and concrete with monomeric impregnates which are subsequently polymerized. Though this was developed in Japan [96], U.S.A [97] and European countries during 1960s and the 1970s, the high cost and complicated process technology involved made it increasingly unpopular.

i) Principle

In this type of polymer cement composites the water or air filled pores in the hardened cement structures are fully or partially replaced by polymers. These composites have a microstructure in which the cement hydrate matrix phase, aggregate phase and the continuous polymer phase interpenetrate each other. As a result, the bonds between the cement paste and aggregates are stronger than those in the conventional ones. Consequently, these composites exhibit higher strength, chemical resistance and freeze-thaw resistance.

The properties of a typical PIC [98] depends mostly on:

1. Impregnation efficiency of the monomers,
2. Degree of conversion of the monomers into polymer,
3. Polymer impregnation depth and polymer loading and
4. The properties of the polymers used.

ii) Materials

The materials used for PIC consist of monomeric impregnants, base mortar and concrete. The polymers most widely used in the impregnation of concrete are vinyl types such as methyl methacrylate, styrene, acrylonitrile, tert butyl styrene and vinyl acetate. MMA and its mixtures with acrylonitrile are preferred due to their low viscosity, good wettability, high reactivity, relatively low cost and superior properties of the resulting composite. These polymers could be crosslinked with suitable agents such as trimethylolpropane trimethacrylate to form a three dimensional network in the pores thereby resulting in enhanced chemical and mechanical properties of the polymer cement composites. Thermosetting resins are very viscous. Hence less impregnation is possible though they increase the resistance of the composites to heat.

iii) Processing

PIC is made by impregnation of precast hardened Portland cement concrete with low viscosity monomers (in either liquid or gaseous form) that are converted to solid polymer under the influence of physical agents (ultraviolet radiation or heat) or chemical agents (catalysts) [99]. It is produced by drying conventional concrete, displacing the air from the open pores (by vacuum or monomer displacement and pressure), saturating the open pore structure by diffusion of low viscosity monomers or a prepolymer-monomer mixture (viscosity 10 cps; 1 x 10-2 Pa•s) and in situ polymerization of the monomer or prepolymer-monomer mixture, using the most economical and convenient method (radiation, heat or chemical initiation). The important feature of this material is that a large proportion of the void volume is filled with polymer, which forms a continuous reinforcing network. The concrete structure may be impregnated to varying depths or in the surface layer only, depending on whether increased strength and/or durability are sought.

iv) Properties

The properties of the PIC depend on the polymer loading or polymer penetration depth [100]. The main properties of a PIC [101] are:

1. High strength similar to PC and PM,

2. Excellent water tightness and freeze-thaw durability,
3. Good chemical resistance depending on the degree of polymer penetration,
4. Excellent abrasion resistance and impact resistance and
5. Poor thermal resistance and fire resistance.

v) Applications

Applications include structural floors, high performance structures, food processing buildings, sewer pipes, storage tanks for seawater, desalination plants and distilled water plants, marine structures, wall panels, tunnel liners, prefabricated tunnel sections and swimming pool walls. Partially impregnated concrete is used for the protection of bridges and concrete structures against deterioration and repair of deteriorated building structures such as ceiling slabs, underground garage decks and bridge decks [102].

Though composites of polymers show improved properties when low viscosity monomers are impregnated in hardened concrete, PIC is very expensive due to the high cost of the monomers. This is one of the main reasons why research and applications in this area are limited [103]. Studies carried out on PIC using acrylic acid monomer [104], with different W/C ratios and cured for various durations indicated that the intrusion of polymer into the cement paste matrix does not affect the phase composition of the hydrated phases. It also revealed the dependence of the compressive strength on the initial W/C ratio, curing time and gel/space ratio. The properties of PIC are dependent on the glass transition temperature of the polymers or the copolymers used [105, 106]. Also the addition of crosslinking agents increases the strength at high temperatures. Investigations on the impregnation of surface of highway bridge decks with polymers revealed that it increased the durability and more study is underway [107] to develop a practical method of application and evaluation of different treatments by various testing procedures.

1.7.3 Polymer Cement Interaction Theories and Models

Chemical admixtures are often used to alter the course of the cement hydration reactions and the properties of fresh and hardened concrete. These admixtures mostly undergo various types of physico-chemical interactions with the hydrating cement phases. The admixture-cement interactions could be explained as reactions between two complex chemical systems (as shown in the Fig.1.21) - one being Portland cement which is a multicomponent multiphase inorganic material and the other the organic polymer. Two types of the latter exhibit an affinity towards the cement particles or the hydration products which results in adsorption. These types include - polymers having charged groups like SO_3^-, COO^- that can interact with the particle surface via electrostatic forces and those having polar functional groups like OH^- which interact strongly with the highly polar hydrated phases [108]. Polymers containing hydrophobic groups similar to surfactants can interact with the hydrating surface either through their polar groups or through their hydrophobic counterparts.

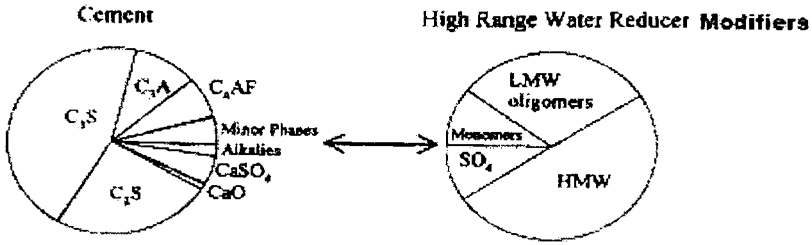


Fig.1.21.- Schematic illustration of the interaction between a cement (multi-phasic mineral system) and a chemical admixture (multi-component organic system).

a) *Chemical interactions between polymer and cement grains*

The interactions between Portland cement, a common building material and polymer are very complex. These interactions have been studied under two heads based on the nature of the addition of polymers to the Portland cement viz. - impregnation of concrete and mixing in concrete [87].

i) Interactions when polymers are impregnated in concrete

In this case the effective polymer loading is about 1.5-7.5%, which is much smaller as compared to that used in polymer cement concrete (which is about 15%) [100,109,110]. This lower effective loading is because the impregnation of the polymer takes place after the hardening of the cement and there is no possibility of any interaction between the two phases. The polymer fills the voids and bridges the microcracks of the cement concrete structure and strengthens the concrete. The strength of the PIC is therefore due to the cumulative strength of the concrete as a whole and the adhesive bond provided by the polymer.

ii) Interactions when polymers latexes mixed in concrete

Ideally when the polymer is mixed with the cement *concrete* the latex does not undergo interactions with the cement and forms a film over the cement particles and bridges the microcracks while drying.

In actual practice when the polymers are mixed with cement concrete there are reactions between the two phases which results in the coagulation of the latex. Thus, the latex loses its film forming ability and this coagulation interferes with the normal hydration of the cement. This formation of complexes may results in acceleration or retardation of the cement hydration [111].

When water is added to the cement, $Ca(OH)_2$ is released into the water. In the case of cement modified by acrylic polymers there is a reaction between the Ca^{2+} ions in the water and carboxylate ions present in the polymer [112, 113, 77, 114, 115]. Chemical analysis of the pore solution indicated a comparable amount of OH ions in it [116]. XRD and thermal analysis of the cement pastes modified by acrylic polymers indicate a decrease in the amount of Ca^{2+} ions and an increased amount of SO_4^{2+} compared to the unmodified cement paste [77].

The relevant reaction takes place in two stages - first an attack on the carboxylate group (ester linkage) of the polymer by the hydroxide ions, known as saponification (or alkaline hydrolysis) followed by a reaction of Ca^{2+} ions with the carboxylic group [117] as depicted in Fig. 1.22.

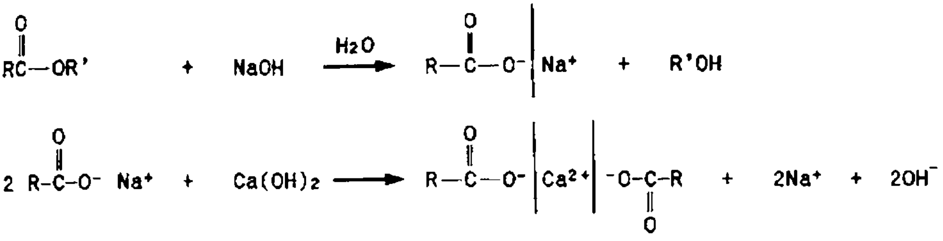


Fig.1.22. Alkaline hydrolysis of the acrylic polymers

Ohama [78] suggested that the reaction between the Ca^{2+} ions and the carboxylic group could either result in chemical bonding between the aggregate surface and the SiO_2 group or in crosslinking of polymer chains by the Ca^{2+} ions as depicted in Fig.1.22.

Investigations into the possibility of a polymer (styrene acrylate) film in the presence of $Ca(OH)_2$ revealed that there is a decrease in the extent of formation as the level of the $Ca(OH)_2$ increased. When the P/C ratio is less than 1:4 the polymer adheres on to the $Ca(OH)_2$ particle and loses its film forming capacity [74]. This phenomenon is not observed in the presence of NaOH. Therefore the interaction between the two phases results in an ionic bonding between Ca^{2+} ions and the carboxylate ions of the polymer forming crosslinks which also inhibit film formation. This indicates further that the polymer latex does not undergo destabilization due to the alkalinity of the solution.

The interaction between the reactive parts of the polymer and the Ca^{2+} ions has been under study by many research groups [77, 118]. The analysis of the pore solution and the amount of Ca^{2+} ions in the modified and unmodified cement concrete revealed a different mechanism in the presence of polymer chains. The influence of this chemical interaction on the final properties has however not been investigated.

Though the polymer particles or film influences the microstructure of the hydration products, the final structure depends on the polymer and P/C ratio. It has been observed that a continuous film formation is not possible if the percentage of polymer is less than 5% and behaves as an additive [119, 120]. Depending on its type the polymer deposits, as droplets, on the surface of the hydrated and unhydrated cement particles and coalesces to form a film. In this way the polymer partially or completely hinders the hydration of cement particles. Therefore, the structures of the bulk binder phase of the modified and unmodified phases differ in the degree of crystallinity and the morphology of the $Ca(OH)_2$.

In the unmodified cement the formation of crystals of $Ca(OH)_2$ are distorted and accommodated to spaces formed by the structure of the unhydrated particles and the primary hydration products. However the formation of $Ca(OH)_2$ crystals in the presence of polymers takes place without any deformation [121]. Therefore the polymer acts as a bonding agent trying to bridge the different layers thereby increasing the interparticle bonding. The existence of chemical bonds however cannot be concluded from structural investigations. Su, Bijen and Larbi [77, 119] found that $Ca(OH)_2$ crystals are formed at the interface between the cement hydrates and limestone or aggregates in the presence of the polymer latexes.

b) Models of polymer modification

Many authors have proposed theories on the formation of the microstructure of polymer mortar and concrete [119, 122, 123, 124]. They have explained the structure of the matrix consisting of the interpenetrating polymer phase and hydrated cement with random dispersion of the aggregates. SEM studies revealed the presence of the polymer film in capillary pores, bridging opposite sides of propagation cracks and around the aggregates [125].

Ohama [123] proposed the basic model of polymer modification of cement concrete and many refinements were proposed. Though the models gave a good idea about the micro and meso structures, the chemical interactions between the two phases still remain uncertain.

i) Three step model proposed by Ohama

This is already described in Section 1.7.3 a) ii)1).

ii) Modification of the three-step model proposed by Bijen and Su [119, 122]

This theory was based on observations made on an Environmental Scanning Electron Microscope and suggested some refinements and additions to Ohama's model.

In the first step it is assumed that there is equilibrium between the polymer particles in the liquid phase and the adsorbed polymer particles on the cement surface. This depends on the type of the polymer and cement, dispersing agents in the polymer and the P/C ratio. The efficiency of the polymer modification is more when there are fewer polymer molecules adsorbed on the cement particles. This is so because they hinder the movement of the capillary water to the unhydrated cement. This slows the hydration process of the cement and is observed in the case of many polymers [126].

As the degree of hydration proceeds with water consumption, the layer of adsorbed polymer molecules also thickens. Therefore, it takes a long time for the cement products to penetrate the polymer layer. The morphology of the cement hydration products in the pore regions is more crystalline and is influenced by the polymers dispersed in the liquid phase. Plate and needle shaped products are formed in the pore regions and consist of inorganic and organic polymeric materials. At this stage the polymer forms bridges between different particles. As the formation of the cement hydration products takes place the amount of free available water is restricted to areas where capillary pores are in the unmodified state.

Depending on the minimum film forming temperature, the amount of the polymer and the existing temperature, the polymer molecules coalesce to form a film. When the P/C ratio increases the film is continuous and forms an interlinked, uniformly distributed skeleton in between the cement hydrate layers [127]. With lesser percentage of polymer molecules, they get distributed evenly with or without mutual contacts. A minimum of 5% of the polymer is essential for continuous film formation [128]. Above 9% of polymer in the whole volume (P/C = 6.4%, with sp.wt of cement= 3.01 kg/m^3 and polymer emulsion=1 kg/m^3 and 350 kg cement) a continuous phase is formed which is intimately mixed with the cement hydrate phase. Above 18% (P/C ~ 14%) the two phases still exist with a polymer phase free of cement hydrates which result in increase in ductility in compression as well as in tension.

iii) Modification of three-step model by Puterman and Malorny [124]

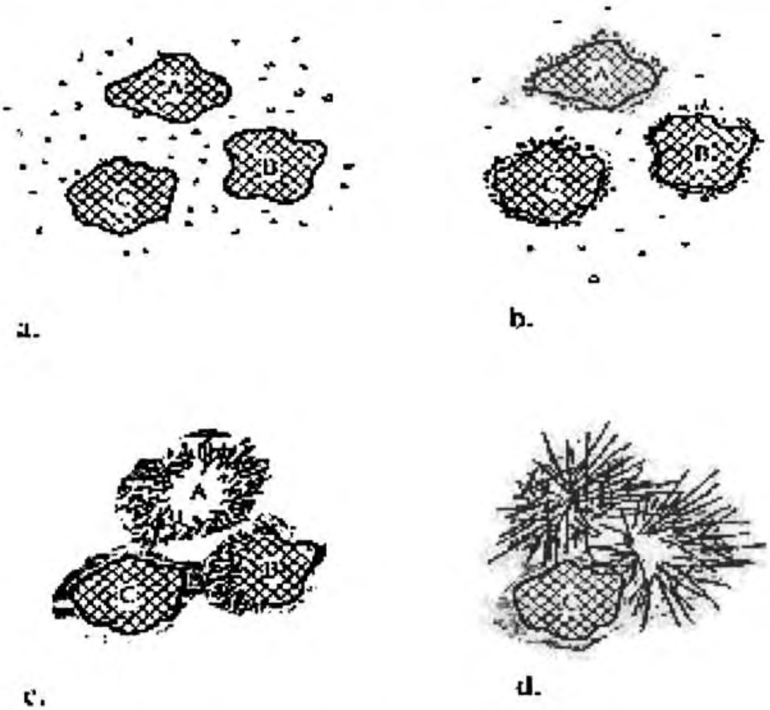


Fig.1.23 Modification by Puterman and Malorny [124]

This theory was propounded by studying the interactions of the polymer dispersion and cement particles at the early stages of hydration using SEM. It revealed a microstructure of hydrated cementitious matrix as shown in Fig. 1.23 in which the polymer, which at the first stage coated. The cement particles is incorporated and contained within the cementitious phase.

The first stage is similar to the model proposed by Ohama where the polymer gets adsorbed on the mineral surfaces forming a layer of coated particles on the available surfaces. Depending on the type of the polymer it gets partly or completely adsorbed on the surfaces and the unabsorbed polymer remains in the free water phase.

In the second stage, the closely packed polymer particles coalesce to form a film provided its minimum film temperature (MFT) is lower than the hydration temperature. MFT is the minimum temperature during which the polymer particles coalesce to form a film. The cement hydration takes place where the cement particles have access to free water. An external layer of hydrated products is formed on some parts of the cement grains which results in some of the cement particles remaining unhydrated.

As the hydration goes to the final stage, the cement particles grow into products that sometimes penetrate the polymer film. The particles connect to each other incorporating the polymer film around and within the cement gel particles. Investigations on the polymer film on the cement surfaces by Sasse [111] revealed that the cement particles penetrated it during the hydration process. Therefore, the polymer film does not contribute to the properties though, however, it improves the workability and hydration rate during the start of the cement hydration.

The P/C ratio is a major factor in determining the ability of cement hydration products to penetrate the polymer film and to finally access the free water and complete the hydration [129]. When the P/C is lower than 16% the penetration of the film by the cement particles takes place. At higher percentages, the polymer forms an impermeable membrane around the partially hydrated cement particles which have no access to free water.

This theory lays emphasis on the minimum film formation temperature (MFT) of the polymer used in the polymer cement composite. If the MFT of the polymer is above the curing temperature of the cement, the polymer remains as a thick layer of stacked droplets on the surface and does not form a film. This layer is permeable and may improve the properties and toughness of the composite.

1.8 Current status of polymer cement composites

Of late significant work on the development and application of new polymer cement composites have been carried out [130, 131]. These composites are mostly used as repair and construction materials and possess excellent mechanical and durability related properties.

After the oil crisis in 1970's it was clear that mineral oil was no longer available as the cheap basis for polymer production. Therefore, the use of polymers in construction industry became limited and became focussed on to scenarios where high durability and sustainability were considered important. Polymers are thus currently used in areas where their specific properties are required to contribute to a synergistic effect with the classical construction materials [132].

Polymers are added either to the fresh concrete mix or to the hardened Portland cement concrete in the form of a complete polymer (premix polymerised latexes - elastomers or thermoplastics) or chemically reactive synthetic resins - prepolymers or monomers that may be polymerised or polycondensed (post-mix polymerised) by thermocatalytic or other systems. Some of the premix polymers used are polyacrylic esters, styrene butadiene rubber, polyvinyl alcohol and copolymers of styrene with acrylic esters and butadiene. Epoxy resins are the widely used as a post mix polymer.

In Japan, research and development in the field of polymer modified mortar and concrete have been carried out for the several years. These are used mostly for their high performance, multifunctional applicability and sustainability compared to conventional cement concrete or mortar. Styrene butadiene rubber (SBR) latex, polyethylene vinyl acetate (EVA) and poly acrylic esters emulsions are some of the dispersions used. Commonly used resdispersible powders include poly(vinyl acetate- vinyl versatate) and EVA. PMM is mostly used for repair and finish works [20] but PMC has limited applications.

In Korea, polymer cement concrete is mainly used for bridge overlay while polymer cement mortar is used for repairing buildings, bridges and concrete pavements [133]. Polymer concrete and mortars are employed in the manufacture of manhole covers, cable troughs and reinforced plastic composite pipes. The use of MMA modified UP polymer concrete and mortar in bridge decks, sewage manholes and oceanic pile are also being investigated [134]. PICs are mostly used for job site impregnation and have very limited applications due to their high cost. Most of the polymers used, as construction admixtures are SBR, PAE, waste polyethylene terephthalate [135]. Waterproofing is done with cement blended rubber latexes like synthetic rubber, natural rubber and rubber asphalt.

In China, use of polymer modified mortars, including latex modified mortars and mortars modified with redispersible powders in various civil applications are being investigated [136]. The main PMC based products are tile adhesives, concrete interface treatments, adhesives and surface protecting mortars, polystyrene foam boards for thermal insulation of buildings and water proofing materials. Polymer concrete and polymer modified mortar and concrete are mostly used for repair of roads, dams and buildings. Some of the polymers used are SBR, specially developed carboxylic butadiene/styrene copolymer [137] (for oil well consolidation), copolymer of vinyl acetate with methacryloxyethyl trimethylammonium chloride [138] and steel fibre reinforced concrete.

In India, around 6% of polymeric materials have been used in construction [139] and in the production of pipes, gutters, window and door profiles, insulation, bridges and building panels. Polymer modified mortar and concrete are used as repair materials and investigations have revealed that steel fibre reinforced natural rubber latex concrete has superior durability and ductility [140]. SBR and polyacrylic rubber latex modified concrete with and without the use of steel fibre with normal aggregate viz. sintered fly ash aggregate are being developed. The latex modified RC beams showed increased initial crack load and improved load deflection behaviour. Epoxy and polyester resins are now employed in polymer cement and concrete and are applied as repair materials in airfields; cement concrete highway pavements and dumper platforms for iron ore handling plants. The resins used as binders for cement are MMA and polyester. Fibre reinforced polymer composites are also used in the RC plates and laminates [107].

In Europe, the use of polymers have gradually extended from concrete crack injection to repair mortars for concrete and stone, consolidation of masonry, repair of timber structures, piping and waterproofing materials [141]. On an average about 8% of the polymer consumption concerns thermosets, the rest being thermoplastics. In 2003, 7350000 tons or 18.5% of the total market of polymers in Western Europe (European Union, Norway and Switzerland) were used in building and construction industry [142].

Table 1.9 European Consumption of Polymers in Construction

Application field	Type	Consumption
Textiles in architecture	Polyester/ glass	280000 tons
	PVC/ polyester	100000 tons
	Carbon/ Kevlar	Not significant
Impermeable membranes	PVC	200000 tons
	PE (HD+ LD)	250000 tons
	EP,PU, UP Resins	50000 tons
Road paintings	SBS, APP bitumen modified	88000 tons
Tubing for optical fibres	Liquid, hot melt, strips	280000 tons
	PEHD	200000 tons (2001)
		600000 tons (expt. 2010)
Tubes for sewers, gas, water …	PVC, PE, PP, UP	2761000 tons
		486000 tons
Concrete modification		

1.9 Objectives and Scope of the work

The main objective of this research work was to prepare and evaluate the macroscopic and microstructural properties of polymer modified cement (PMC) composites and cement-sand *mortars* that could possibly yield low-cost indigenous construction materials. It was envisaged to use various thermoplastics, rubbers and thermosets along with Portland cement to prepare PMCs that would enhance some properties of virgin cement. Subsequent studies of their macroscopic properties, microstructure and the polymer–cement interactions in the cement matrix were also one of the objectives. An attempt to correlate the structures of the polymers used with the properties of the PMC would also aid in the development of tailor-made composites.

The scope of the work was:

- preparation of chemically resistant PMCs
- determination of their macroscopic properties – mechanical and chemical resistance
- microstructural studies of these polymer–cement composites
- study of interactions between the polymer and the cement in the polymer-cement matrix
- effect of polymer structure on the properties of polymer-cement composites.

References

[1] P. C. Hewlett (Ed.); Lea's *Chemistry of Cement and Concrete,* 4th Ed, Arnold, 1998, ISBN 0-340-56589-6.

[2] Robert H. Bogue; *The Chemistry of Portland Cement,* Reinhold Publishing Co., New York, 1947.

[3] Robert H. Bogue, *Ind. Eng. Chem., Anal. Ed.* 1, 1929, pp. 192-197.

[4] Robert H. Bogue, *Concrete,* Vol.30 No.3, 1927, pp. 33-36.

[5] http://www.epa.gov/ttn/chief/ap42/ch11/final/c11s06.pdf

[6] Bye G.C.; *Portland cement: composition, production and properties,* Pergamon Press, Oxford, 1983, pp.149.

[7] Shetty M.S.; *Concrete Technology theory and practice,* S.Chand and company Ltd., 2003.

[8] Barbara Lothenbach, Frank Winnefeld, Corinne Alder, Erich Wieland and Peter Lunk; *Cement and Concrete Research*, Vol. 37, No. 4, April 2007, pp. 483-491.

[9] *Standard Specification for Portland Cement,* ASTM C-150, Annual Book of ASTM Standards, Vol. 04.01, Cement, Lime and Gypsum, American Society for Testing and Materials, West Conshohocken, PA, 1999.

[10] http://guides.ce.washington.edu/WSDOT/Modules/03_materials/03-4_body.htm

[11] http://www.fhwa.dot.gov/infrastructure/materialsgrp/cement.html

[12] Neville A.M; *Properties of concrete*, IV Edition, Addison Wesley Longman Ltd., England, 1997.

[13] http://www.cement.org/basics/concretebasics_concretebasics.asp

[14] http://www.cement.org/basics/concretebasics_*aggregate*.asp

[15] Nan Su, Buquan Miao and Fu-Shung Liu; *Cement and Concrete Research*, Vol.32, No.5, May 2002, pp. 777-782.

[16] F.M. Lea. *The Chemistry of Cement and Concrete*, Arnold, London, 1956.

[17] Sunil Kumar ; *Cement and Concrete Research*, Vol.30, No.3 , March 2000, pp. 345-350.

[18] B.C. Doell; *J. Am. Concr. Inst.*, Vol.51, 1954, pp. 333–342.

[19] M. Moukwa; *Cement and Concrete Research*, Vol.20, No.3, May1990, pp. 439-446.

[20] Clifton J., Knab L.; Service life of concrete, *National Institute of Standard and technology Interagency Report 89-4086*, Gaithersburg Md, 1989.

[21] Czarnecki L. et al; *Proceedings of VIII International Congress on Polymers in Concrete*, Belgium, 1995.

[22] Garvin, S. L.; Ridal, J. P.; *Proceedings of 5th International Symposium & Exhibition on Environmental Contamination in Central & Eastern Europe*, Prague, Czech Republic, Sept. 12-14, 2000 (2001), pp. 2390-2397.

[23] Surlaker, Samir; Journal of Chemical Engineering World, Vol. 31, No.8, CODEN: CEWOAY ISSN: 0009-2517, 1996, pp. 95-102.

[24] H.H.Green; *Proc. of Inst, Civ. Eng.*, 28, London, July 1964, pp. 383-96.

[25] ACI 210R-93, *ACI manual of concrete Practice: Materials and General properties of concrete*, Detroit, Michigan 1994, pp.41.

[26] M.J. Kenn, *TN001M*, CIRIA, London, July 1968.

[27] Kopycinski, Bronislaw ; *Proc. of Colloq. Intern. Durabilite Betons,*

Rappt. Prelim., Prague, CAN 58:38714 AN 1963:38714, 1961, pp. 331-8.

[28] Balazs, Gyorgy; Csanyi, Erika; Tamas, Ferenc.; *Proceedings of the 10th International Congress on the Chemistry of Cement,* Gothenburg, June 2-6, CODEN: 65IBAI, 1997, pp.8.

[29] Powers, T.C.; *ASTM Sp. Tech. Publ. No. 169*, 1956, pp. 182-187.

[30] Helmut, R.A.; *Proc. of the 4th Int. Sym. On the Chemistry of Cement*, Washington D.C., 1960, pp. 855-869.

[31] http://irc.nrc-cnrc.gc.ca/pubs/cbd/cbd116_e.html

[32] http://irc.nrc-cnrc.gc.ca/pubs/cbd/cbd020_e.html

[33] Mehta, P.K.; *Materials Science of Concrete III, Ed. J. Skalny*, American Ceramic Society, 1993, pp. 105-130.

[34] ACI Committee 201.2R-92; *Guide to Durable Concrete Part I: Materials and General Properties of Concrete*, ACI Manual of Concrete Practice, 1994.

[35] Proposed revision of: Guide to durable concrete reported by ACI committee 201. *ACI Mater J,* Vol.88, No. 2, 1991, pp. 544–582.

[36] O.S.B. Al-Amoudi, Rasheeduzzafar, M. Maslehuddin and S.N. Abduljauwad, *Mag. Concr. Res,* Vol.46, 167, 1994, pp. 113–123.

[37] P.K. Mehta; *Cement Concrete Research, Vol.* 3, No.1, 1973, pp. 1–6.

[38] G. Frigione and R. Sersale; *Cement Concrete Research,* Vol.19, No.6, 1989, pp. 885–893.

[39] F.M. Lea; *The Chemistry of Cement and Concrete* 3rd Edition, Ed. Edward Arnold, London, 1970.

[40] G.L. Kalousek, L.C. Porter and E.J. Benton; *Cement Concrete Research,* Vol.2, No.1, 1972, pp. 79–89.

[41] E.R. Dunstan, Jr., *Cement Concrete Research,* Vol.10, No.1, 1980, pp. 20–30.

[42] M. Regourd; *Mater Struct* , Vol.18,1985, pp. 223–226.

[43] G. Wong and T. Poole; *Proc. of Int. Conf. Concrete Durability, ACI SP-100–109*, American Concrete Institute, Detroit, 1987.

[44] *IS: 456-1978, Code of Practice for Plain and Reinforced Concrete,* Bureau of Indian Standards, New Delhi.

[45] T. Miyagawa; *Mag Concr. Res.* Vol. 43, 156, 1991, pp. 155–170.

[46] S. Kumar and C.V.S.K. Rao; *Cement Concrete Research*, Vol.25, No.1, 1995, pp. 1–8.

[47] Noel Mailvaganam; *Chemical Admixtures for Concrete*, Taylor & Francis; 3rd edition, August 4, 1999.

[48] Cement admixtures association/ cement and concrete association; *Superplastics for concrete*, 1975, pp. 88.

[49] Vollick, C.A.; *ASTM SP.Tech.. Publ.,* No. 266, 1960, pp. 182-200.

[50] US Patent, 643 7401960.

[51] Kondo, Y. et al.; *ACI Journal,* Vol. 56, 1959, pp. 299-312.

[52] Morgan, R.D.; *Proc. of the first Australian conference on Engineering materials,* University of New South Wales, 1974, pp. 97-108.

[53] Neville, A.M.; *Properties of concrete*, Pitman, London, 1963.

[54] Nishi, T.;. *Proceedings of the International symposium on admixtures for Mortar and concrete*, Brussels, 1967, pp. 112-117.

[55] Sutherland, A.; *Air entrained concrete. Publication 45 022*, Cement and concrete Association, 1974.

[56] Keene, P.W.; *Technical report TRA 331*, Cement and concrete Association, 1960.

[57] Anon; *ACI bibliography,* No.10, 1970, pp. 1966-70.

[58] Rosenburg, A.M.; *ACI journal*, Vol. 71, 1974, pp. 1261-1268

[59] Shildeler, J. J.; *ACI journal*, No. 48, 1952, pp. 537-59.

[60] Hope, B.B.; *ACI journal,* No.68, 1971, pp. 361-365

[61] http://irc.nrc-cnrc.gc.ca/pubs/cbd/cbd103_e.html

[62] Ohama, Y.; Proc. of the V Asian Symposium on Polymers in Concrete, ASPIC, Sept.11-12, Chennai, India, 2006, pp. 3-11.

[63] Brydson, J.A., *Plastics Materials*, 4th edition, Butterworth Scientific publishers, London, 1999.

[64] Crawford, R.J.; *Plastics engineering*, 3rd edition, Butterworth-Heinemann Publishers, Oxford, 1998.

[65] http://irc.nrc-cnrc.gc.ca/pubs/cbd/cbd158_e.html

[66] Cresson, L.; *British Patent 191, 474*, 1923.

[67] Venuat, M. and Alexandre, J.; *Rev. Mater. Constr.*, 639, 1968, pp. 469.

[68] J.A. Mason; *ACI Publication SP-69*, American Concrete Institute, Detroit, Michigan, 1981.

[69] Dikeou J.T.; *Proc. of Second International Congress on Polymers in Concrete*, Austin, Texas, October, 1978.

[70] Ohama, Y.; *Cement and concrete composites*, Vol. 20, 1998. pp. 189-212.

[71] Wagner, H.B. and Grenley; D.G., *J. of Appl. Polym. Sci.*,Vol. 22, ,1978, pp.813-822.

[72] Crisp, S.Prosser, H.J., and Wilson, A.D.; *J. Mater. Sci.*, Vol. 11, , 1976, pp. 36.

[73] Rodger, S.A., Brooks, S.A., Sinclair, W., Groves, G.W., and Double, D.D.; *J. Mater. Sci.*, Vol.20, 1985, pp. 2853.

[74] Chandra, S., Berntsson, L., and Flodin, P., *Cement Concrete Research*, Vol.11, 1981, pp. 125-129.

[75] Ohama,Y.; *Bosui J.*, Vol.21, No.11, ,1990, pp. 104 (In Japanese)

[76] Volkwein,A., Petri,R., and Springenscmid, R.; *Bet5onwerk Fertigeteil-Tech.*, Vol.54, No.8, 1988, pp. 30 and Volkwein,A., Petri,R., and Springenscmid, R.; *Bet5onwerk Fertigeteil-Tech.*, Vol.54, No. 9, 1988, pp. 72.

[77] Larbi, J.A. and Bijen, J.; *Proc. of 6th Int. Congr. Polymers In Concrete*, International Academic Publishers, Beijing, 1990, pp.185.

[78] Yoshihiko,O; *Proc. of the Third Beijing International Symposium on Cement and Concrete*,Vol.2, 1997, International Academic Publishers, Beijing, pp. 918-923.

[79] Ohama, Y. et al.; *Proc. of the 9th International Cong. on the Chemistry of Cement,* Vol.5, National Council for Cement and Building Materials, 1992, pp. 221.

[80] Schulde, V.F.; *Beton, Herstellung, Verwendung*, Vol.39, No.9, 1989, pp. 377.

[81] Conrad, H.K.; *RILEM International Seminar of Adhesion between Polymers and Concrete (ISAP'89)*, 1989.

[82] Joaoa.R. et al.; *Cement and Concrete Research*, Vol.32, No.3, March 2002, pp. 329-334.

[83] Kim et al.; *Cement and Concrete Research,* Vol.29, No.3, March1999, pp. 407-415.

[84] L.K. Aggarwal, P.C. Thapliyal and S.R. Karade; *Construction and Building Materials,* Vol. 21, No. 2, 2007, pp. 379-383.

[85] Bing Chen and Juanyu Liu, Mechanical properties of polymer-modified concretes containing expanded polystyrene beads *Construction and Building Materials,* Vol. 21, No. 1, January 2007, pp.7-11.

[86] Leisegand, H.; *Plastics,* Vol.27 (297), 1962, pp. 62.

[87] Ohama, Y., Chandra, S.; *Polymers in concrete*, 5th chapter, Noyes Publications, 1994.

[88] Kobayashi, K., and Ito, T.; *Proc. of first Int. Cong. Polymers in concrete*, Construction Press, Lancester, U.K., 1976, pp. 236.

[89] Ohama, Y., IV-1, Improvement of the Quality of concrete, 60. Resistance of resins concretes to rapid freezing and thawing in water, research work for the period, 1st April, 69- 31st march '70, Building research Institute, Tokyo, 1970, 304.

[90] Vipulanandan et al., *ACI Materials Journal*, Vol.87, No.3, May-June 1990, pp. 241-250.

[91] Fowler, D.W, *SP-116*, ACI, Detroit, pp. 129-143, 1989.

[92] Vaidya, U.R. and Nadkarni,V.M., *Indus. And Egg. Chem. Res.*, Vol.26, No.2, 1987, pp. 194-198,

[93] Wang Xinyou et al, *Concrete and Cement Products*, No.1, 13, 1995, pp 8-10.

[94] Gorninski, J.P., Denise C. Dal Molin and Kazmierczak, Claudio S.; Cement and Concrete Research, Vol. 34, No.11, November 2004, pp. 2091-2095.

[95] Pratap, Arun; *Progress in Crystal Growth and Characterization of Materials,* Vol. 45, No. 1-2, 2002, pp. 117-125.

[96] Tazawa, E., and Kobayashi, S., *Polymer conc., ACI spec. Publ., SP-40,* 1973, pp.57.

[97] Steinberg, M. et al, *BNL 50134(T509)*, Denver, 1968.

[98] Chandra S., Justnes, H., Ohama, Y.; Concrete Polymer composites, Polymeric Materials Encyclopedia, Vol. 2C, 1994, pp. 1389-1402.

[99] Lin Tu and Deon Kruger; *Journal of Mechanical Technology*, Specialist Press association, Aug. 1994, pp. 22-26.

[100] Cheng-Hsin Chen, R. Huang, J.K. Wu and Chien-Hung Chen; *Construction and Building Materials*, Vol. 20, No. 9, November 2006, pp. 706-712.

[101] Fowler, D.W.; *Cement and concrete composites*, Vol. 21, 1999, pp. 449-452.

[102] Ohama, Y., *Proc. of Advances in Concrete Technology*, Canada Centre for Mineral and Energy Technology, Ottawa, 1992, pp.775.

[103] Kyu-Seok Yeon; *Proc. of V Asian Symposium on Polymers in Concrete, ASPIC*, Sept. 11-12th, 2006, Chennai, India, pp. 13-28.

[104] Gad, E. A. M., El-Sukkary, M. M. A., Sayed., W. M., Abo-El-Enein, S. A.; *Journal of Chemical Technology & Biotechnology*, Vol.62, No.3, 1995, pp. 310-316.

[105] Liu, Y.-N., Manson, J. A., Chen, W. F., Vanderhoff, J. W.; *Cement and Concrete Composites*, Vol. 27, No.9-10, October-November 2005, pp. 926-933.

[106] Zeldin, L. E. Kukacka, N. Carciello; *Journal of Applied Polymer Science*, Vol. 24, No.7 , 1979, pp.1759 – 1765.

[107] Neelamegam, M., Subrahmanyam, B.V.; *Proc. of the V Asian Symposium on Polymers in Concrete, ASPIC,* Chennai, India, 2006, pp.39-52.

[108] Santhanam, M., *Proc. of the V Asian Symposium on Polymers in Concrete, ASPIC,* Chennai, India, 2006, pp. 71-78.

[109] T. Sebök and O. Strán; *Cement and Concrete Research,* Vol. 34, No. 10, October 2004, pp. 1853-1858.

[110] Swamy, R.N.; *Journal of Materials Science,* Vol. 14, 1979, pp. 1521–155.

[111] Sasse, H.R., *Proc. of first Int. Cong. Polymers in concrete*, 5-7 May 1975, pp. 168-173.

[112] Chandra, S.; *Proc. of 9th Int. Cong. Polymers in concrete*, Bologna, 14-18 Sept. 1998, pp. 245-254.

[113] Justnes, H. et al; *Proc. of 9th Int. Cong. Polymers in concrete*, Bologna, 14-18th Sept. 1998; pp. 225-238.

[114] Ohama, Y.; *ACI Materials Journal,* Vol.84, No.6, 1987; pp. 511-518.

[115] Zhenping Li et al; *Proc. of 6th Int. Cong. Polymers in concrete*, Shanghai, 24-27th Sept. 1990; pp. 193-198.

[116] Larbi, J.A. and Bijen, J.M.J.M.; *Cement and Concrete Research,* Vol.20, No.1, 1990, pp. 139-147.

[117] Rodger, S.A., Brooks, S.A., Sinclair, W., Groves, G.W., and Double, D.D.; *Journal of Mater.*, SCI., Vol.20, 1985, pp. 2853.

[118] Janotka, J. Madejová, L. Stevula and D.M. Frt'alová; *Cement and Concrete Research,* Vol.26, No.11, 1996, pp. 1727–1735.

[119] Su, Zao; *Microstructure of polymer cement concrete*, Doctoral thesis, Deft University of Technology, Deft, 1995, pp. 174.

[120] Afridi, M.U.K.; *Cement and Concrete Composites,* Vol.12, No.3, 1994, pp. 163-173.

[121] Su, Zhao; Larbi J.A. and Bijen J.M.; *Cement and Concrete Research,* Vol.21, No.6, 1991, pp. 983-990.

[122] Bijen, J.M. and Su, Z.; *Proceedings of the technical committee TC-113, Symposium on properties and test methods for concrete-polymer composites*, Oostende, 3-5 July 1995, pp. 19-27.

[123] Ohama, Y.; *Handbook of Polymer modified concrete and mortars, properties and process technology*; Noyes Publication, 1995.

[124] Puterman, M. and Malorny; *Proc. of 9th Int. Cong. Polymers in concrete,* Bologna, 14-18th Sept. 1998, pp. 165-178

[125] Isengerg, R.L. and Vander Hoff, J.W.; *Am. Chem. Soc. Polymer reprints*, Vol.14, No. 2, 1973, pp. 1197.

[126] Semerand, E. et al; *Proc. of 5th Int. Cong. Polymers in concrete*, Brighton; 22-24 Sept.1987; pp. 223-228.

[127] Lutman, M. et al; *Proc. of 9th Int. Cong. Polymers in concrete*, Bologna, 14-18th Sept. 1998, pp. 239-243.

[128] Bell, R.L. and Dingley, R.G.; *Proc. of 1st Int. Cong. Polymers in concrete*; 3-5 May 1975, pp. 162-167.

[129] Dingley, R.G.; *Dissertation, University of Southhampton,* in Microstructure of polymer cement concrete by Su; 1974.

[130] L.K. Aggarwal, P.C. Thapliyal and S.R. Karade; *Construction and Building Materials*, Vol. 21, No. 2, February 2007, pp. 379-383.

[131] Bing Chen and Juanyu Liu; *Construction and Building Materials*, Vol. 21, No.1, January 2007, pp. 7-11.

[132] Nutt, W.O.; *British Patent 1,065,053,* April 12 1967.

[133] Yun,K.K., Lee, J.H., Choi, S.L., Kim, K.H.; *J of Korea Concrete Institute*, Vol. 13, 2001, pp. 507-515.

[134] Jeon, C.S. et al; *Proc. of Korea Concrete Institute*, Vol.11, 1999, pp. 355-400.

[135] Jo, B.W. et al; *Journal of Korea Concrete Institute*, Vol. 17, 2005, pp. 335-342.

[136] Zhong, S., Chen; Z., *Proc. of 5th Asian Symposium on Polymers in Concrete,* Chennai, India, 2006, pp. 29-38.

[137] Ma, J. et al; *Journal of Gansu Science and Technology,* Vol.21, No.12, 2005, pp. 101-104.

[138] Wang, P. et al; *New building materials*, Vol. 1, 2005, pp. 32-36.

[139] Verma, S.K.; *Proc. of the Symp. on Advances in Polymeric building materials*, Roorkee, India, 2003, pp.1-4.

[140] Ganesan.N and Shivananda K.P; *Journal of Structural Engineering,* Vol. 27, No.2, July 2000, pp. 111-116.

[141] Gemert, D.V. and Knapen, E.; *Proc. of 5th Asian Symposium on Polymers in Concrete,* Sept.11-12, Chennai, India, 2006, pp. 61-70.

[142] Plastics Europe; *Proc. of the 10th Int. Cong. On Polymers in Concrete,* Hawai, USA, 2004.

Chapter 2

CEMENT COMPOSITES OF THERMOPLASTICS AND RUBBERS

2.1 Introduction

Both thermoplastics and rubbers constitute an important class of synthetic materials used in a wide variety of applications. In the building and construction sector, they are used to make light structural and decorative components and in civil engineering applications as adhesives, modifiers and matrix materials. Cement composites of thermoplastics and rubbers are used to increase the durability of the concrete structures that are exposed to chemical pollution. In general, thermoplastic lattices have greater strengthening effects on the mortars then elastomeric lattices [1].

A description of the thermoplastics and rubbers used in the current work and procedures for mixing and testing together with the results of macroscopic studies carried out are presented in this chapter.

The polymers used for this study are broadly categorized as -

(i) Thermoplastics

This category of polymers was studied under two sections –

a Water soluble polymers and
b Emulsions.

The water-soluble polymers used in the present study were (1) polyvinyl alcohol (PVAL) and (2) two different molecular weights of polyethylene glycol (PEG). The polymer emulsions used were polyvinyl acetate (PVAC), acrylic polymer (PA) and acrylic styrene polymer (AS). Water insoluble compounds formed by combining PVAL with borax (PVA-B) as also PVAL with phenol formaldehyde resin (PF-PVAL) were added separately to cement pastes and the leachability of these composites on exposure to water was studied.

(ii) Rubbers

These were studied under two sections

a Lattices and

b Solid rubbers.

The lattices used were natural rubber (NR), styrene butadiene rubber (SBR) and nitrile rubber (NBR). In the class of solid rubbers, composites of uncrosslinked linear nitrile rubber (L-NBR) were investigated.

2.2 Materials and specifications

2.2.1 Portland cement

Portland cement used for the preparation of these composites had the following specifications:

Brand: Ramco Cements Super, India.

Fineness = 361 m^2/kg

Normal consistency = 33%

Setting time (min): Initial = 70

Final = 160

Soundness:

Le Chatelier expansion = 0.50mm

Autoclave expansion = 0.03%

Chloride content = 0.013% by mass

Insoluble residue = 22.01% by mass

Magnesia = 0.84% by mass

Sulphuric anhydride = 2.79% by mass

Total loss on ignition = 2.44% by mass

2.2.2 Thermoplastics

The specifications of the thermoplastics used are given below.

a. Polyvinyl alcohol

Supplied by Central Drug House, Mumbai, India.

Molecular weight = 14,000

Appearance: Dense, white flakes

Viscosity of 4% aqueous solution ~ 4-6 cps

Ash = max 1%

b. Polyvinyl acetate

Supplied by Pidilite India Limited, Mumbai, India.

Emulsion in Water

Total solids content (TSC) = 50%

c. Polyethylene glycol

Two different samples of polyethylene glycol supplied by Loba chemie Indoaustranal Company, Mumbai, India.

(i) Mol. wt. = 3500-4000

Hydroxyl no. = 25-32

Melting range = 54°-58° C

(ii) Mol. wt. = 5000-7000

Hydroxyl number = 16-32

Melting point = 55°-62°C

d. Acrylic polymer-ASC 261

Supplied by Rohm and Hass Company, Mumbai, India.

Total solids content (TSC) = 50%

e. Acrylic-Styrene polymer-AS 398

Supplied by Rohm and Hass Company, Mumbai, India.

Total solids content (TSC) = 50%

f. Borax

Sodium borate decahydrate $Na_2B_4O_7.10\ H_2O$

2.2.3 Rubbers

The rubbers employed for the study were in the form of lattices and solids.

a. Lattices:

The SBR and NBR lattices were supplied by Apar Industries, Mumbai, India.

(i) SBR

Total Solids Content (TSC) = 42-46%

pH = 9.6

Viscosity = 50 cps with Brookfield viscometer

Surface tension = 37 at 50°C

Anionic type stabilizer was used.

(ii) NBR

Total Solids Content = 48-52%

pH = 8.5-10

Viscosity = 100 cps with Brookfield viscometer

Surface tension = 36-43 at 50°C

(iii) Prevulcanised NR Latex

Details is given in Section 2.3.1 b)

b. Solids

Uncrosslinked linear NBR Spheres

Supplied by Apar Industries Ltd., India.

Grade: P6422C

Acrylonitrile = 33%

Linear Structure

Mooney Viscosity ML(1+4)100°C = 80

Partition Agent = $CaCO_3$

Median Particle Size = 40

Sp. Gravity = 1.0

Ash (%) = 7 ± 2

2.3 Polymer Cement Formulations

This section deals with the formulations for the prevulcanisation of rubber lattices and the procedures employed for the preparation of cement composites of thermoplastics and rubbers.

2.3.1 Rubber latex prevulcanisation and mixing

a. **Prevulcanised NBR was prepared in the laboratory using the following formulation.**

NBR latex = 200g

10% KOH = 5

Vulcastab = 2.5

10% Pottassium oleate = 5

Zinc oxide = 3

ZDC = 3

ZMBT =1

Sulphur = 3

Dry rubber content = 50g in 100g of latex

Initially the dry rubber content of the NBR latex was determined. Vulcanising chemicals were mixed in water and dispersed in porcelain containers with porcelain pebbles using ball mills. Sulphur was ball-milled for 72 hours and the rest of the chemicals for 48 hours at room temperature to get a stable dispersion. These dispersions were then added to the latex in appropriate proportions shown above. This mixture was prevulcanised by heating it to 60°C for half an hour with continuous stirring at the rate of 30 rpm.

b. **Prevulcanised NR was prepared in the laboratory using the following formulation.**

60% NR Latex = 167

10% KOH = 1.0

20% VL = 0.5

10% K Oleate = 0.5

50% ZnO = 0.5

50% ZDC = 1.5

50% Sulphur = 2.0

The latex to be prevulcanised was sieved through a 60 mesh sieve and deammoniated to 0.2% (w/w) of the latex. The dry rubber content was determined and the correct quantities of vulcanising dispersions were added to it. The latex was cured at 55°C for 2 hours with continuous stirring. The completion of vulcanisation was determined by coagulating a sample with 5% formic acid and noting the condition of the coagulam.

Table 2.1 Proportions of the components for cement composites of latex

% of rubber in cement	Weight of the cement (g)	Weight of rubber latex taken (g)
2.5	200	10
3.75	200	15
5	200	20
6.25	200	25
7.5	200	30

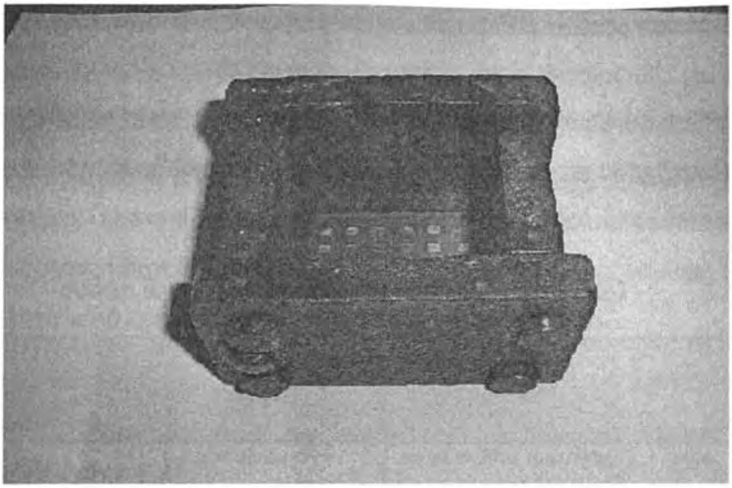
The latex cement composites were prepared in five percentages of latex in cement viz. 2.5, 3.25, 5, 6.25, 7.5 as shown in Table 2.1. At percentages higher than 7.5 the latex showed a tendency to coagulate in the alkaline cement matrix. The W/C ratio for all the composites was maintained at 0.325. The amount of water calculated included the water present in the latex.

Table 2.2 Formulations of cement composites of rubbers

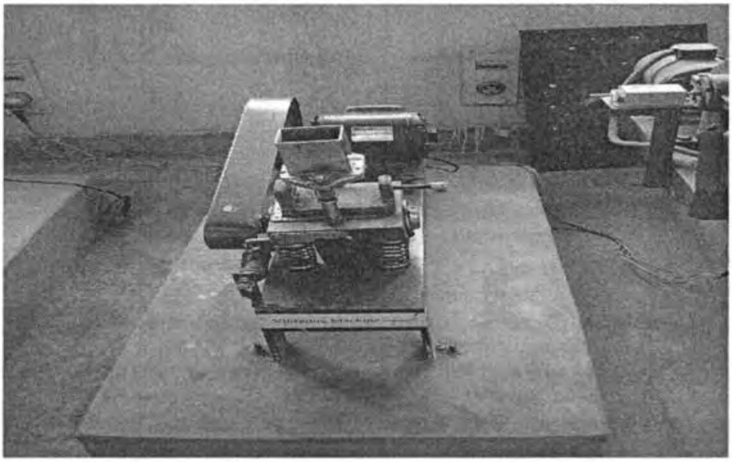
Components	Chemicals	Types	Percentage by weight of cement depending on the total solids content in latex
Rubber latex	(1) Natural rubber latex	Prevulcanised	2.5 3.75 5 6.25 7.5
	(2) Styrene butadiene rubber latex	Construction grade	2.5 3.75 5 6.25 7.5
	(3) Acrylonitrile butadiene rubber latex	Prevulcanised	2.5, 3.75 5 6.25 7.5
	(4) Linear uncrosslinked Acrylonitrile butadiene rubber		2.5 3.75 5 6.25 7.5
Water		Potable	32.5
Cement	Portland cement	Ordinary Portland cement	100
Accelerator	Calcium chloride	Fused	0.1

Hand mixing was employed to prepare the cement composites of rubbers. As indicated in Table 2.2 a known weight of cement was separately mixed with the latex-water blends to form uniform and homogenous pastes. 0.1% calcium chloride was added to these pastes and blended well.

The pastes were cast into cubical mild steel moulds of dimension 50mm x 50mm x 50 mm shown in Fig. 2.1(a). The moulds used were of mild steel, thick enough to prevent distortion. The compaction was done in a vibration mixer [2].



(a)



(b)

Fig.2.1 (a) and (b) show the mould and the vibration mixer used

Description of Vibrator

The vibrator shown in Fig.2.1 (b) conforms to IS: 10080-1982 and was Lawrence and Mayo make. The vibrating table consists of a vibrator, housing a revolving eccentric shaft supported on four springs. The shaft is coupled to a 2800 RPM motor using a nylon belt on its pulley. The eccentric shaft carries a cubical mould with a base plate and hopper. This arrangement is mounted on a channel base with four adjustable legs. The centre of gravity of the whole vibrator, including the mould, is brought to the centre of the eccentric shaft (or within a distance of 25 mm below it) by means of a balance weight attached rigidly to the frame beneath the base plate. The running speed of the eccentric shaft is 12000±400 rpm. A timer is provided to set the time for running of the machine. The machine is powered by a 230V, 50Hz single phase supply.

The composites were kept at room temperature for 24 hours for the initial hydration of cement particles after which the composites were heated for around 2 hours at 110°C. Subsequently, the samples were immersed in water for a period of 28 days to complete the hydration.

2.3.2 Mixing of cement and thermoplastics

All the cement composites of thermoplastics were prepared in four percentages of the polymer in cement viz. 0.5, 1, 1.5, and 2.0. The W/C ratio was maintained at a constant value of 0.325 to enable comparison of all the composites. In the case of thermoplastic polymers that were available in the form of emulsions the total solids content was determined by heating a definite weight of the emulsion in a hot-air oven at 100°C till a constant weight was attained.

$\%\ \text{Moisture} = (m_w/m_{sample}) \times 100$

m_{sample} = Initial mass of the emulsion taken

m_w = Mass of water in the emulsion

= (Initial mass of the emulsion – Final mass of the emulsion after heating)

In the present study, the water present in the polymer emulsions was about 50%. This was taken into consideration while calculating the W/C ratio.

Tables 2.3 and 2.4 give details of each component utilised for different thermoplastics while Table 2.5 gives mix designs for different thermoplastics.

Table 2.3 Proportions of components for cement composites of water-soluble thermoplastics (PVAL and PEG)

% of polymer	Weight of the cement taken (g)	Weight of the polymer taken (g)	Weight of the water taken (g)
0	200	0	60
0.5	200	1	60
1.0	200	2	60
1.5	200	3	60
2.0	200	4	60

Table 2.4 Proportions of components for cement composites of thermoplastic emulsions (PVAC, PA and PAS)

% of polymer	Weight of the cement taken (g)	Weight of the polymer emulsions taken (g)	Weight of the water taken (g)
0	200	0	60
0.5	200	2	59
1.0	200	4	58
1.5	200	6	57
2.0	200	8	56

Table 2.5 Mix design of thermoplastics modified cement paste

Components	Chemicals	Type	Percentage by weight
Thermoplastic	(1) Polyvinyl alcohol	Solution in hot water	0 0.5 1 1.5 2.0
	(2) Polyethylene glycol (a) Mol. wt. = 3500-4000 (b) Mol. wt. = 5000-7000	Solution in water	0 0.5 1 1.5 2.0
	(3) Acrylic polymer	Emulsion in water	0 0.5 1 1.5 2.0
	(4) Acrylic-styrene polymer	Emulsion in water	0 0.5 1 1.5 2.0
	(5) Polyvinyl acetate	Emulsion in water	0 0.5 1 1.5 2.0
Water		Potable	30
Cement	Portland cement	Fly ash based Portland cement	100
Accelerator	Calcium chloride	Fused	0.1

Polyvinyl alcohol used was of the hot water soluble grade. It was weighed, added to hot water (80°C) and dissolved by stirring over a period of 15 minutes. As indicated in Table 2.3 and 2.4 the amount of water used for preparing the solution was kept constant to ensure a uniform W/C ratio of 0.325. Since this ratio is less than that conventionally employed for ordinary cement (0.4) it results in fewer voids leading to higher strength of the composite [3].

Table 2.5 indicates the mix design parameters for cement composites of thermoplastics. Polyethylene glycol solution was prepared by dissolving it in water at room temperature. Since the TSC of the acrylic and acrylic styrene polymer and PVAC were found to be 50% the weights of the emulsion was taken accordingly. The calculated amount of water was then added to the emulsions so as to maintain the same W/C ratio and homogenised using a mechanical stirrer. This dispersion was then added to the cement during mixing.

2.3.3 Polyvinyl alcohol cement composites

Initially PVAL cement pastes were prepared and their properties evaluated. These cement pastes were mixed separately with borax and phenol formaldehyde resin as given below and their properties were studied. Table 2.6 gives details of all PVAL based composites.

a. PF–PVAL-cement (PFVA) composites:

The quantities of the ingredients are given in Table 2.6. The phenol and formaldehyde were mixed in the ratio of 1:2.75 with 33% sodium hydroxide in water as catalyst and heated to 90°C for 45 min to form the PF resin. A known weight of cement was hand- mixed with a solution of PVAL in water to form a homogenous paste. A pre-weighed quantity of PF resin was blended with the above paste. 0.1% calcium chloride was mixed to this paste until a uniform consistency was obtained. This was cast into cubical mild steel moulds of dimension 50mm x 50mm x 50mm. The compaction was carried out using a vibration mixer [1].

b. Polyvinyl alcohol–borax–cement (PVAL-B) composites:

Borax and boric acid form cyclic esters with PVAL as shown in Fig.2.2. This reaction is extremely sensitive to pH and an insoluble gel is formed at pH values above 4.5-5 [4]. Since it is difficult to mix this gel with cement, the borax solution was added to the cement before adding the solution of PVAL in water. 1% PVAL by weight of cement was later used to prepare the composite.

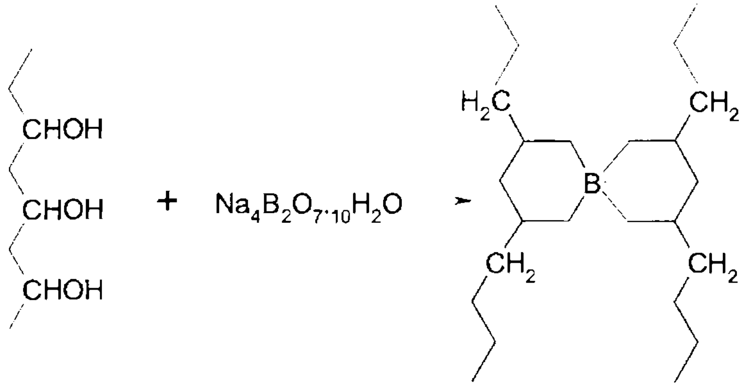


Fig.2.2 Reaction between borax and polyvinyl alcohol

Table 2.6 Formulations of PVAL cement composites

Ingredients	Type	Percentage by weight
Phenol formaldehyde resin	1:2.75	2.5
PVAL solution	Mol. wt. = 14000	1
Portland cement	Fly ash based Pozzolana	100
Accelerator, calcium chloride	Fused	0.1
Borax as saturated solution in water (5.1g in 100ml of water)	--	3 ml

A known weight of cement was hand-mixed separately with 3ml of saturated solution of borax and 5g of PF resin. Table 2.6 shows the formulations of these PVAL cement composites. A 1% solution of PVAL was added to the above blend to form a homogenous paste. 0.1% calcium chloride was mixed to this paste till a uniform consistency was obtained. This paste was cast into cubical mild steel moulds of dimensions 50mm x 50mm x 50 mm. The compaction was performed in a vibration mixer [2].

2.3.4 Curing

The polymer-cement paste cubes thus prepared were kept at room temperature for 24 hours to allow the initial setting of the Portland cement. In the case of the PF resin composites, the samples were heated in a hot air oven at 120°C for 6 hours to facilitate the crosslinking of the phenolic resin. After the samples were annealed to room temperature, they were immersed in water for 28 days to complete the curing of the cement.

2.4 Experimental Techniques

The macroscopic properties evaluated in this study were bulk density, compressive strength and resistance of the cement composites of thermoplastics and rubbers to 1% nitric acid, 1% sodium hydroxide and kerosene.

2.4.1 Bulk density measurements

The bulk density measurements were carried out by determining the weight of the specimen and dividing it by its volume. Measurements were made before and after the hydration of each specimen to determine the change in density during the hydration of the virgin cement and the polymer cement composites. The loss of weight after exposure of these composites to acid, alkali and kerosene environments was also evaluated.

2.4.2 Compressive strength

Compressive strength of hardened concrete is one of the basic properties generally evaluated. The compressive strength of the cement composites of thermoplastics and rubbers was evaluated after curing the samples for 28 days in water. This evaluation of the cubical specimens of 5cm X 5cm X 5cm dimension was performed in accordance with BIS 4031 Part 6 1988 [5]. The maximum load needed to break the polymer cement composite samples was determined using a Universal Testing Machine, Model No. TUNS 1000 of Fine Spavy make.

The cubes were tested by placing them between the two flat steel platens of the testing machine without any packing. The load was uniformly and steadily applied from zero at the rate of 35 N/mm^2/min. The compressive strength was evaluated in N/mm^2 by dividing the maximum load by the cross sectional area of the specimen.

The development of strength during the hydration period was studied by testing the specimens of virgin cement paste and cement composites of SBR, PEG and PVAC at 7, 14, 21 and 28 day intervals after mixing. The samples immersed in water for hydration were removed and dried. The bulk density and compressive strength of these samples were determined within an hour after removal from water.

2.4.3 Chemical resistance

The cured samples of virgin cement paste and polymer cement composites were separately immersed in 1% nitric acid, 1% sodium hydroxide and kerosene for 24 hours at room temperature. These samples were subsequently washed with running water, dried and their mechanical properties determined. The chemical resistance was studied by comparing the percentage retention of mass and compressive strengths of the composites before and after they were exposed to the acid, base and kerosene environments.

Nitric acid was employed for this study since the dissolution of calcium ions in it is higher than other acids like hydrochloric and sulphuric acids. Though it is not as strong as sulphuric acid it is very destructive and causes extensive damage even in the diluted form [6]. Sodium hydroxide was chosen since it is a typical and widely employed alkali.

Kerosene, a mixture of hydrocarbons, was used to test the resistance against deterioration of the composites in an organic environment. Kerosene is obtained from the fractional distillation of petroleum between 150°C and 275 °C and comprises of a mixture of carbon chains containing 12 to 15 carbon atoms.

2. 5 Results and Discussion

This section deals with the inferences and the interpretations arrived at based on the data obtained from the experimental work. It focuses on the macroscopic properties of the polymer cement composites evaluated herein viz. bulk density, compressive strength and resistance to various chemical environments.

2.5.1 Effects of addition of polymers

Polymer modification influences the properties of a fresh concrete mixture as well as the properties of its hardened version. Some effects of polymer addition are reduction in the amount of water required for mixing, higher air entrainment, improved workability and retardation of the cement hydration [7-9]. The first two effects are due to the presence of surfactants in the polymer emulsion. These surfactants also enhance dispersion and workability of the fresh concrete mix. Consequently, porosity and drying shrinkage of the hardened cement concrete decrease. The encapsulation of cement particles by the polymer molecules and the retention of water by the surfactants cause partial or complete retardation of the hydration of the cement.

The modification of the hardened concrete is mainly due to the formation of the polymer film, which results in improved adhesion between the cement particles. The flexural and tensile strengths are also enhanced. The polymer modification also contributes to reduced porosity, bridging of micro fractures and improved bonding between the cement and the aggregates. The presence of the polymer particles prevents the formation of large crystals that are formed during the cement hydration. The distribution and development of the polymer in the cement matrix also contribute greatly to the improvement of mechanical properties of the cement concrete.

2.5.2 Mixing of various polymers with Portland cement

Most polymers were added to the cement either by dissolving in or emulsifying with the water used for the cement mixing.

In this study the maximum percentage of the thermoplastics used was 2%. Beyond this percentage the polymer solution became too viscous and made the mixing a cumbersome process. In case of cement composites of SBR and NBR lattices, at percentages higher than 7.5% coagulation of the latex took place.

Prevulcanised natural rubber latex when added to cement underwent coagulation and formed lumps. The same was observed even when diluted latex. These lumps could not be blended to form a homogeneous mix. The rubber particles being negatively charged [10] coagulation took place due to the following factors -

a Absorption of the water in the latex by the cement for hydration.

b Release of Ca^{2+} ions during hydration

c Dissipation of heat when the water is added to the cement

The linear NBR spheres used in this study had low density. Uniform mixing with cement was thus difficult. The linear NBR spheres bloomed to the surface of the composite especially at higher percentages.

2.5.3 Mechanical properties

This section deals with the performance of the composites on application of load and their resistance to damage when exposed to external chemical environments.

a. Bulk density

Bulk density was measured to find out the change in density before and after hydration. During the curing of cement paste, the matrix becomes denser due to the formation of various hydration products. Hydration is a continuous process. The rate of hydration is high in the initial period but decreases with time. On the contrary, in the case of polymer modified cement, hydration proceeds gradually due to the formation of the polymer film around the cement particles.

Table 2.7 Bulk density after 7,14,21,28 days of hydration before and after immersion in water

	Cement in kg/m^3		SBR in kg/m^3		PVAC in kg/m^3		PEG in kg/m^3	
No. of Days	Before*	After	Before*	After	Before*	After	Before*	After
7	2023.82	2145.36	1777.32	1864.10	1970.95	2062.75	2049.74	2145.87
14	1934.40	2050.00	1759.73	1823.13	1990.41	2073.97	2037.08	2137.20
21	1996.70	2131.34	1773.92	1883.74	1957.01	2070.82	1986.25	2106.78
28	2013.70	2116.55	1788.97	1882.80	1992.79	2119.10	2013.79	2116.55

*Measurements were taken within 24 hours after mixing

Table 2.7 and Fig.2.3 show density variations for some polymer composites as hydration proceeds. Values are given for density values after 7, 14, 21 and 28 days of hydration.

In the case of virgin cement paste, the percentage increase in bulk density is high in the first 7 days [11] after which there is no significant change till 14 days. The initial increase in the rate of cement hydration after mixing is due to the formation of the hydration products of C_2S and C_3S in the early stages and hydration of C_3A and C_4AF at the later stages.

In all the composites studied, an initial 4.5- 6% increase in bulk density in the first 7 days was observed. The presence of the polymer causes a slow increase of density in the polymers containing samples [12]. The rate of increase in density is somewhat steeper in the case of these composites after 7 days. In the period from 7 to 21 days the hydration has taken place in spite of the polymer film around the cement particles.

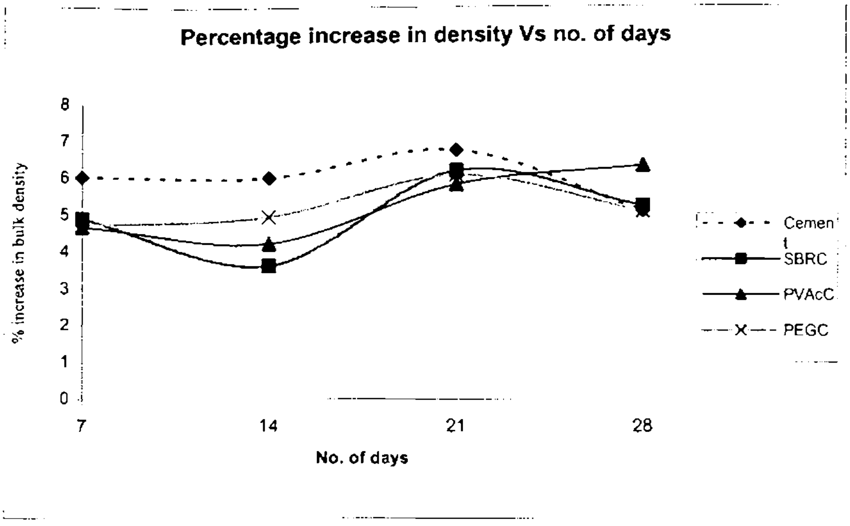


Fig.2.3 Percentage increase in density Vs no. of days of hydration

SBR and PVAC emulsions contain surfactants which have presumably enhanced the air entrapment. Hence the slightly lower values of bulk density for these cases. Table 2.8 gives density changes undergone during cure of different polymer composites.

Table 2.8 Density values in kg/m^3 before and after the hydration and the % increase in the density for:

(i) Thermoplastics

% of Polymer	ACRYLIC			AS			PEG-A			PEG			PVAC		
	BEFORE	AFTER	% INCREASE	BEFORE	AFTER	% INCREASE	BEFORE	AFTER	% INCREASE	BEFORE	AFTER	% INCREASE	BEFORE	AFTER	% INCREASE
0	1996.62	2104.57	5.41	1996.62	2104.57	5.41	1996.62	2104.57	5.41	1996.62	2104.57	5.41	1996.62	2104.57	5.41
0.5	1958.20	2027.90	3.56	1818.97	2055.69	10	2037.42	2077.54	1.97	1989.39	2101.08	5.61	2035.80	2079.32	2.14
1	2063.60	2126.49	3.05	1918.93	2100.00	9	1987.35	2094.11	5.37	2075.33	2146.30	3.42	2050.00	2107.12	2.79
1.5	2018.04	2077.79	2.96	1785.40	1880.00	5	2048.04	2127.43	3.88	2056.97	2127.26	3.42	1879.66	1973.58	5.00
2	1958.20	2070.14	5.72	1875.15	1959.00	5	1964.32	2075.84	5.68	2037.08	2108.82	3.52	1907.20	1998.40	4.78

(ii) Rubbers

% of polymer	NBR			SBR			NBR SPHERES		
	BEFORE	AFTER	% INCREASE	BEFORE	AFTER	% INCREASE	BEFORE	AFTER	% INCREASE
0	1996.62	2104.57	5.40	1996.62	2104.57	5.40	1996.62	2104.57	5.40
2.50	1769.67	1882.12	6.35	1762.36	1780.81	1.05	1945.53	1979.19	1.73
3.75	1696.66	1806.39	6.47	1761.17	1800.00	2.20	2023.39	2074.27	2.51
5.00	1705.16	1827.04	7.15	1771.97	1809.62	2.13	1923.94	1944.09	1.05
6.25	1770.78	1879.74	6.15	1692.49	1720.80	1.67	1776.90	1835.97	3.32
7.50	1732.70	1817.02	4.87	1785.06	1815.74	1.72	1755.31	1806.31	2.91

i. Thermoplastics

Polyvinyl acetate, acrylic polymer and acrylic styrene polymers were added to the cement as emulsions. These contained surfactants as emulsifiers that entrapped air during mixing with the cement. This resulted in decrease in the percentage increase in density of the composite in many cases as seen in Table 2.8 (i). In the case of a water-soluble polymer such as polyethylene glycol, the molecular weight has an influence on its reaction with the Ca ions in the cement [13]. The polymer with lower molecular weight forms coordinate bond with the Ca ions thereby forming a denser network of the polymer cement matrix leading to greater density.

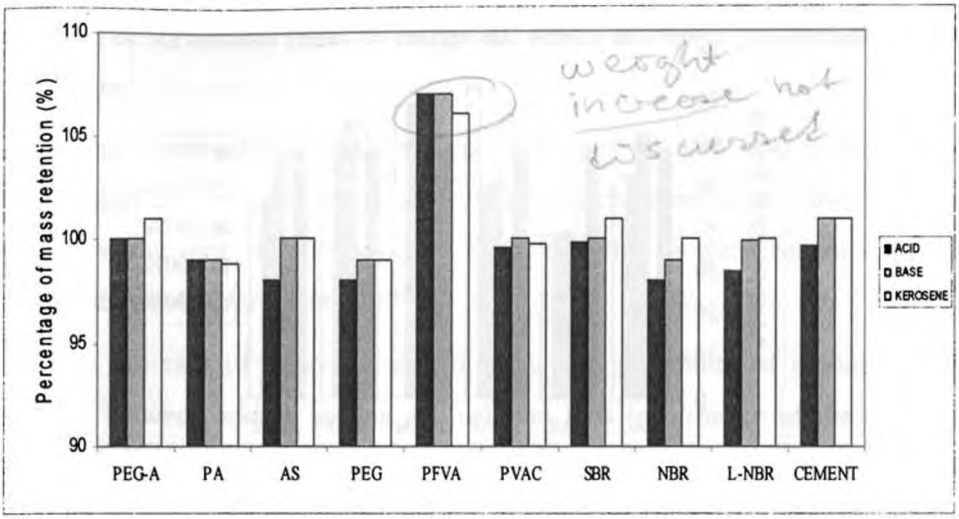
ii. Rubbers

Among the rubber lattices, the percentage increase in bulk density as indicated in Table 2.8 (ii) is more in the case of the NBR than SBR. This may be attributed to the fact that the NBR latex is prevulcanised [14]. The low density of the linear uncrosslinked NBR spheres does not contribute to the overall density of the composite. This may be due to air entrapped during mixing or blooming of some of the spheres on the surface.

b. Surface erosion

Exposure of cement concrete to external chemical environments results in interactions between the two phases and formation of microcracks and progressive scaling of the outer layers. This surface erosion results in loss of weight of the structure.

In this study, the composites were exposed to 1% nitric acid, 1% sodium hydroxide and kerosene.



weight
increase not
discussed

Fig.2.4 % Mass retention after exposure to chemical environments

From Fig.2.4 it is seen that polymer modified cement pastes have undergone minimum weight change on exposure to chemicals. This may be due to the sealing of the pores and voids by the polymer which possibly prevents the entry of external chemicals into the polymer cement matrix thereby inhibiting chemical interactions. These results indicate resistivity of the composite against deterioration when exposed to polluted environments [15].

c. Compressive strength

From the studies carried out herein, it has been found that the load bearing capacities of cement composites of thermoplastics are superior to that of rubbers and thermosets.

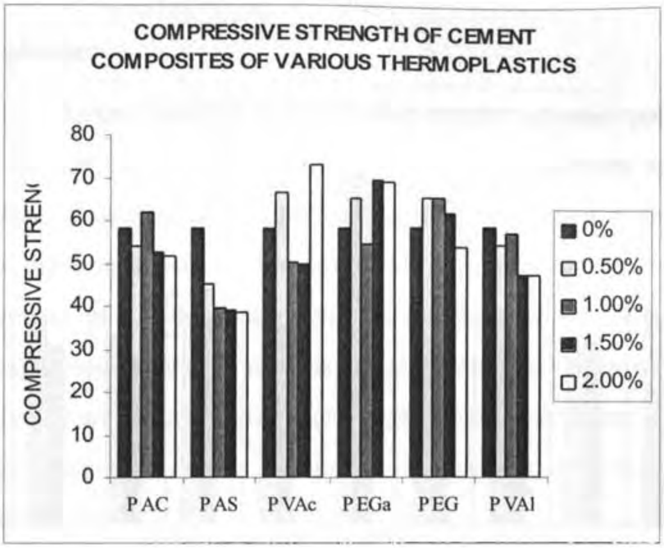


Fig.2.5 Compressive strength of cement composites of various thermoplastics for different P/C percentages

Fig.2.5 shows the compressive strengths of the various composites. This graph reveals that in most of the thermoplastic polymers used, after an initial increase in compressive strength there is a marginal decrease at higher percentages of P/C. This is probably due to the decrease in the rate of hydration of cement particles which in turn is because of the presence of the polymers in the cement-polymer matrix. Further, except for PAS and PVAL, there is a marked improvement in compressive strength due to addition of the polymer.

The minimum film forming temperatures of thermoplastics are generally less than or equal to room temperature [7]. Therefore, the polymer particles coalesce to form a film around the cement particles [16,17]. This film either retards or prevents the percolation of water to the cement particles thereby decreasing or preventing hydration. The thickness of the film and its permeability to water molecules depend mainly on the type and percentage of the polymer used [18].

Polyvinyl acetate, lattices of SBR and NBR, acrylic and acrylic styrene polymers were added to the cement as polymer dispersions in water. In polymer dispersions, the surfactants hold the water needed for hydration more compactly since their hydrophilic parts are partially bound to the water molecules. The presence of surfactants tends to entrap air, which decreases the strength of the composite.

The water-soluble polymers viz. polyvinyl alcohol and polyethylene glycol used for the preparation of polymer cement composites seem to have bonded to the water by the hydrogen bonds resulting in water retention in the matrix just as cited by Gemert [19].

In the case of polyvinyl acetate there is a possibility of saponification reaction between acetate groups and calcium ions in presence of the alkaline cement medium [20]. This interaction may be the real cause that enhances the strength of the composite at 2% P/C ratio. It is known that at lower molecular weights polyethylene glycol forms coordination compounds with Ca^{2+} ions [13] and also increases the workability of the mix by acting as a lubricant [21]. For molecular weights higher than 6000 (i.e. PEG-A in the graph) PEG induces the nucleation of calcite crystals. This could be one of the positive factors that contribute to strength performance of the composite.

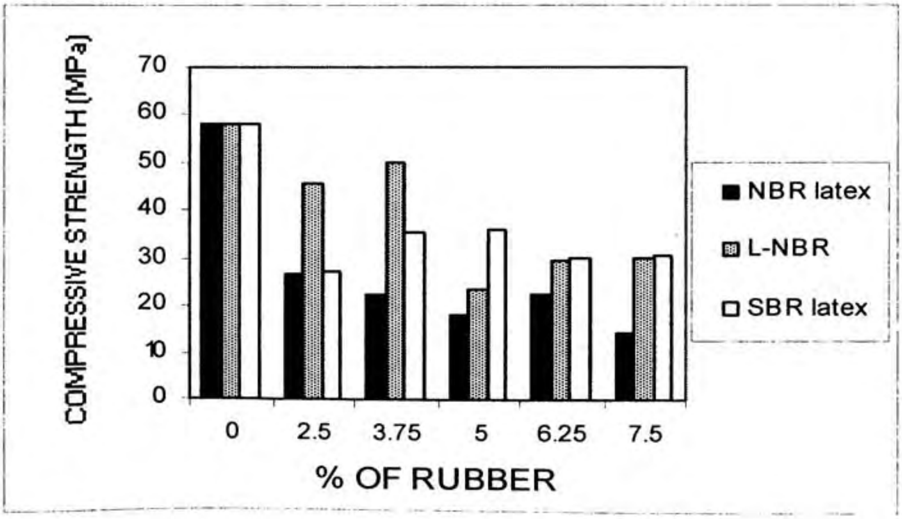


Fig.2.6 Compressive strength of cement composites of rubber

As seen in Fig.2.6, the compressive strength of the cement composites of rubber lattices is lower than that of virgin cement. The polymer lattices contain surfactants that entrap air during its mixing with cement. Some of these air voids remain in the matrix even after compaction with vibrator. Though air voids decrease the strength of the cement, they contribute to its durability during the freeze thaw cycles. This is because the air voids help to decrease the damage caused during expansion and contraction.

Since the minimum film forming temperature of rubbers is below room temperature the rubber particles coalesce to form a film around the cement particles. As the hydration proceeds with time the thickness of the film increases thereby reducing the permeation of water through the film to the cement particles.

In the case of linear NBR spheres, the compressive strength initially increases at lower percentages and then decreases at higher P/C percentages. This could be because the polymer particles behave as ball bearings that no doubt help to improve workability but also introduce microvoids in the matrix [22, 23]. These microvoids reduce the properties of the composite.

Among the polymer lattices, SBR forms better cement composites than NBR though it is a non-polar rubber. Referring to Fig.2.4, the compressive strength of SBR cement composites is superior to the NBR cement composites. The strength reaches a maximum at around 5% after which it decreases gradually. It may be surmised that the minimum percentage required for the formation of a film around the cement particles may be around 5% by Moshe as indicated in_[18]. The gradual decrease may be due to the polymer envelope around the cement particle which cuts off the supply of water required for hydration. It may also be observed that the compressive strength of NBR cement composites is less than that for both virgin cement and its composites with SBR.

d. Strength development of various polymer cement composites

The polymer composites studied in this part were SBR, PVAC and PEG. The properties of these composites were compared with those of virgin cement.

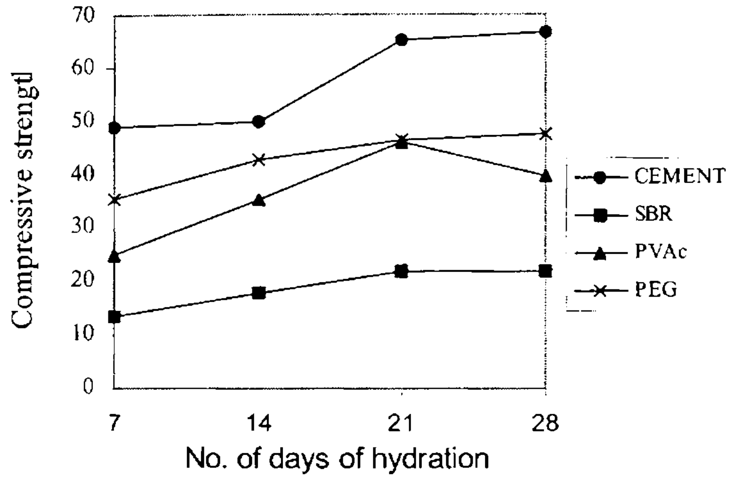


Fig. 2.7 Development of strength of cement and its composites with polymer

Fig.2.7 shows the percentage increase in strength development of cement composites of various polymers in terms of compressive strength at regular intervals during hydration.

Referring to Fig.2.7, the variation of strength as cure proceeds is broadly similar in all the cases studied. The strength also follows a similar pattern as that of density (Fig. 2.1) in the case of cement and polyvinyl acetate while in the other two cases viz. cement composites of SBR and PEG, the increase is gradual throughout the hydration. Compressive strengths in the case of PEG and PVAC are much higher than that of SBR based samples. This can be attributed to a greater probability of chemical interaction between PEG and cement and PVAC and cement [13, 20]. In the case of PVAC ther e is a possibility of a chemical interaction with cement, which is explained, in Section 4.3.1 in Chapter IV. SBR has only limited possibility for interaction with cement due to the diene structure of butadiene.

Build up of strength after the 14th day is rapid in the case of both virgin cement and PVAC. This goes to show that PVAC does not form an inhibiting polymer film around the cement particles at lower P/C percentages. Possible chemical interactions between cement and PVAC may also be responsible for this. PEG makes water accessible to cement for hydration at all stages. This could be possibly the reason for the smoothness of the curve. SBR is seen to be a poor candidate for modification of cement from the strength values obtained.

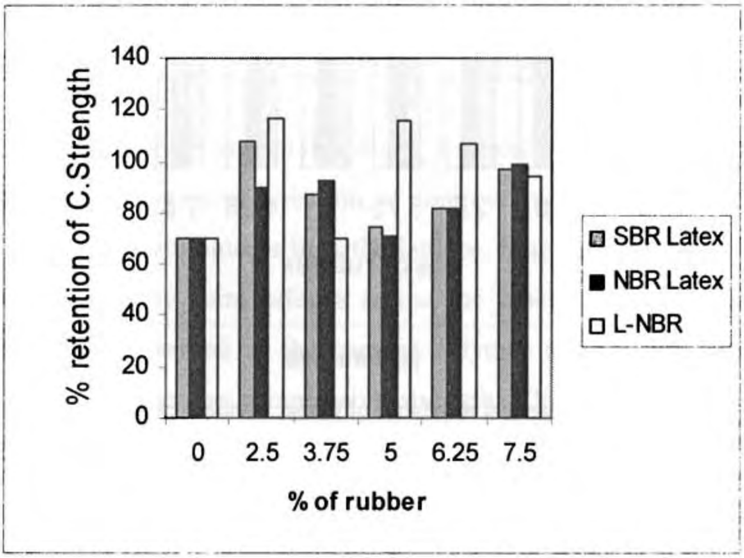
2.5.4 Chemical resistance

Durability of concrete structures is one of the most outstanding problems due to increasing environmental pollution. Many admixtures are being employed to increase their durability. Polymers are one of the materials used to decrease the porosity in the cement matrix thereby preventing the external chemicals from interacting with the cement particles. In this study polymer composites of cement pastes were exposed to acidic, basic and kerosene environments and the chemical resistances of these composites were evaluated based on the degree of retention of compressive strength. This study gave an estimate of the applicability of the composites to structures that may be exposed to chemical environments like refineries, chemical silos, floorings of cattle houses and chemical laboratories and effluent drains.

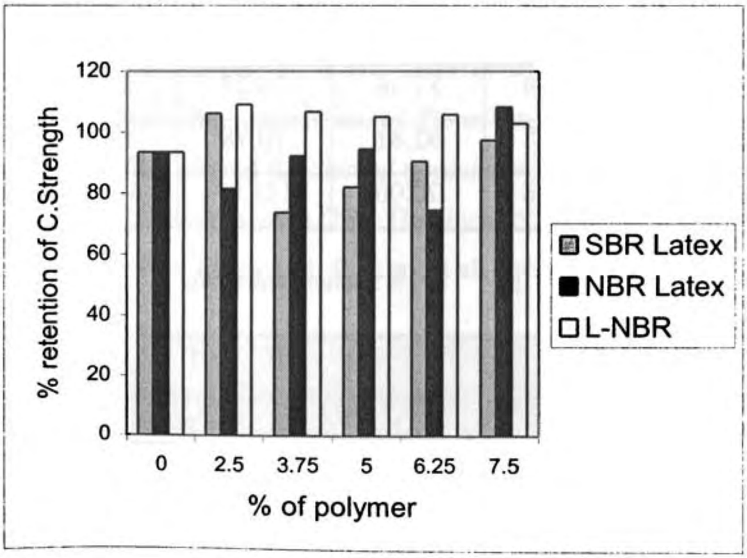
In this study the chemical resistance was evaluated by calculating the percentage retention of compressive strength after immersion of the composites in each of acid, base and kerosene. These values were compared with the values obtained for virgin cement pastes.

(i) Rubbers

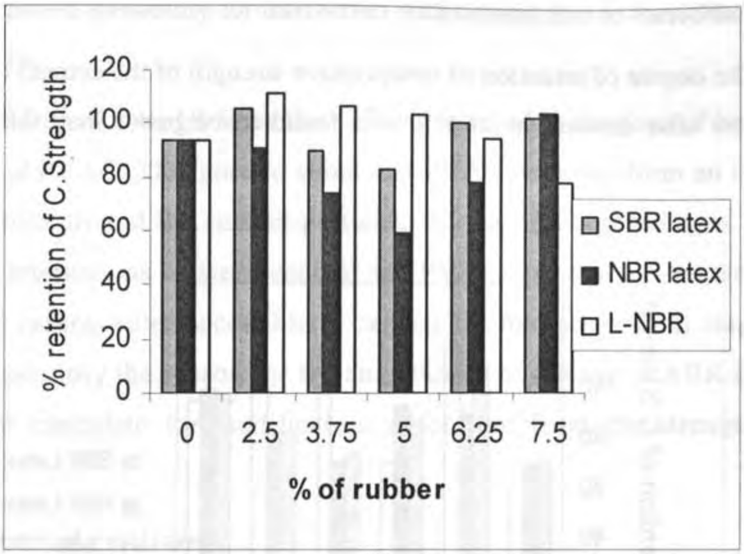
The degree of retention of compressive strength of the cement composites of rubbers after immersion in acid was found to be better than that of virgin cement.



(a) In acid



(b) 1% sodium hydroxide



(c) Kerosene

Fig.2.8 Chemical resistance of rubber modified cement paste

Table 2.9 Degree of retention of compressive strength of cement composites of rubbers

(a) In 1% nitric acid

Rubber	P/C (%)				
	2.5%	3.75%	5%	6.25%	7.5%
SBR	107.69	87.06	74.27	81.94	96.55
NBR	90.07	92.81	70.78	81.46	98.83
Linear NBR	116.36	70.00	116.07	107.14	94.44

(b) In 1% sodium hydroxide

Rubber	P/C (%)				
	2.5%	3.75%	5%	6.25%	7.5%
SBR latex	106.15	73.53	81.87	90.28	97.24
NBR latex	81.37	92.05	94.34	74.22	108.19
L-NBR	109.09	106.67	105.04	105.71	102.78

(c) **In kerosene**

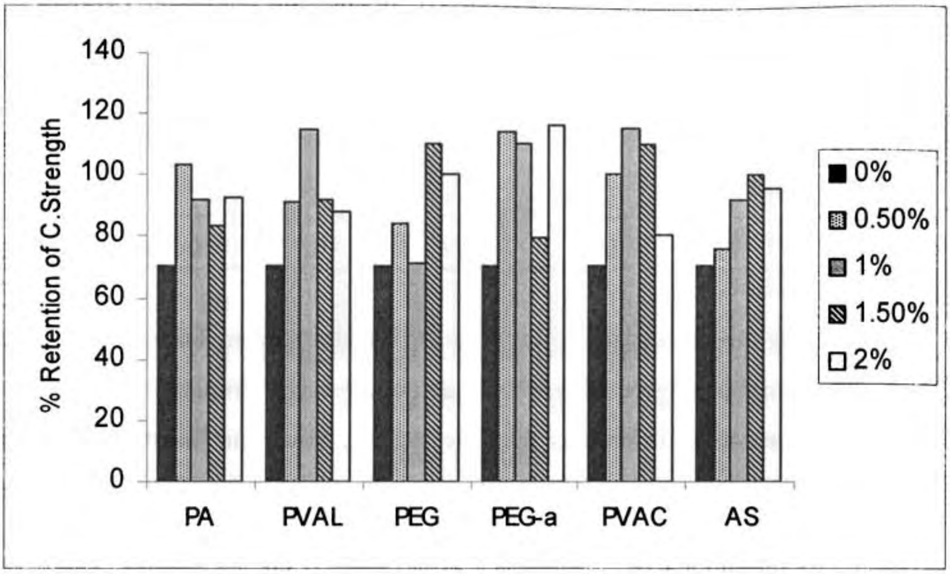
Rubber	P/C (%)					
	0	2.5	3.75	5	6.25	7.5
SBR	93.48	105.38	90.00	82.46	100.69	102.07
NBR latex	93.48	90.38	73.49	58.95	77.77	104.70
L-NBR	93.48	110.91	106.67	103.57	94.29	77.78

Among the rubbers used in this study, it is noted from Table 2.9 that linear NBR has a higher degree of retention of compressive strength on exposure to external chemical environments than the lattices. Since the linear NBR spheres are uncrosslinked they form bridges across the cracks formed in the cement matrix. This was observed in the cement polymer matrix after breaking the specimen to determine the compressive strength. This also contributes to the superior strength of these cement composites.

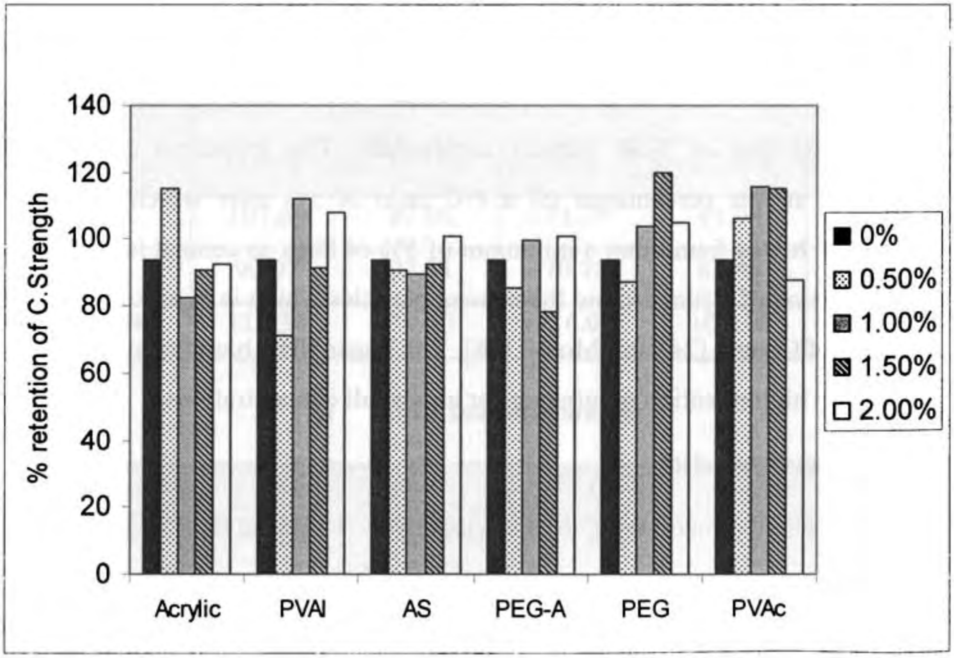
From Fig.2.8 it is inferred that among the rubber lattices used for this study, NBR latex enhances the resistance of the composites to 1% sodium hydroxide. The resistance of these composites to acid and kerosene is however lower than that of SBR cement composites. The resistance to chemicals decreases at low percentages till a P/C ratio of 5% after which it gradually increases. It was found that a minimum of 5% of latex in cement is required for the formation of a film around the cement particles which is in accordance to the theories of Ohama [24] and Moshe [18]. The linear NBR based composites show uniformly high retention of strength for almost all concentrations.

(b) Thermoplastics

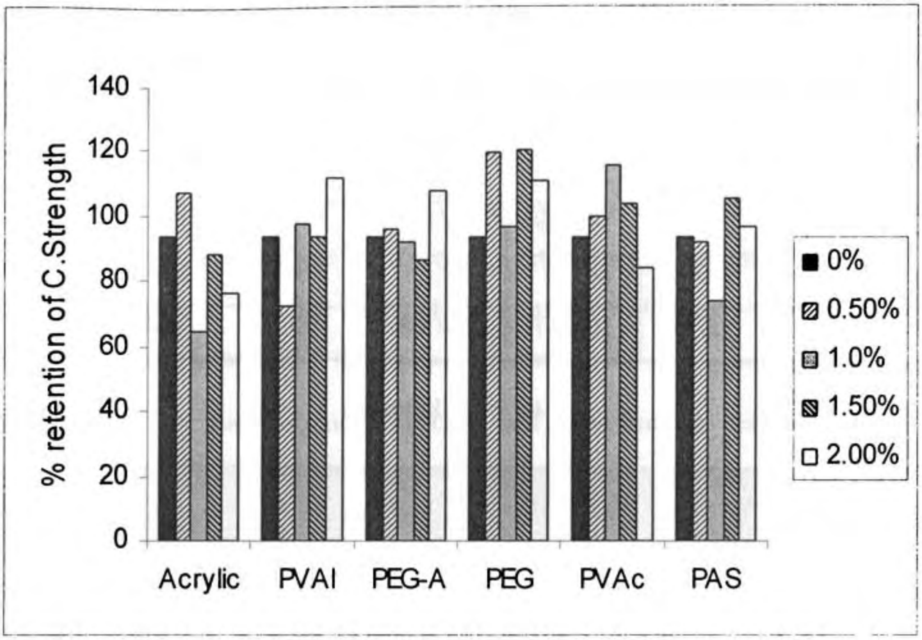
As already mentioned, the thermoplastics studied in this work, PAVL and PEG are water-soluble polymers while the others were added in the form of emulsions. Figs. 2.9 (a), (b) and (c) and Table 2.10 (a), (b) and (c) show the percentage of retention of compressive strengths when the samples were immersed in 1% nitric acid, 1% sodium hydroxide and kerosene.



(a) 1% nitric acid



(b) 1% sodium hydroxide



(c) Kerosene

Fig.2.9 Chemical resistance of thermoplastics modified cement paste

Table 2.10 Degree of percentage retention of compressive strength of cement composites of thermoplastics

(a) In 1% nitric acid

% of polymer	Acrylic	PVAL	PEG	PEG-A	PVAC	AS
0%	70.17	70.17	70.17	70.17	70.17	70.17
0.5%	103.39	91.07	84.51	114.07	100.00	76.09
1.0%	91.95	114.50	71.52	110.14	115.70	91.67
1.5%	83.33	92.00	110.10	79.36	110.00	100.00
2.0%	92.74	88.36	100.02	116.45	80.00	95.70

(b) In 1% sodium hydroxide

% of polymer	Acrylic	PVAL	AS	PEG A	PEG	PVAC
0.00	93.48	93.48	93.48	93.48	93.48	93.48
0.50	115.38	71.39	90.88	85.68	87.32	106.25
1.00	82.55	112.39	89.47	99.85	104.10	115.70
1.50	90.48	91.51	92.55	78.25	120.04	115.00
2.00	92.74	108.17	101.08	100.73	104.71	88.00

(c) In kerosene

% of polymer	Acrylic	PVAL	PEG-A	PEG	PVAC	PAS
0	93.48	93.48	93.48	93.48	93.48	93.48
0.5	106.71	72.31	95.91	119.90	100.00	91.75
1	64.16	97.71	92.20	97.06	115.70	73.68
1.5	88.10	93.63	86.54	120.00	104.17	105.32
2	76.61	111.66	107.88	110.96	84.00	96.77

Referring to Fig. 2.9 most of the polymers show a slight decrease in the chemical resistance properties till a certain percentage beyond which the same increases. This may be due to the fact that the polymers act as cement admixtures at lower percentages while after a certain percentage they coalesce at the surface of the cement particles to form a film. This film may be responsible for sealing the micropores and bridging the microcracks in the cement matrix.

According to Gemert [19], water-soluble polymers form a film around the cement particles at percentages lower than the conventional P/C ratio of 5% applicable to polymer emulsions. This film prevents the external chemicals from interacting with the cement particles thereby increasing the durability of the composite.

PVAC cement paste exhibits better properties than the other thermoplastics used in this study because it undergoes saponification in the alkaline cement medium forming calcium salt of the acetate ions from $Ca(OH)_2$ as explained in Section 4.3.1. $Ca(OH)_2$, a by-product of the cement hydration reaction is chiefly responsible for the deterioration of the cement structures as it undergoes reactions with the external environment and forms water leachable salts. This results in cracks in the composite matrix.

Acrylic styrene polymer forms a self crosslinking network at room temperature. PEG also undergoes interaction with the Ca ions when its molecular weight is below 5500 [13].

(iii) Polyvinyl alcohol based cement composites

PVAL is widely used in dry wall joint cements, stucco finishes, thin bed tile mortars and cement paint. It improves water retention and promotes bonding but the polymer can get leached on exposure to water resulting in poor durability of the structures [25].

This part presents results of studies done on PVAL cement composites containing -

a Only polyvinyl alcohol,

b Polyvinyl alcohol and phenol formaldehyde resin (phenol formaldehyde, a thermoset resin forms a three dimensional network in the polymer cement matrix thereby preventing the leaching of PVAL) and

c Polyvinyl alcohol and small amounts of borax (The formation of an insoluble gel in the presence of borax prevents the leaching of the polymer when exposed to water).

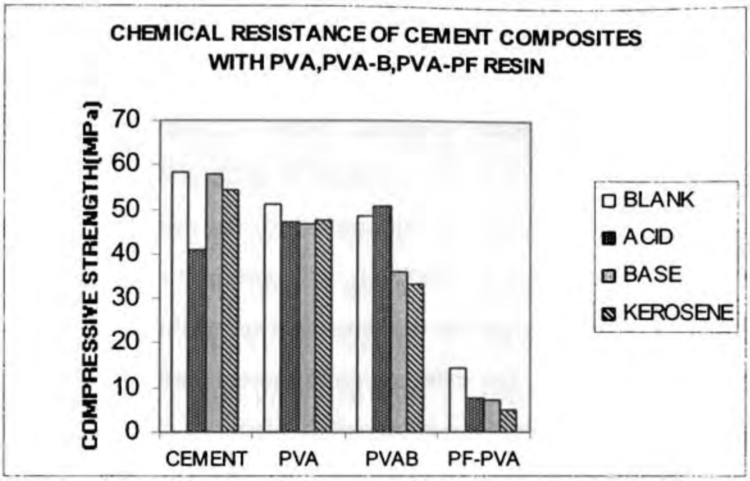


Fig. 2.10 Chemical resistance of thermoplastics modified cement paste

Referring to Fig. 2.10 the compressive strength of virgin cement was found to be better than that for its composites with polyvinyl alcohol and PF resin before exposure to chemicals [26]. The slight reduction in the initial compressive strength on addition of polymeric matter is presumably due to less than perfect hydration of the cement particles because of the formation of a polymer envelope. The compressive strength of virgin cement undergoes considerable deterioration after 24 hours of immersion in acid at room temperature compared to that of polymer cement composites, with the exception of PF-PVAL.

The addition of PF-PVAL has in general resulted in deterioration of the chemical resistance properties. The addition of PVAL-borax has improved the acid resistance (percentage retention) considerably over that of virgin cement. No noticeable improvement was seen in the percentage retention of compressive strength when these composites were exposed to base and kerosene.

2.6 Conclusions

From the above study on the cement composites of thermoplastics and rubbers the following conclusions were arrived at. Mixing of the virgin cement with water is better on addition of the polymer and this is mainly due to the ball bearing action of the polymer particles.. The density of the cement paste decreases on addition of the polymer due to air entrapment during mixing. The rate of cement hydration on addition of the polymer decreases due to polymer film formation around the cement particles. The percentage retention of compressive strength of polymer cement composites is more than that of virgin cement due to sealing of the micropores in the cement matrix by the polymer particles. Some specific conclusions arrived at while using rubbers and thermoplastics are summarized below.

a Rubbers: Preparation of cement composites of prevulcanised natural rubber latex was cumbersome as it coagulated to form lumps even when diluted latex was used. Mixing of the cement paste is more effective when SBR and NBR latex were added due to the presence of surfactants present in them. Bulk density values of the cement composites of rubber lattices were found to be lower than that of virgin cement due to the entrapment of air in the cement matrix during mixing. The cement composites of SBR and NBR lattices have better acid resistance properties than virgin cement. The fall in compressive strength due to addition of polymer latex is only marginal. Linear NBR shows a uniform retention of compressive strength when exposed to all three chemical environments.

b Thermoplastics: Mixing of thermoplastics cement pastes was cumbersome at higher percentages of the thermoplastics due to their viscous nature. Among the thermoplastics used in this study, the properties of cement polyvinyl acetate composites were found to be better than others. The addition of PVAL does not affect the compressive strength to any considerable extent. The addition of PF resin to PVAL cement composites decreased its macroscopic properties.

References

[1] Giest, J.M., Amaga, S.V. and Meller,B.B.; *Ind. Eng. Cem.*, Vol. 45, 1953, pp. 759.

[2] ACI 309R-87; Guide for consolidation of concrete, *ACI Manual of concrete practice, Part 2: Construction practices and inspection pavements,* Detriot, Michigan, 1994, pp. 19.

[3] Schulze, Joachim, *Cement and Concrete Research*, 29, No.6, 1999, pp. 909-915.

[4] Vinyl alcohol polymers; *Encyclopaedia of polymer science and engineering*, Vol.17, John Wiley and Sons; pp. 175.

[5] BIS 4031 : Part 6 : 1988 Methods of physical tests for hydraulic cement: Part 6 Determination of compressive strength of hydraulic cement (other than masonry cement).

[6] V. Pavlík; *Cement Concrete Research,* Vol.24, No. 8, 1994, pp. 1495–1508.

[7] Beeldens, A., Influence of polymer modification on the behaviour of concrete under severe conditions, *Ph.D dissertation*, Faculty of Engg., Kotholike Universiteit Leuven (2002).

[8] Swamy, R.N., *Proceedings of the VIII ICPIC*, Oostende, Belgium, July 3-5 1995, pp. 21-26.

[9] Moteny, J. et al; *Journal of Materials and Structures*, Vol. 36, May 2003, pp. 242-249.

[10] Ravindrarajah, R; *Proc. of III ICPIC*, Japan, May 13-15, 1981, pp. 380-394.

[11] Shetty M.S.; *Concrete Technology theory and practice*; S.Chand and company Ltd., New Delhi, 2003.

[12] Ohama, Y., Chandra, S., *Polymers in concrete*, 6th chapter, CRC Press, USA, 1994.

[13] An-Jian Xie, Chun-Yan Zhang, Yu-Hua Shen, Ling-Guang Qiu, Pei-Pei Xiao and Zhao-Yang Hu.; *Cryst. Res. Technol.*, Vol. 41, No. 10, 2006, pp. 967 – 971.

[14] Viswanath, Priya and Thachil, E.T.; *Proc. of 5th ASPIC*, Sept.11-12, Chennai, India, 2006, pp. 125-132.

[15] C. T. Sumathy, M.Dharakumar, M.Saroja Devi, and s. Saccubai; *Journal of Applied Polymer Science*, Vol. 63, No. 10, 7 March 1997, pp. 1251-1257.

[16] Su, Zao: Microstructure of polymer cement concrete, *Ph.D dissertation*, Deft University of technology, Deft, 1995; pp. 174.

[17] Justnes, H. et al; *Proc. of 9th ICPIC*, Bologna, 14-18th Sept. 1998, pp. 225-238.

[18] Puterman, M. and Malorny; *Proc. of 9th ICPIC*, Bologna, 14-18th Sept. 1998, pp. 165-178.

[19] Knapen, E. and Gemert, D.V.; *Intl. Sym. of Polymers in concrete*, Portugal, 2-4 April 2006, pp. 85-95.

[20] Silva, D.A. et al; *Cement and concrete research*, Vol. 32, 2002, pp. 1383-1390.

[21] *Encyclopaedia of Polymer Science and Engg.*, Vol.6, Wiley Interscience; 2nd edition, January 19, 1990, pp. 254.

[22] Sugama, T.; Kukacka, L. E.; Horn W. (1980); *Journal of Materials Science*, Vol. 15, No.6, pp. 1498-508.

[23] W. J. Lewis and G. Lewis; *Construction and Building Materials*, Volume 5, Issue 4, December 1991, pp. 201-207.

[24] Ohama, Y. and Chandra, S., Mechanisms of concrete – polymer interactions, *Polymers in concrete*, CRC Press, New York, 1994.

[25] Jae-Ho Kim, Richard E. Robertson and Antoine E. Naaman; *Cement and Concrete Research*, Vol. 29, No. 3, March 1999, pp. 407-415.

[26] Adnan Çolak, Cement and Concrete Research, Vol. 35, No. 8, 2005, pp. 1510-1521.

Chapter 3

CEMENT COMPOSITES OF THERMOSETTING POLYMERS

3.1 Introduction

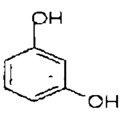
Thermosetting materials are usually preferred over thermoplastics and rubbers for structural applications as they have a three-dimensional network and hence do not have a tendency to cold flow (creep) at room temperatures [1]. The tightly cross-linked structure of thermosetting polymers immobilizes the molecules, providing hardness, strength at relatively high temperatures, insolubility, good heat, chemical and creep resistance. Epoxies and unsaturated polyesters are generally used in the manufacture of polymer-modified cement composite [2] but they often require crosslinking agents or catalysts, which may or may not influence the final properties of the composite.

Phenolic resins have been chosen for detailed investigations in this project for several reasons. This part of the thesis describes synthesis of phenolic resins, preparation of cement composites of formaldehyde based resins and the evaluation of properties of such composites. These resins were used because of their superior resistance against degradation when exposed to chemicals and high temperatures [3]. Since resole-type resins were employed for the preparation of the composites, external crosslinking agents that aid the formation of a three dimensional network were not required. Furthermore, the water formed during the synthesis of these resins could be utilised for the hydration of cement. Resole-type phenolic resins were synthesised in various ratios of the phenolic compound to formaldehyde, with sodium hydroxide as the catalyst.

The resins used for the present study are listed below:

1. Resorcinol formaldehyde resin -RF
    - i. R: F = 1:1.75 (molar ratio)
    - ii. R:F = 1:2.0 (molar ratio)
    - iii. R: F = 1:2.3 (molar ratio)
2. m- cresol formaldehyde resin - CF
    - i. C: F= 1:1.75 (molar ratio)
    - ii. C: F= 1:2.0 (molar ratio)
3. Phenol formaldehyde resin – PF
    - i. P: F= 1:2.25 (molar ratio)
    - ii. P: F= 1:2.5 (molar ratio)
    - iii. P: F= 1:2.75 (molar ratio)
4. Cashew nut shell liquid phenol formaldehyde resin – CNSL PF resin
5. PF microspheres
6. Melamine formaldehyde- MF

The chemical structures of four different co-monomers of formaldehyde used in this study to prepare different thermoset resins are depicted in Fig. 3.1.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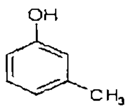
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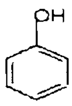
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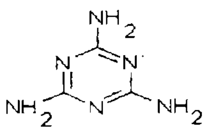

MELAMINE

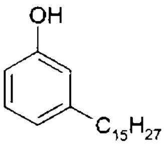

CARDANOL

Fig. 3.1 Chemical structures of different substances reacting with formaldehyde

3.2 Experimental

This part of the section describes the materials used and synthesis of the phenolic resins, preparation of the cement composites of various thermosetting resins and evaluation of their properties.

3.2.1 Materials

a. Chemicals used for the preparation of the polymer cement composites were laboratory grade resorcinol, phenol, m-cresol, formaldehyde, sodium hydroxide and calcium chloride supplied by Merck India Ltd. The specifications are given below:

(i) Phenol

Form: Solid

Colour: Colourless

pH value at 50g/l H_2O (20°C) ~ 5

Viscocity (dynamic) at 50°C = 3.437 mPas

Melting point = 40.8°C

Boiling point = 181.8°C

Density at 20°C = 1.06 g/cm^3

(ii) Resorcinol

Form: Solid

Colour: White

pH at 100g/l H_2O (20°C) ~ 4-6

Melting point = 109-111°C

Boiling point = 281°C

(iii) m-Cresol

Form: Liquid

Colour: White to yellowish

Odour: Phenol-like

pH value at 20g/l H_2O (20°C) ~5

Melting point = 11.5°C

Boiling point = 203°C

Density = 1.03g/cm^3

(iv) Formaldehyde (37%)

Ignition temperature ~ 300°C

Melting point < -15°C

pH value = 2.8 -4.0 (20°C)

Density = 1.09 g/cm^3 (20°C)

Boiling point = 93 -97°C

(v) Sodium hydroxide

Melting point = 323°C

Density = 2.13 g/cm^3 (20°C)

Boiling point = 1390°C

pH = 14 (50 g/l, H_2O, 20°C)

(vi) Calcium chloride

Solubility in water = 740 g/l (20 °C)

Melting point = 772 °C

Molar mass = 110.99 g/mol

Density = 2.15 g/cm^3 (20 °C)

pH value at 100 g/l, H_2O, 20 °C ~8 - 10

Boiling point > 1600 °C

Water absorption: Hygroscopic

b. Portland cement

Portland cement used for the preparation of these composites had the following specifications:

Brand: Ramco Cements Super, India.

Fineness = 361 m^2/kg

Normal consistency = 33%

Setting time (min): Initial = 70

Final = 160

Soundness:

Le Chatelier expansion = 0.50 mm

Autoclave expansion = 0.03%

Chloride content = 0.013% by mass

Insoluble residue = 22.01% by mass

Magnesia = 0.84% by mass

Sulphuric anhydride = 2.79% by mass

Total loss on ignition = 2.44% by mass

c. Melamine formaldehyde resin-MF

Supplied by TFC Corporation, Jalgaon, India.

Appearance: Dry finely divided white powder

Moisture = 3% max

Nitrogen content = 37% app

Bulk density = 0.65 g/cc

c. Cashew nut shell liquid

Supplied by Satya Cashew Company, Chennai, India.

d. PF microspheres

Supplied by Naval Physical and Oceanographical Laboratory (NPOL), Kochi, India.

3.2.2 Preparation of resins

The thermosetting resins synthesised during this study were alkali catalysed phenol formaldehyde, m-cresol formaldehyde, resorcinol formaldehyde and cardanol phenol formaldehyde.

a. Phenolic resins [4]

The phenolic resins were prepared in different ratios of phenolic compound and formaldehyde (37% v/v in water) with sodium hydroxide as a catalyst. Fig.3.2, 3.4 and 3.5 show the chemical reactions involved.

(i) Resorcinol formaldehyde (RF) resin

As shown in Fig.3.2 the synthesis of resorcinol formaldehyde resin was initially carried out at room temperature with 33% sodium hydroxide (w/w in water) as catalyst. The reaction was very quick [5] and exothermic resulting in immediate crosslinking of the resin.

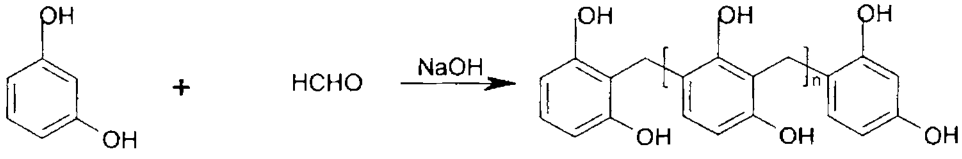


Fig.3.2 Formation of RF resin

The resin was initially light yellow in colour and gradually became deep maroon on crosslinking. This made mixing of the resin with the cement water blend impossible. The concentration of the catalyst viz. sodium hydroxide had to be thus optimised so as to facilitate an adequate time lag for the mixing to be carried out. The preparation of the resin at different catalyst concentrations showed that at lower values (0.5-9% w/w in water), the reaction mixture comprising of resorcinol and formaldehyde remained colourless and did not crosslink. Further investigations revealed that when 12.5% sodium hydroxide was added to 1:1.5 resorcinol-formaldehyde, the mixture turned deep maroon and crosslinked only after approximately 2 hours at room temperature. This time gap was sufficient for the preparation of 1:1.5 resorcinol–formaldehyde cement composites. Similarly, 10% sodium hydroxide was found to be the optimum concentration for the preparation of both 1:1.75 and 1:2.0 resorcinol–formaldehyde resins. The quantites of chemicals taken for the in-situ synthesis of the resin in the composites are indicated in Table 3.1.

Table 3.1 Reaction mixtures for preparation of RF resin

Ratio R:F	Resorcinol in g	Formaldehyde in ml	NaOH in ml
1:1.5	1.272	3.97	3.0
1:1.75	1.272	4.632	3.0
1:2.0	1.272	5.75	3.0

Fig.3.3 shows the experimental setup used for the synthesis of m-cresol formaldehyde and phenol formaldehyde.

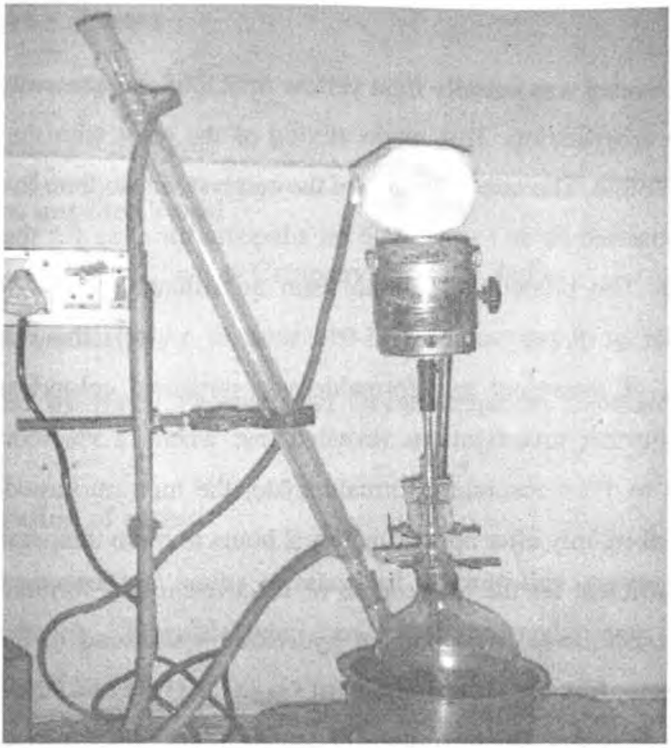


Fig. 3.3 Experimental setup for the synthesis of m-cresol formaldehyde and phenol formaldehyde resins

The reaction mixture was taken in a round bottomed flask fitted with a stirrer and water condenser. A water bath was used to heat the mixture.

(ii) m-cresol formaldehyde (CF) resin

Since m-cresol formed ortho and para isomers at room temperature it had to be vacuum distilled before the preparation of the CF resin. The resin was synthesised in two ratios of m-cresol and formaldehyde – 1:1.5 and 1:1.75 with 33% sodium hydroxide (w/w in water) as a catalyst.

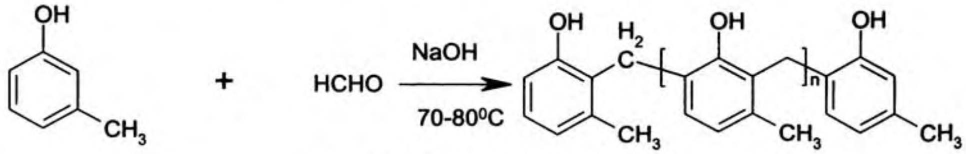


Fig.3.4 Synthesis of CF resin

m-cresol formaldehyde resin (Fig.3.4) was prepared by heating the reaction mixture at 70°-80°C for 1.5 hours. The quantities of chemicals taken for synthesis of the resin in the composites are indicated in Table 3.2.

Table 3.2 Reaction mixture for the synthesis of CF resin

Ratio C:F	m-cresol in ml	Formaldehyde in ml	30% NaOH in ml
1:1.5	9.67	40.5	5.0
1:1.75	9.67	47.3	5.0

(iii) Phenol formaldehyde (PF) resin

The phenol formaldehyde resins were synthesised in three ratios of phenol and formaldehyde viz. 1:2.25, 1:2.5 and 1:2.75 with 33% sodium hydroxide (w/w in water) as a catalyst. The relevant reaction is shown in Fig.3.5.

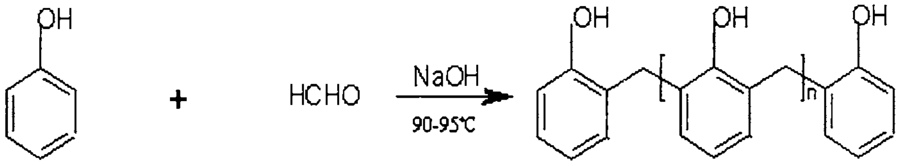


Fig.3.5 Preparation of PF resin [3]

The quantities and proportions of the reaction mixtures are indicated in Table 3.3. The reaction mixture was taken in a round bottomed flask fitted with a condenser and heated to 90°C. The rate of reaction increased with increasing proportions of formaldehyde. The approximate reaction times for 1:2.25, 1:2.5 and 1:2.75 were found to be 2 hours, 1.5 hours and 45 minutes respectively by acetone solubility tests.

Table 3.3 Amounts of chemicals taken for the synthesis of PF resin

Ratio P:F	Phenol in ml	Formaldehyde in ml	30% NaOH in ml
1:2.75	94	206.25	36
1:2.5	94	187.5	36
1:2.25	94	168.75	36

Since these resins crosslinked at high temperatures the addition of an external cross-linking agent was not necessary.

(iv) Cardanol phenol formaldehyde resin

Cardanol was separated from commercial CNSL by distillation under reduced pressure (1mm Hg). Cardanol was collected as a pale yellow fraction at 206-208°C [6]. The copolymer, phenol-cardanol-formaldehyde (PCF) resin was synthesised by reacting mixtures of phenol, cardanol and formaldehyde [7]. A resole-type resin was preferred as it is heat-reactive. The resin was prepared with a molar stochiometric ratio of 1:1.7 of total phenols to formaldehyde. Phenol and cardanol were taken in the ratio 3:2 (by weight) in a three necked round bottomed flask equipped with a water condenser. This ratio was selected to make the resultant resin less hydrophobic than cardanol formaldehyde which is highly immiscible with water. Formaldehyde was added to the blend of phenol and cardanol and the reaction mixture was refluxed for one hour at 95°C with 6 ml of 33% NaOH as catalyst. The reaction was stopped when the mixture became viscous and hydrophobic. The resole-type resin obtained was neutralised with oxalic acid and washed with hot water to remove unreacted phenol and then vacuum dried.

(v) Melamine formaldehyde (MF) resin

700 ml of water and 41g of concentrated hydrochloric acid were mixed and melamine formaldehyde resin powder (100g) was added to the above mixture. This was stirred continuously for 8 to 12 hours till a solution was formed. This solution was kept overnight before it was added to the cement [8].

Studies on the MF powder cement composites were also carried out after the MF powder was added as such to the cement in various percentages.

3.2.3 Formulations

The following sections give details of the preparation of cement composites of thermosetting resins.

a. *Moulds:* Moulds designed for the preparation of the standard composite samples had inner dimensions of 50mm x 50mm x 50mm (as per IS specifications) as shown in Fig.2.1 (a). They were used for the determination of compressive strength.

b. *Compaction*: The polymer cement composites were prepared by hand mixing the components viz. cement, water, accelerator and resin. They were cast to cubical moulds and compacted initially by hand. Since the latter procedure was cumbersome due to the viscous nature of the resin, compaction of the composite in the moulds was done using a vibrator [9]. The vibrator is shown in Fig.2.1 (b).

c. *Preparation:*

(I) Resorcinol formaldehyde Cement Composite (RFC)

To prepare resorcinol formaldehyde resin cement composite the blend of resorcinol and formaldehyde was added to the water-cement mix before the catalyst was added. This in situ preparation of the resin was carried out to avoid the formation of the three-dimensional crosslinked network during the preparation of the composite itself.

Initially cement and water were mixed well along with calcium chloride as accelerator to form a uniform paste. A mixture of resorcinol and formaldehyde as per Table 3.1 was added to the cement water blend before adding sodium hydroxide. The above ingredients were mixed well to form a homogenous mix which was then cast into moulds. The proportions and percentages of RF resin used for the preparation of the resin cement composite are given in Table 3.4.

Table 3.4 Mix design of RF cement composites (W/C – 0.25)

Components used for the preparation of the resin	Chemicals	Types	Percentage by weight
Monomers	Resorcinol (R) Formaldehyde (F)	1:1.5 (R: F)	5 7.5 10
		1:1.75 (R: F)	5 7.5 10
		1:2.0 (R: F)	5 7.5 10
Catalyst	Sodium hydroxide	12.5% for 1:1.5 10.0% for 1:1.75 & 1:2.0	3ml
Water	--	Potable	25
Cement	Portland cement	Ordinary Portland cement	100
Accelerator	Calcium chloride	Solution in water	0.1

(II) Resorcinol-formaldehyde sand cement composites (RFSC)

In this section, the preparation of composites, from cement–sand–water mixture with different percentages of resin, and their curing are described. The amounts of the materials taken for the synthesis of the RF resin are indicated in Table 3.1.

The following proportions of sand to cement ratios were employed for preparation of the RFSC.

(a) Sand:Cement = 70:30

This proportion is generally used to prepare cement mortars but the compressive strength properties of these sand composites with RF resin were found to be poor compared to RFC.

(b) Sand:Cement = 50:50

The properties of polymer composites of the cement mortar with these proportions were better than those of the 70:30 composite.

The RF resin with ratio 1:1.5 was not employed for this study since its properties were noticeably bad. The components and proportions of materials used to prepare these composites are given in Table 3.5.

Table 3.5 Mix proportions for RFSC composite.

Components	Ingredients	Types	Percentage by weight
Monomers	Resorcinol (R) Formaldehyde (F)	1:1.75 (R: F)	5 7.5 10
		1:2.0 (R: F)	5 7.5 10
Catalyst	Sodium hydroxide	10.0%	3ml
Water	--	Potable	50 30
Cement	Ordinary Portland cement	--	50,30
Sand	River bank sand	Particle size < 600 micron	50,70
Accelerator	Calcium chloride	Fused	0.1

Water was initially added to the cement-sand mixture to form a uniform paste. The mixture of resorcinol in formaldehyde was blended to this paste to form a uniform slurry. 3 ml of sodium hydroxide was added to the mix as the catalyst. This mixture was poured into the moulds and the compaction was performed in a vibrator according to ACI 309R-87 [9].

(III) m-cresol formaldehyde cement composites (CFC)

Portland cement was mixed with water and 0.1% calcium chloride was added as an accelerator. The prepolymer of CF resins, prepared in different ratios of m-cresol and formaldehyde as described in Section 3.2.2. (ii) was blended with the cement-water mixture and moulded into cubical specimens. The compaction was done in a vibration mixer according to ACI 309R-87 [9].

The m-cresol formaldehyde resin cement composite was prepared in three percentages of resin to the weight of cement viz. 5, 7.5 and 10 as shown in Table 3.6.

Table 3.6 Mix proportions for CFC composite (W/C=0.28)

Components	Chemicals	Types	Percentage by Weight
Phenolic resin	m-cresol formaldehyde resin (CF)	1:1.5 (C: F)	5 7.5 10
		1:1.75 (C: F)	5 7.5 10
		1:2.0 (C: F)	5 7.5 10
Water	--	Potable	28
Cement	Portland cement	Ordinary Portland cement	100
Accelerator	Calcium chloride	Fused	0.1

(IV) Preparation of m-cresol formaldehyde sand cement composites

The m-cresol formaldehyde resin sand cement mortars were prepared in three percentages of resin to the weight of cement viz. 5, 7.5,10 (shown in Table 3.7).

Table 3.7 Components of the m-cresol formaldehyde sand cement composite

Components used for the preparation of the composite	Chemicals	Types	Percentage by weight
Phenolic resin	m-cresol formaldehyde resin	1:1.5(MC: F)	5 7.5 10
		1:1.75(MC: F)	5 7.5 10
Water		Potable	30
Cement	Portland cement	Ordinary	50
Sand	River bank sand	Particle size < 600 micron	50
Accelerator	Calcium chloride		0.1

Appropriate quantities of sand and cement (as shown in Table 3.7) were mixed well and water was added uniformly to form a homogenous mixture. As indicated in Table 3.7 appropriate quantities of the resin were blended with the above mixture and cast using the cubical moulds. The compaction was done in a vibration mixer [9].

The polymer sand cement composites were prepared in two different proportions of sand and cement viz. 0:100, 50:50.-

(V) Preparation of phenol formaldehyde cement (PFC) composites

The prepolymer PF resin was blended with the cement-water mixture and moulded into cubical specimens. The phenol formaldehyde resin cement composite was prepared in five percentages of resin to the weight of cement viz. 5, 7.5, 10, 12.5, and 15 as shown in Table 3.8.

Table 3.8 Mix proportions of phenol formaldehyde resin cement composites (W/C = 0.30)

Components	Chemicals	Types	Percentage by weight
Phenolic resin	Phenol-formaldehyde resin	1:2.25	5 7.5 10 12.5 15
		1:2.5	5 7.5 10 12.5 15
		1:2.75	5 7.5 10 12.5 15
	Phenol formaldehyde resin microspheres		5 7.5 10 12.5 15
Water		Potable	30
Cement	Portland cement	Ordinary Portland cement	100
Accelerator	Calcium chloride	Fused	0.1

Weighed quantities of the resin was added to the mixture containing cement and water in five percentages of the resin to the cement and moulded using cubical moulds of dimensions 50mm X 50mm X 50mm.

(IV) Preparation of cardanol-phenol formaldehyde cement (CNSL-PFC) composites

PVAL was added as a compatibiliser during the preparation of cardanol PF resin cement composite because the cardanol PF resin is not misible with cement. The prepolymer of cardanol PF resin was blended with the PVAL-cement-water mixture and moulded into cubical specimens. The cardanol-phenol formaldehyde resin- cement composite was prepared only at a concentration of 5% of the resin to the weight of cement since the mixing and compaction was very cumbersome at higher percentages.

(D) Melamine formaldehyde resin cement composite (MFC)

Two cases were studied. The solution and powder of MF resins were separately blended with the cement-water mixture in five percentages of resin to the weight of cement viz. 5, 7.5, 10, 12.5, and 15. The mixture was moulded using cubical moulds. The mixture was compacted using a vibration mixer according to ACI 309R-87 [9]. The formulation and mix proportions of MFC are indicated in Table 3.9.

Table 3.9 Preparation of MF resin cement composite

Components	Chemicals	Types	Percentage by Weight
Resin	Melamine formaldehyde resin	Solution	5, 7.5 10 12.5 15
		Powder	5 7.5 10 12.5 15
Water		Potable	35
Cement	Portland cement	Ordinary Portland cement	100
Accelerator	Calcium chloride	Fused	0.1

3.2.4. Curing

The cubical specimens of cement composites of phenolic resins were kept at room temperature for 24 hours to allow the initial setting of the Portland cement accelerated by calcium chloride. The samples were then heated to 100°C in a hot air oven for 6 hours to facilitate the crosslinking of the phenolic resin. Phenolic compounds crosslink at the two ortho positions and the para position of the phenolic structure and enable formation of a three dimensional network.

After the samples were annealed to room temperature, they were immersed in water for 28 days to complete the hardening of the cement.

3.2.5. Evaluation of properties of the polymer cement composites

The properties studied in this part of the work include bulk density, compressive strength, porosity and durability of the polymer cement composites when exposed to acid, base and kerosene. A number of pulse velocity measurements were done in the case of RFC and CFC composites.

(a) Bulk density measurements:

The bulk density measurements were carried out by determining the weight of the specimen and dividing it by its volume. This was performed before and after the hydration of each specimen and before and after the exposure of the specimens in chemical environments. It was done to determine the change in density during the hydration of the virgin cement and the polymer cement composites. The weight loss due to exposure of these composites to acid, alkaline and kerosene environments was also evaluated.

(b) Pulse velocity measurements

Testing using ultrasonic pulse velocity method was carried out using Proceq manufactured Tico Model equipment. This test helps to establish uniformity and detect cracks in the samples. The velocity of an ultrasonic pulse travelling in a solid material depends on the density and the elastic properties of that material [10]. Specimens were tested according to IS 13311(Part 1) 1992

[11]. The pulse velocities were determined for fresh samples and for samples immersed in various chemicals. These tests were limited to RFC and CFC composites. The travel time of the ultrasonic pulse through the test specimen under direct transmission was recorded and pulse velocity was calculated by dividing the length of the specimen by the travel time.

The dynamic Young's modulus is given by

$$E = \frac{\rho(1+\mu)\,(1+2\mu)\,V^2}{(1-\mu)}$$

E=Dynamic Young's Modulus of elasticity in MPa

μ= Dynamic Poison's ratio

ρ= Density in kg/m^3

V= Pulse velocity in m/sec

(c) Compressive strength

Compressive strength is a basic property of the hardened concrete. The test was performed in accordance with BSI 4031[12].

The maximum compressive load before breaking of the polymer cement composite samples was determined using a Universal Testing Machine Model No. TUNS 1000 of Fine Spavy make. The compressive strength was evaluated after curing the samples for 28 days in water.

The cubical specimens were tested by placing them between the flat steel platens of the testing machine without any packing. The load was uniformly and steadily applied from zero at a rate of 35 N/mm^2/min. The compressive strength was evaluated by dividing the maximum load by the cross sectional area in terms of N/mm^2.

(d) Chemical resistance measurements

The cured samples of the virgin cement and polymer cement composites were separately immersed in 1% nitric acid, 1% sodium hydroxide and kerosene for 24 hours at room temperature. The procedure followed was the same as the previous section (Section 2.4.3). The chemical resistance was studied by comparing the compressive strengths of the composites before and after they were exposed to the acid, base and kerosene environments.

3.3 Results and discussion

Thermosetting resins form a brittle three-dimensional network on crosslinking that do not degrade easily on heating. Composites of thermosetting resins are resistant to deterioration due to heat and chemicals. The following section discusses the compressive strength characteristics of cement composites of thermosetting resins and the resistance of these composites to damage on exposure to acid, base and kerosene respectively. The compressive strength properties of CNSL–PFC composites were found to be very poor. Hence only their microscopic aspects were studied.

3.3.1 Mixing

Most of the thermosetting resins used in the present study were synthesized as prepolymers and viscous liquids. Therefore, uniform mixing was difficult to achieve though a vibration mixer was employed for compaction especially at higher percentages of resin to cement.

a. Mixing of cement composites of formaldehyde resins

Prepolymers of all the resins, except CNSL PF resin, were highly hydrophilic so that mixing of the two phases i.e. cement and resin was not difficult. The thermosetting resins were added to the cement water mix. Beyond 15% of the resin in cement, mixing was found to be cumbersome due to the viscous nature of the resins.

The in situ synthesis of the resorcinol formaldehyde resin, performed to prevent its crosslinking during the preparation of the composite, facilitated the uniform mixing of the resin with the sand cement and water.

The addition of MF powder to cement at higher percentages was difficult due to blooming of the resin to the surface of the specimens.

Further, the cement composites of MF powder cracked when subjected to wet curing for 28 days. Therefore, the MF powder cement composites were not immersed in water for 28 days for cement hydration and were instead, dry cured.

The PF micro spheres were also very difficult to blend with the cement at higher percentages. Since the strength of cement composites of PF microspheres at higher percentages was already found to be very low the evaluation of their compressive strength after exposure to acid and base environments was not done.

The amount of water used for preparing the solution was kept constant to ensure a W/C ratio of 0.325. Since this ratio is less than that employed for ordinary cement (0.40) it results in fewer voids leading to higher strength of the composite [12]. In the case of latexes and emulsions water already present was also included while calculating the W/C ratio.

b. Mixing of resorcinol formaldehyde resin sand cement composites (RFSC)

The in situ synthesis of the resorcinol formaldehyde resin, performed to prevent its crosslinking during the preparation of the composite, facilitated the uniform mixing of the resin with the sand cement and water. The W/C ratios corresponding to 0:100, 50:50 and 70:30 ratios of sand: cement in phenolic resin sand cement composites were found to be 0.25, 0.30 and 0.5 respectively. This shows that as the proportion of the cement in the composites increases the water required to obtain a workable mix also decreases. One can also infer that at higher proportions of cement the imperfections and voids are less due to lower amounts of water which improves the mechanical properties [13].

The m-cresol formaldehyde resin sand cement composite (CFSC) was prepared for 50:50 of sand to cement ratio.

The macroscopic properties of the polymer cement composites evaluated in this study include pulse velocity measurements, bulk density, compressive strength and resistance to various chemical environments. These were performed on cubical samples that were cured for 28 days in water.

3.3.2 Bulk density

Bulk density measurements were carried out to find the change in the density before and after the hydration.

The percentage weight retention of the specimens was also determined by finding the weight before and after exposure to 1% nitric acid, 1% sodium hydroxide and kerosene respectively.

Table 3.10 Bulk density measurements of the cement composites of thermosetting resins

% OF RESIN	MFC			PF 1:2.25			PF 1:2.5			PF 1:2.75			RFC 1:2.0		
	BEFORE	AFTER	% INCREASE	BEFORE	AFTER	% INCREASE	BEFORE	AFTER	% INCREASE	BEFORE	AFTER	% INCREASE	BEFORE	AFTER	% INCREASE
0	1996.61	2104.57	5.41	1996.617	2104.57	5.41	1996.61	2104.57	5.41	1996.61	2104.57	5.41	1870.394	2088.501	5.41
5	1812.17	2068.44	14	1728.02	1847.87	6.94	1818.12	2030.62	11.69	1589.47	1901.42	19.63	1808.855	1991.177	11.66
7.5	1773.58	2072.27	16	1602.22	1830.87	14.27	1642.17	1996.62	21.58	1473.88	1745.87	18.45	1827.81	2013.447	10.08
10	1779.87	2069.21	16.5	1573.32	1830.02	16.32	1573.32	1964.32	24.85	1589.47	1875.07	17.97	1632.398	1905.924	10.16
12.5	1885.52	2095.47	11	1587.77	1779.87	12.10	1582.67	1766.27	11.60	1491.73	1641.32	10.03	1662.913	1956.243	16.76
15	1855.77	2057.99	10.9	1592.02	1832.57	15.11	1950.72	1722.92	-11.68	1525.72	1662.57	8.97	1870.394	2088.501	17.64

The percentage increase in bulk density is maximum in the case of cement composites of thermosets. This may be due to the formation of a dense three dimensional crosslinked structure of the polymer in the cement matrix. From Table 3.10 it can be inferred that the percentage of bulk density increases to a maximum at 10% of resin in the cement composite and then decreases due to the creation of microcracks and voids during the escape of excess formaldehyde from the resin. These voids and cracks decrease the bulk density of the polymer cement composite.

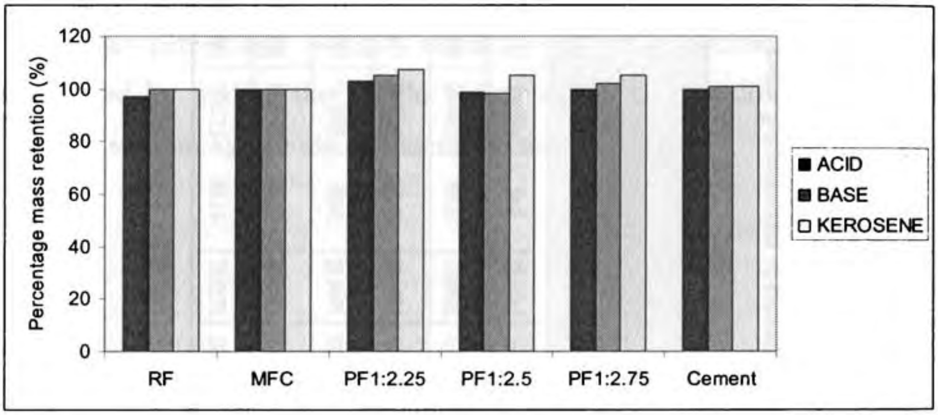


Fig.3.6 Percentage mass retention of cement composites of thermosetting resins after exposure to acid, base and kerosene

As shown in Fig.3.6 the percentage mass retention of polymer modified cement composites after exposure to chemical environments is found to be good. This may be due to the sealing of the pores and voids by the polymer which in turn prevents the entry of external chemicals into the polymer cement matrix and subsequent reactions with the cement particles. The results obtained point to the effectiveness of polymers in enhancing chemical resistance.

3.3.3. Pulse velocity measurements

These tests were limited to the cement and cement sand composites of RF and CF resins.

Table 3.11 Dynamic Young's modulus of elasticity values of

(a)RFC composites

Ratio	Percentage (%)	Dynamic Young's modulus of Elasticity X 10^{-10} in MPa			
		Blank	1% HNO_3	1% NaOH	Kerosene
1:1.5	5.0	1.813	1.690	1.614	1.824
1:1.5	7.5	1.779	1.802	1.882	1.905
1:1.5	10.0	1.859	1.690	1.712	1.824
1:1.75	5.0	2.01206	1.779	1.905	1.882
1:1.75	7.5	2.0115	1.779	1.636	1.79
1:1.75	10.0	1.768	1.668	1.679	1.79
1:2.0	5.0	1.882	1.802	1.976	2.012
1:2.0	7.5	2.060	1.847	2.012	1.824
1:2.0	10.0	2.035	1.779	1.882	1.882

(b) CFC composites

Ratio	Percentage (%)	Dynamic Young's modulus of Elasticity X 10^{-10} in MPa			
		Blank	1% HNO_3	1% NaOH	Kerosene
1:1.75	5.0	1.882	1.734	1.779	1.757
1:1.75	7.5	1.882	1.592	1.779	1.614
1:1.75	10.0	1.572	1.468	1.734	1.572
1:2.0	5.0	1.79	1.712	1.69	1.813
1:2.0	7.5	1.779	1.712	1.779	1.712

(c) RFSC (50:50) Composites

Ratio	Percentage (%)	Dynamic Young's modulus of Elasticity X 10^{-10} in MPa			
		Blank	1% HNO_3	1% NaOH	Kerosene
1:1.75	5.0	19.52	20.96	20.961	19.756
1:1.75	7.5	19.52	18.819	20.114	16.142
1:1.75	10.0	18.35	18.131	17.455	16.357
1:2.0	5.0	18.75	17.9	19.051	16.972
1:2.0	7.5	17.70	19.285	18.588	
1:2.0	10.0	19.28	18.819	18.359	19.051

(d) RFSC (70:30) composites

Ratio	Percentage (%)	Dynamic Young's modulus of Elasticity X 10^{-10} in MPa
1:1.75	5.0	1.976
1:1.75	7.5	1.928
1:1.75	10.0	1.509
1:2.0	5.0	1.367
1:2.0	7.5	1.251
1:2.0	10.0	0.9425

The results of the ultrasonic pulse velocity tests shown in Table 3.11 indicate uniform mixing and absence of voids or cracks. The presence of such voids or cracks results in poor macroscopic mechanical properties. Results after

24 hours of exposure to chemicals indicate that the degree of damage due to chemicals is only marginal and did not induce cracks. This was observed for all the ratios and percentages of resin in the cement.

3.3.4 Compressive strength

The compressive strengths of cement composites of thermosets employed for this study were found to be generally lower than that of virgin cement. This may be due to the dense and brittle nature of the resin after the formation of the three dimensional crosslinked structures. Moreover there is a possibility that hydration of cement could be inhibited by the presence of the resin. Therefore, the composites are unable to withstand the load applied on them.

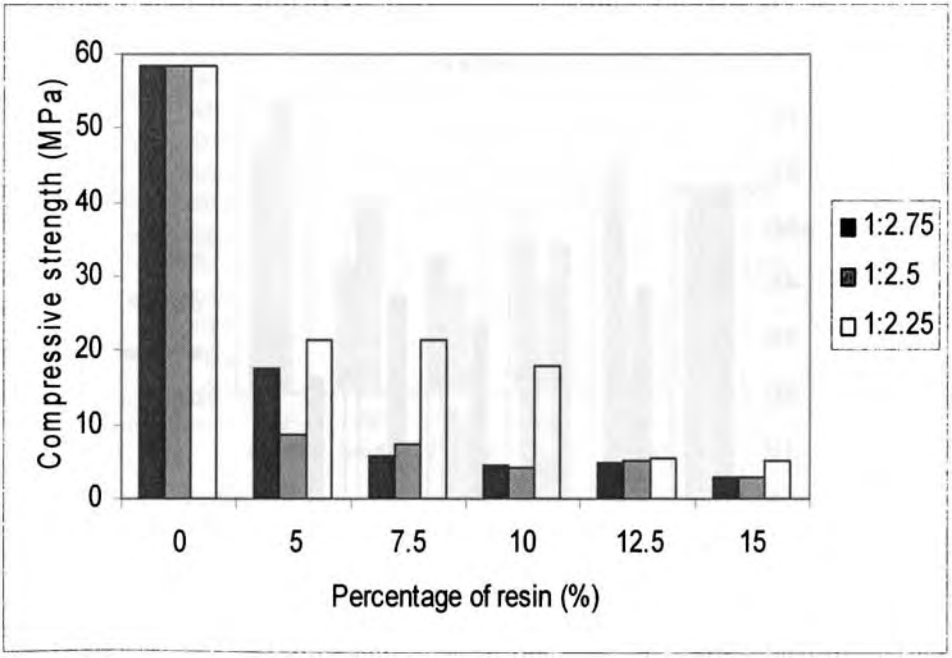


Fig.3.7 Variation of compressive strength of cement composites of PF resins of different ratios (0% is virgin cement taken as reference)

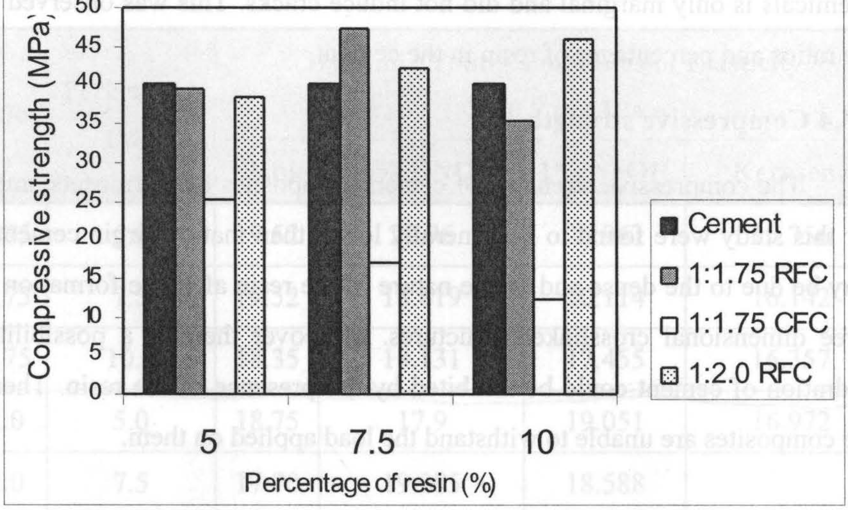


Fig. 3.8 Compressive strength of RFC and CFC composites

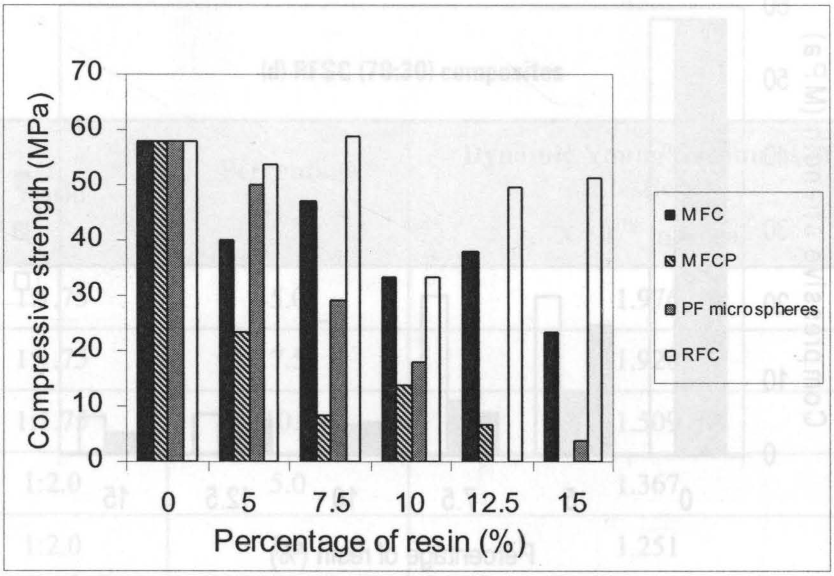


Fig.3.9 Compressive strength of cement composites of thermosetting polymers

(0% is virgin cement taken as reference)

Among the thermosetting resins cited in Fig.3.7, 3.8 and 3.9, it was observed that RFC has better compressive strength properties than cement composites of phenol formaldehyde and m-cresol formaldehyde resins. It was observed that as the ratio of the formaldehyde in the phenolic resins increases, the compressive strength of the composites decreases. This may be due to the brittle nature of the resin when a three-dimensional crosslinked structure is formed and also due the microvoids that are formed when excess formaldehyde escapes from the composite.

The MFC powder and PF microspheres act as flexible ball bearings [14] incorporating non-coalescing air bubbles during the mixing thereby decreasing the compressive strength at higher percentages. The bulk density of these microspheres and powders at higher percentages is also less than those of other composites due to the same reason.

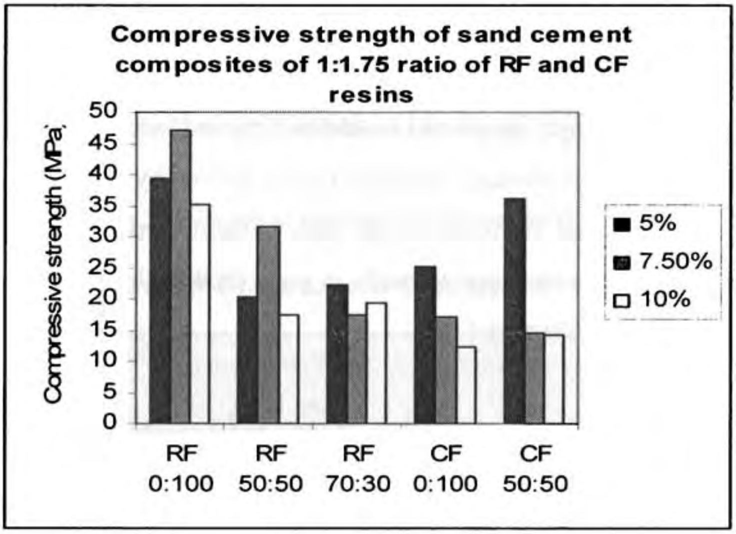


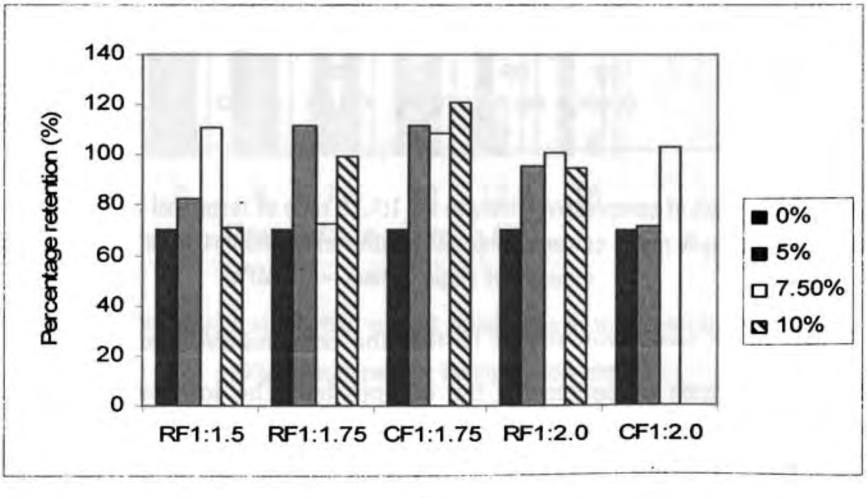
Fig. 3.10 Variation of compressive strength for 1:1.75 ratio of resorcinol formaldehyde and m-cresol formaldehyde resins cement composites with various proportions of sand (Compressive strength of virgin cement = 39 MPa)

It can be seen from Fig. 3.10 that the compressive strength is higher for higher proportions of cement in the composites. The load bearing capacity at higher percentages of the cement in the RF composite is high because the resin undergoes interactions with the cement resulting in a strong bond between the two. It shows that the compressive strengths increase as the proportion of the cement in the polymer sand cement increases. This is because the binding of the polymer and the cement is greater in polymer cement composites than in composites of polymer sand and cement.

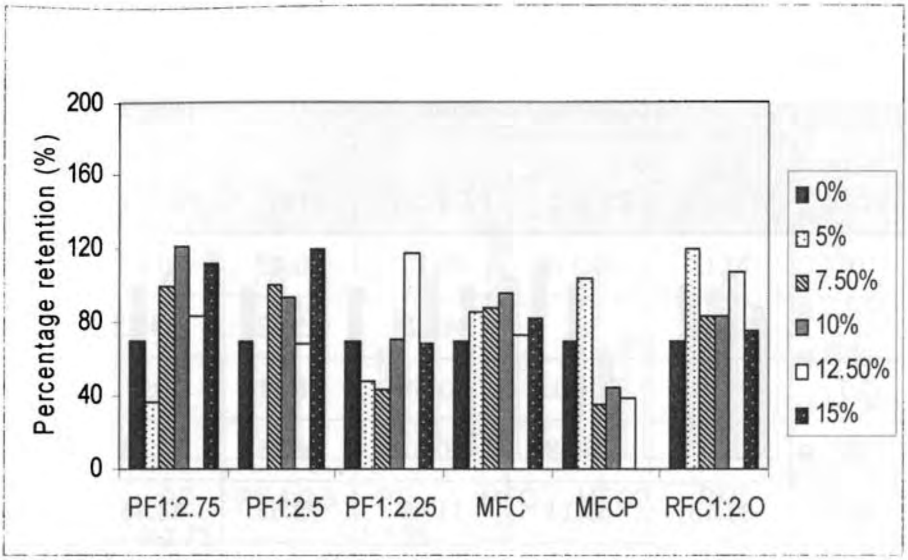
The strength of the resin cement sand composite formed using 70:30 sand:cement ratio, is less than that of other proportions. The addition of higher proportions of sand also increases the micro voids which in turn decreases the effective area that can resist the applied load.

3.3.5. Chemical resistance of the composites

In this work, it is assumed that a period of exposure of 24 hours of the polymer cement composites to the acid, base and kerosene is sufficient to cause degradation of the properties, if any. In a chemical or petrochemical industry where the polymer cement composites would be exposed to various chemical vapours the macroscopic properties would be retained better than when they are exposed to the various chemical liquids. This is proved by the presence of dense microstructure without voids in the polymer cement composite. In the case of cement concrete, its resistance to acids is poor though the same to alkalis and organic liquids is satisfactory [15].



(a)



(b)

Fig.3.11 Acid resistance of cement composites of (a) phenolic resins (b) thermosetting resins

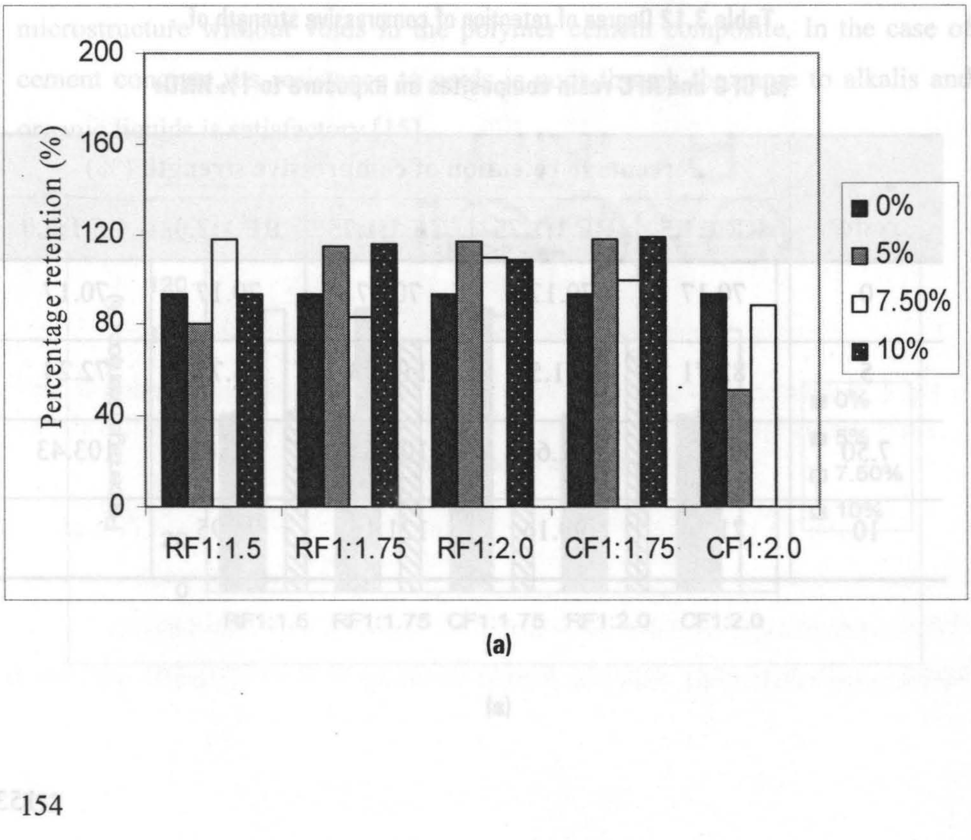
Table 3.12 Degree of retention of compressive strength of -

(a) CFC and RFC resin composites on exposure to 1% HNO_3

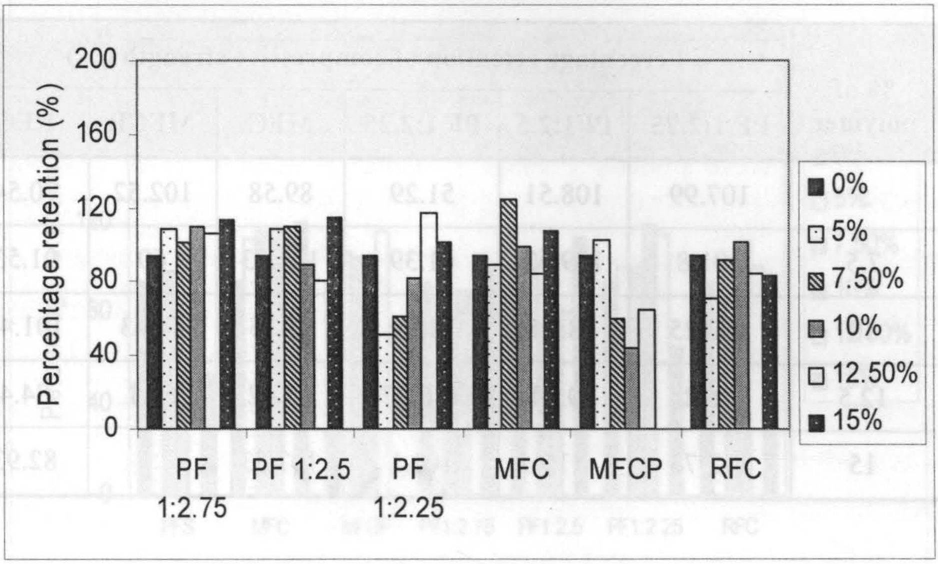
% of resin	Percentage retention of compressive strength (%)				
	RF 1:1.5	RF 1:1.75	CF 1:1.75	RF 1:2.0	CF 1:2.0
0	70.17	70.178	70.17	70.17	70.17
5	82.71	111.53	111.93	95.77	72.24
7.50	110.61	72.64	108.81	100.82	103.43
10	71.24	99.16	121.16	94.95	

(b) Thermosetting resin composites on exposure to 1% HNO_3

% of resin	Percentage retention of compressive strength (%)					
	PF 1:2.75	PF 1:2.5	PF 1:2.25	MFC	MFCP	RFC 1:2.0
0	70.17	70.178	70.17	70.17	70.17	70.17
5	36.61		48.2	85.42	104.32	120
7.5	99.92	101.05	43.38	88.11	35	83.69
10	121.34	94.08	70.47	96.25	44.43	83.75
12.5	83.13	69.11	117.9	73.63	38.46	107.56
15	112.26	119.85	69.14	82.14		75.61



(a)



(b)

Fig.3.12 Alkali resistance of cement composites of (a) thermosetting resins (b) phenolic resins

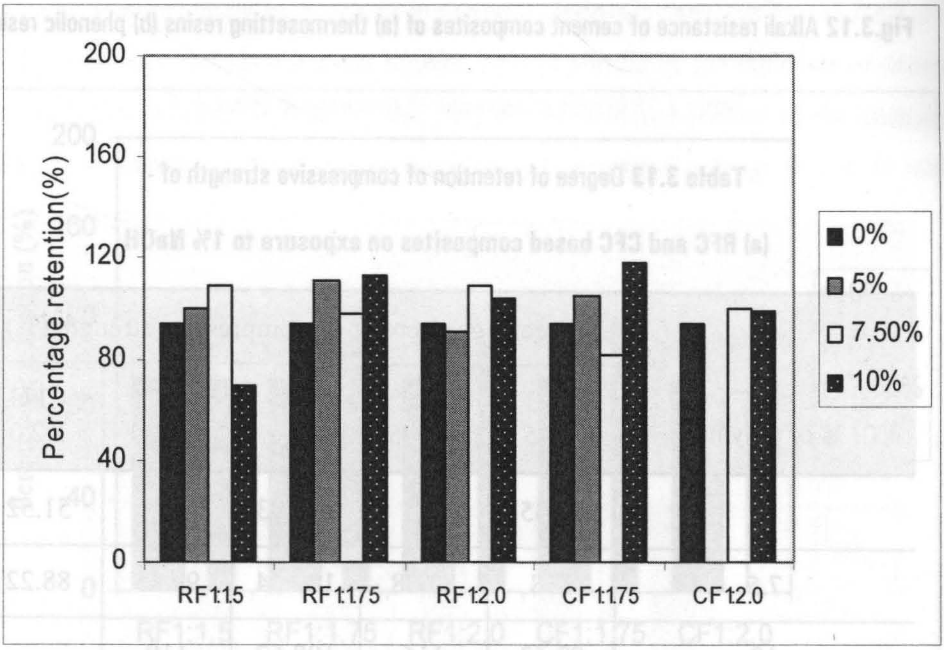
Table 3.13 Degree of retention of compressive strength of -

(a) RFC and CFC based composites on exposure to 1% NaOH

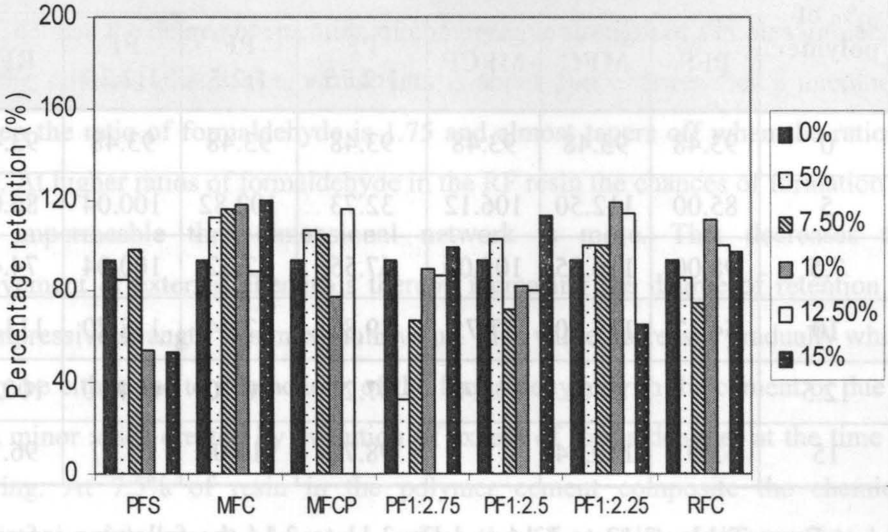
% of polymer	Percentage retention of compressive strength (%)				
	RFC 1:1.5	RFC 1:1.75	RFC 1:2.0	CFC 1:1.75	CFC 1:2.0
5	80.35	115	116.93	118	51.52
7.5	118	83.08	109.64	99.85	88.22
10	93.63	116	108.62	119	

(b) Thermosetting resin composites on exposure to 1% NaOH

% of polymer	Percentage retention of compressive strength (%)					
	PF 1:2.75	PF1:2.5	PF 1:2.25	MFC	MFCP	RFC
5	107.99	108.51	51.29	89.58	102.52	70.54
7.5	101.8	109.62	61.39	124.23	60	91.53
10	110.25	88.46	81.99	98.75	44.43	101.49
12.5	106.24	80.34	116.67	84.62	64.1	84.4
15	113.73	115	101.1	107.83		82.93



(a)



(b)

Fig.3.13 Kerosene resistance of composites of (a) thermosets (b) phenolic resins

Table 3.14 Degree of retention of compressive strength of -

(a) RFC and CFC based composites on exposure to kerosene

% of polymer	Percentage retention of compressive strength (%)				
	RFC 1:1.5	RFC 1:1.75	RFC 1:2.0	CFC 1:1.75	CFC 1:2.0
0	93.48	93.48	93.48	93.48	93.48
5	99.83	111.51	90.77	105.00	
7.5	109.10	98.31	109.00	81.93	100.30
10	69.40	113.00	104.28	118.00	99.32

(b) Thermosetting resin composites on exposure to kerosene

% of polymer	Percentage retention of compressive strength (%)						
	PFS	MFC	MFCP	PF 1:2.75	PF 1:2.5	PF 1:2.25	RFC
0	93.48	93.48	93.48	93.48	93.48	93.48	93.48
5	85.00	112.50	106.12	32.73	102.82	100.04	86.05
7.5	98.00	116.35	105.00	67.55	72.32	100.04	74.47
10	54.17	117.50	77.75	89.85	82.44	118.70	111.11
12.5		89.01	115.43	87.21	80.70	114.10	100.00
15	53.01	119.64		98.76	113.00	65.57	96.75

From Tables 3.12 to 3.14 and Fig.3.11 to 3.14 the following inferences can be made:

a. Phenol formaldehyde resin

Retention of compressive strength after immersion in various chemicals for samples with a P: F ratio of 1:2.25 is, in general, better than those for other ratios. The presence of formaldehyde in excess of 1:2.25 causes brittleness either due to excessive crosslinking of the resin or voids created by evaporation of formaldehyde at the time of curing. These microcracks allow the migration of external chemicals into the matrix and result in interaction with cement particles.

b. MFCS and PFS

The above polymers were added to the cement paste as micro spheres or powders and did not contribute to the properties of the composite. Since the densities of these polymers were very low, the particles bloomed to the surface making mixing difficult. This also created voids in the cement matrix. These voids allow the migration of the chemicals to interact with the cement particles thereby resulting in low retention of compressive strength.

c. Resorcinol formaldehyde resin cement composites

It was found that at 5% of the resin (for R:F ratios of 1:1.75 and 1:2.0) in the cement the degree of retention of compressive strength of samples immersed in the different chemical environments is about 100%. It reaches a maximum when the ratio of formaldehyde is 1.75 and almost tapers off when the ratio is 2.0. At higher ratios of formaldehyde in the RF resin the chances of formation of an impermeable three-dimensional network is more. This decreases the movement of external chemicals thereby increasing the degree of retention of compressive strength to a maximum value. This value decreases gradually which may be either due to interactions of the formaldehyde with the cement or due to the minor voids created by evolution of excess of formaldehyde at the time of curing. At 7.5% of resin in the polymer cement composite the chemical resistance of the samples decreases as the ratio of formaldehyde increases to 1.75 and then increases at higher ratios of formaldehyde due the formation of crosslinks. These crosslinks increase the chemical resistance by sealing the pores of the cement and preventing the reactions between the cement and the chemicals.

At 10% of the resin in the resorcinol formaldehyde resin cement composites, the chemical resistance increases with increase in formaldehyde ratio. This is due to the three-dimensional crosslinked network penetrating the voids of the cement thereby preventing the various chemicals from attacking the composite.

d. m-cresol formaldehyde resin cement composites

As the ratio of the formaldehyde in the resin increases from 1.5 to 1.75, the degree of retention of the compressive strength of the resin cement composite also increases. This is due to increase in the degree of crosslinking of the resin in the composite, which seals the pores in the composite.

The retention increases as the percentage of the resin increases from 5 to 10 due to the increase in the polymer network within the resin cement composite. The polymer network in the m-cresol formaldehyde resin cement composite, augmented by the increased crosslinking, prevents external chemicals from interacting with the cement particles thereby increasing chemical resistance.

e. Melamine formaldehyde resin:

The compressive strength properties of MF resin cement composites are superior to those of PF resin. The resin formed a three-dimensional network without the addition of external chemicals or heating the composite to a high temperature. These crosslinks increase the chemical resistance by sealing the pores of the cement and preventing the reactions between the cement and the chemicals. The degree of retention of compressive strength was found to be around 89% when exposed to acid and base and 95% in case of kerosene.

f. Chemical resistance of m-cresol formaldehyde resin sand cement composites

Some studies were carried out to evaluate the chemical resistance properties of the m-cresol formaldehyde resin sand cement composites.

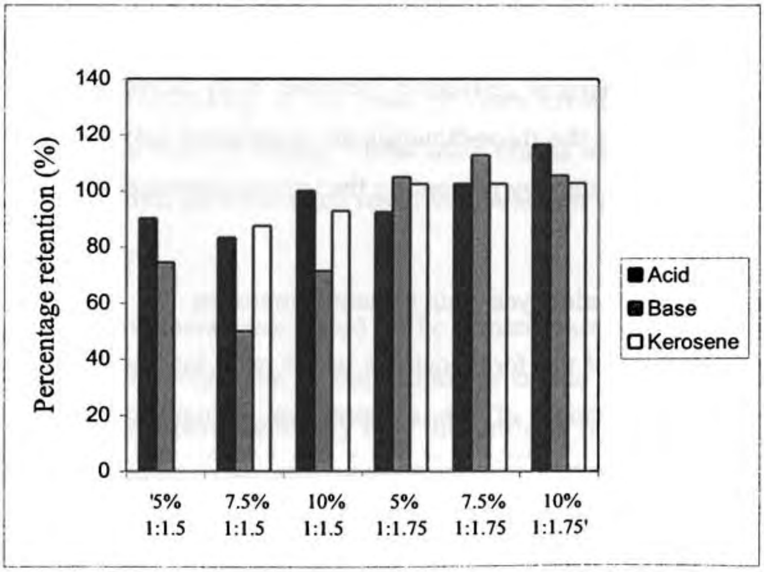


Fig.3.15 Percentage retention of 1:1 cement and sand composites of CF resin

The results shown in the Fig.3.15 reveal the following:

1. The percentage retention of compressive strength of the m-cresol formaldehyde sand cement composites after immersion in various chemical environments for 24 hours at room temperature was found to be better for higher percentages of the resin. This may be due to the dense crosslinked network that sealed the pores in the cement matrix thereby providing an impermeable barrier to the chemical environments.
2. The chemical resistance properties of cement composites of 1:1.75 resin is better than that obtained using 1:1.5 ratio.
3. The phenolic resin thus serves to block the pores in the cement paste preventing external chemical environments from deteriorating its mechanical properties.

3.4 Conclusions

It is possible to blend all the thermoset resins prepared directly with the cement with the exception of resorcinol formaldehyde resin.

Resorcinol formaldehyde resin increases the compressive strength of Portland cement by virtue of interaction with cement as shown in the microstructural study to be presented in Chapter 4. Since there may be a bond formation between OH of resorcinol molecule and the Ca^{2+}ions the overall structure possibly becomes more compact resulting in fewer number of voids.

m-cresol formaldehyde and phenol formaldehyde resins do not undergo significant reactions with the cement particles and consequently do not improve the strength of the cement paste(s).

The hydrophilic nature of the phenolic resins facilitates blending of the polymer and cement and helps in the formation of an interpenetrating network in the phenolic resin-cement matrix.

At high percentages of phenolic resin it forms a brittle network with cement. It, therefore, was unable to undergo deformation on application of stress. This explains the poor compressive strength of the phenol formaldehyde resin cement composites.

The properties of sand cement composites of m-cresol formaldehyde and resorcinol formaldehyde resin are better for 1:1 ratio of sand and cement than for the conventional 7:3 sand to cement ratio. As the proportion of the sand in the resin-cement matrix increases the micro voids also increases and therefore the mechanical and chemical resistant properties decrease.

Melamine formaldehyde resin does not interfere with cement hydration and its presence does not contribute of the properties of the cement paste.

Thermosetting resins increase the degree of retention of compressive strength of cement paste(s) after exposure to acid, base and kerosene due to the formation of a dense three-dimensional network.

References

[1] http://irc.nrc-cnrc.gc.ca/pubs/cbd/cbd159_e.html

[2] Vipulanandan, C; Paul, E., *Journal of Materials in Civil Engineering*, Vol.5, No.1, 1993, pp. 62-82.

[3] Brydson, J.A., *Plastics Materials*, 4th Edition, Butterworth Scientific publishers, London.

[4] Knop, A. and Scheib, W.; *Chemistry and application of phenolic resins*, Chapter 7, Springer Verlag Publishers, New York 1979.

[5] Vam Gills, G.E.; *I & EC Product Research and Development*, 7/2 June 1968, pp.151.

[6] H. P. Bhunia, R. N. Jana, A. Basak, S. Lenka, G. B. Nando R; *J Polym Sci Part A: Polym Chem*, Vol. 36, No. 3, 1998, pp. 391-400.

[7] Lity Allen Vargese, *Ph.D dissertation*, Faculty of Technology, Cochin University of Science and Technology, 2006.

[8] *Technical report of TFC corporation*

[9] ACI 309R-87; Guide for consolidation of concrete, *ACI Manual of concrete practice, Part 2: Construction practices and inspection pavements*, Detriot, Michigan, 1994, pp.19.

[10] Mantrala,Syam K.,Vipulanandan C.; *ACI Materials Journal*, Vol. 92, 1995, pp. 660-8.

[11] BIS 13311 (Part 1):1992 *Non destructive testing of concrete – Methods of test. Part1 Ultrasonic Pulse velocity.*

[12] BIS 4031: Part 6: 1988 *Methods of physical tests for hydraulic cement: Part 6 Determination of compressive strength of hydraulic cement (other than masonry cement)*

[13] Schulze, Joachim; *Cement and Concrete Research*, Vol. 29, No. 6, 1999, pp. 909-915.

[14] A.M. Neville. In: *Properties of Concrete*, 4th Edition, Longman Group, England 1995.

[15] Ohama, Y., Chandra, S., *Polymers in concrete*, Chapter 6, CRC press, USA; 1994.

Chapter 4

MICROSTRUCTURAL STUDIES

4.1 Introduction

Improved properties of polymer cement composites compared to virgin cement concrete has led to the study of the microstructure of the polymer cement matrix. There are two schools of thought about the action of polymers on cement concrete [1].

1. In the first theory, it is suggested that there are no interactions between the two phases and the cement hydration and the coalescence of polymer particles proceed together.
2. Some of the polymers added to the cement undergo chemical interactions and these result in the formation of complexes, which accelerate or retard the cement hydration. According to Janotka et al. [2], chemical interaction could result in the formation of complex structures and in changes in the hydrated cement phases morphology, composition and quantity, especially of calcium hydroxide. This is difficult to predict due to the complex nature of polymer molecules, their structure and reactivity.

The present chapter is an attempt to explain the morphology of the composites, interactions between the cement and polymers used for the present study and influence of the above microstructural aspects on the properties of the composite. Some of the studies done are:

a. thermal studies

b. the leachability of the water soluble components in the composites,

c. morphology of the polymer cement matrix

d. exploring the nature of interactions between the two phases.

The studies were carried out by analysing the relevant thermograms and micrographs, Soxhlet extraction data and EDTA titrations of the composite.

4.2 Experimental techniques

Samples for the microstructural studies (except EDTA titrations) were taken from broken pieces obtained after determination of compressive strength.

4.2.1 Thermo gravimetric analysis (TGA)

TGA was used to ascertain the degree of hydration of cement particles in virgin cement and polymer cement pastes. TA Instruments TGA Q 250 was used to conduct these studies. The samples of polymer cement composites were powdered, weighed and taken in platinum pan. The sample weights were between 5 to 10 mg. The thermo gravimetric curves were obtained after heating them from 20° to 600° C at the rate of 10°C/minute in nitrogen atmosphere.

4.2.2 Soxhlet Extraction

In concrete structures exposed to humid conditions such as dams, bridges, piers and seawalls, percolation of water into the concrete structure results in the washing out of water-soluble components [5]. Water can dissolve many salts and form acid droplets by dissolving gases from the atmosphere. These droplets penetrate the concrete structures and are instrumental in causing chemical deterioration. As a result cracks are formed which in turn allow interactions with external chemical environments. This affects the durability of the structures. Polymers are generally added as admixtures to the cement to seal the cracks and prevent percolation of water and other fluids into the cement matrix. Soxhlet extraction was performed to investigate the amount of water-soluble components within the composite and evaluate their leachability.

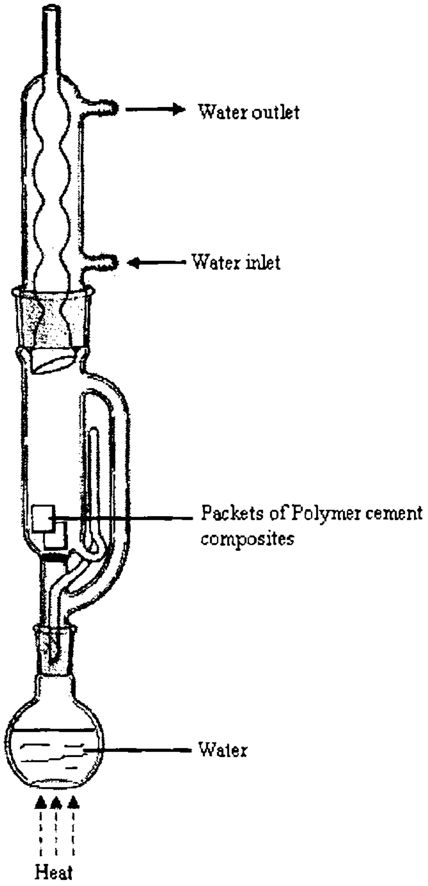


Fig. 4.1 Soxhlet apparatus

Soxhlet extraction apparatus (Fig. 4.1) is used for the continuous extraction of solids with a suitable solvent. The unit consists of a flat bottom boiling flask, Soxhlet extractor and Allihn condenser.

The samples were ground to particles of about 2mm diameter and 2g each of the samples were wrapped in Whatman No.1 filter paper. The solvent used in this case was hot water and the packets containing the accurately weighed polymer cement composite was placed in the middle portion of the apparatus. They were subjected to Soxhlet extraction for 24 hours. The difference in weights of packets gave the soluble matter and the percentage soluble matter was calculated.

4.2.3 Ethylene Diamine Tetra Acetic Acid (EDTA) Titrations

EDTA (Fig.4.2) was used to establish the masking effect of the polymers on the Ca^{2+} ions [3].

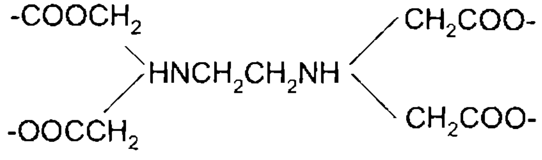


Fig.4.2 Structure of EDTA ion

In this method, a known weight of the polymer sample was added to a standard solution of Ca^{2+} ions and set aside for 24 hours at room temperature for any possible reactions to take place [4]. The amount of calcium ions in a blank solution without the addition of any polymer was initially determined. The changes in the concentration of calcium ions were determined by titrating the standardized solution of EDTA using Eriochrome black T as indicator.

The reactions involved in the determination of Ca^{2+} ions are given below.

$$Ca^{2+} + H_2Y^{2-} \rightarrow Ca\,Y^{2-} + 2H^+$$

where H_2Y^{2-} is the disodium salt of ethylene diamine tetraacetic acid (EDTA).

This procedure was carried out for all samples.

4.2.4 Scanning electron microscope (SEM) Studies:

Investigations using SEM revealed porosity, micro cracks and the extent of hydration of the cement in the composites. A Variable Pressure Digital Scanning Electron Microscope (Model LEO 1430VP) with EDS for X-Ray Microanalysis was used to carry out these studies. Samples of 1-2 mg weight were subjected to gold sputtering to make them conducting. One set of these samples was analyzed by imaging the fractured surface under the SEM. The fracture surface of the composites was studied by imaging the untreated samples. Etching was done on another set of samples with hydrochloric acid for a minute to remove the cement phase and reveal the polymer network within the polymer cement composite. These were then washed and dried prior to SEM observation.

4.3 Results and discussion

The results from the above techniques are presented below in the form of graphs, data and micrographs. The following sections discuss these results and present the conclusions arrived at.

4.3.1 Thermal Analysis of the Cement Polymer Composites

Studies using thermograms revealed the nature of reactions occurring in polymer cement composites and virgin cement at various decompositions temperatures. Using the thermo gravimetric curves a comparison of the significant losses of their weights was made.

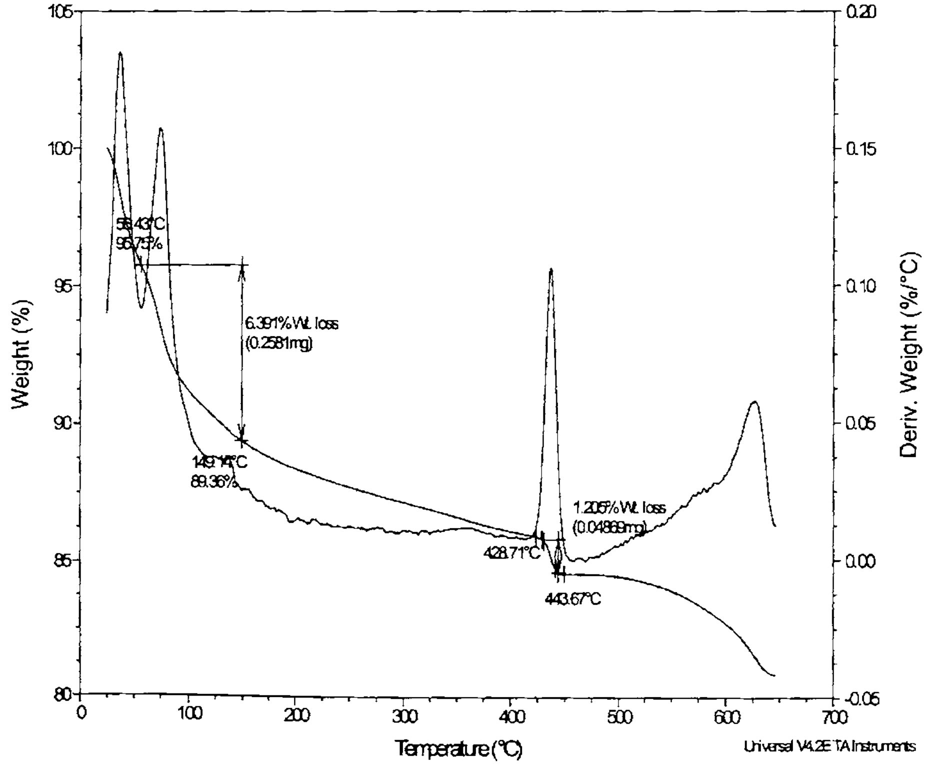


Fig. 4.3 TGA curve of virgin cement concrete

From Fig.4.3, the thermal analysis peaks of virgin cement were studied. The important reactions involved during the major weight losses at various temperatures are given below [6].

1. From about 70°C to 200°C, the endothermal phenomena correspond to the vaporization of free and interlayer water molecules present in the matrix and decomposition of C-S-H and hydrated aluminates.
2. The loss of weight between 400°-500°C corresponds to the decomposition of portlandite and $Ca(OH)_2$. This gave an idea about degree of hydration of the cement
3. The weak signal at about 670°C is due to the decarbonatation of $CaCO_3$.

TGA curves given in Fig.4.4 to 4.16 reveal the thermal transitions occurring in different polymer cement composites. Some of the salient aspects are discussed below.

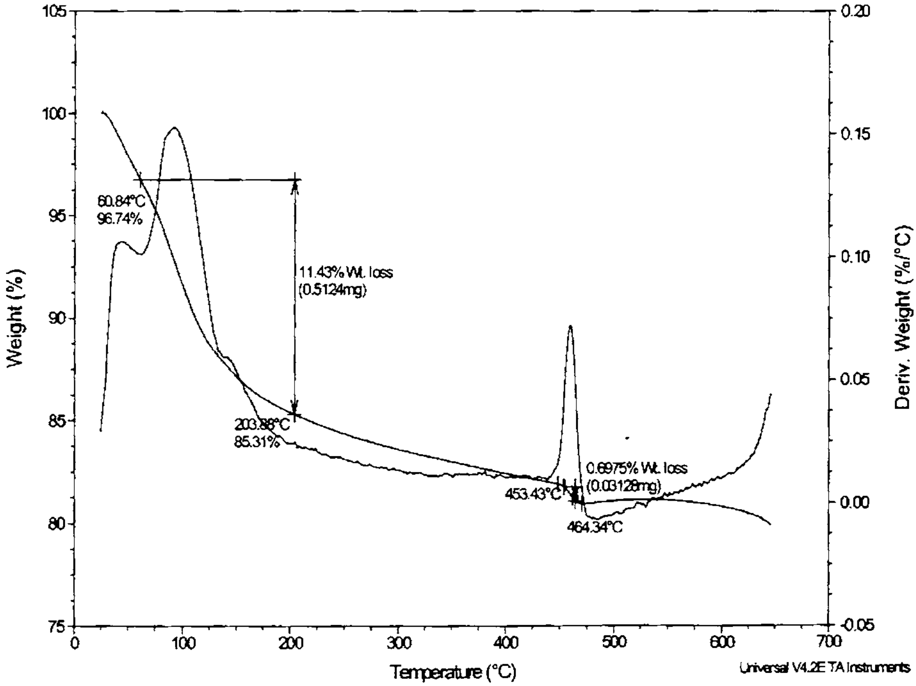


Fig. 4.4 TGA curve of PVAC cement paste

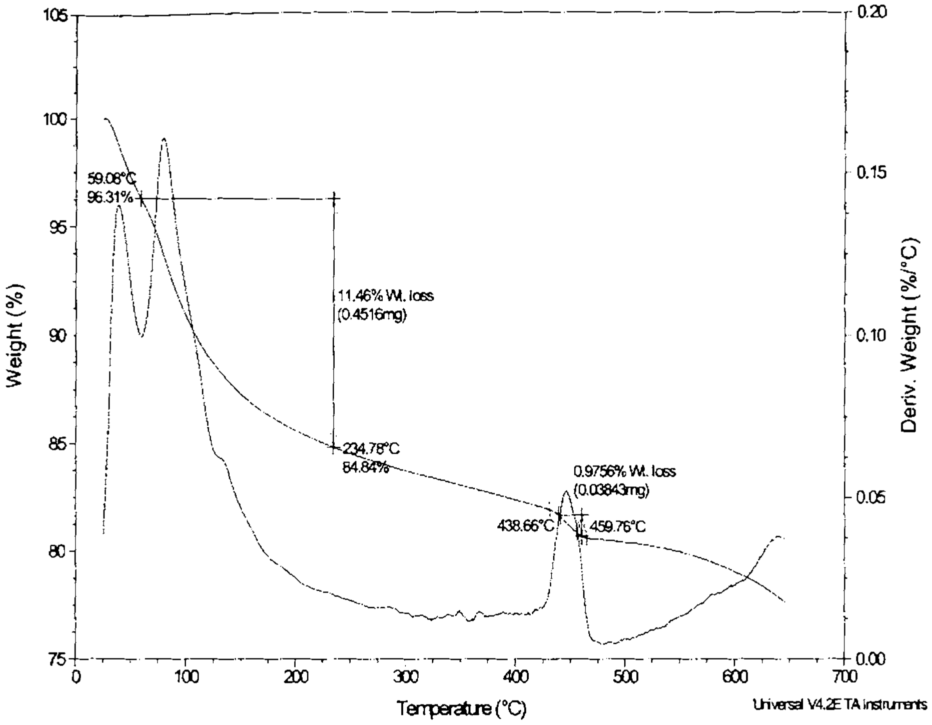


Fig. 4.5 TGA curve of acrylic polymer cement paste

Fig. 4.4 and 4.5 show the thermal curves of cement composites of acrylic polymer and PVAC respectively. In the cases, the polymer undergoes saponification. PVAC forms acetate ions and poly vinyl alcohol in the presence of cement. The pore water contains $Ca(OH)_2$ which is a byproduct of cement hydration. When dispersed in pore water the acetate ions form calcium acetate.

$$Ca(OH)_2 + 2\ CH_3COO^- \rightarrow Ca(OOCCH_3)_2 + H_2O$$

The loss of weight at around 200°C in Fig.4.4 and 4.5 respectively may be due to the decomposition of calcium acetate forming calcium carbonate [7].

$$(CH_3COO)_2Ca \rightarrow CaCO_3 + CO_2 + H_2O$$

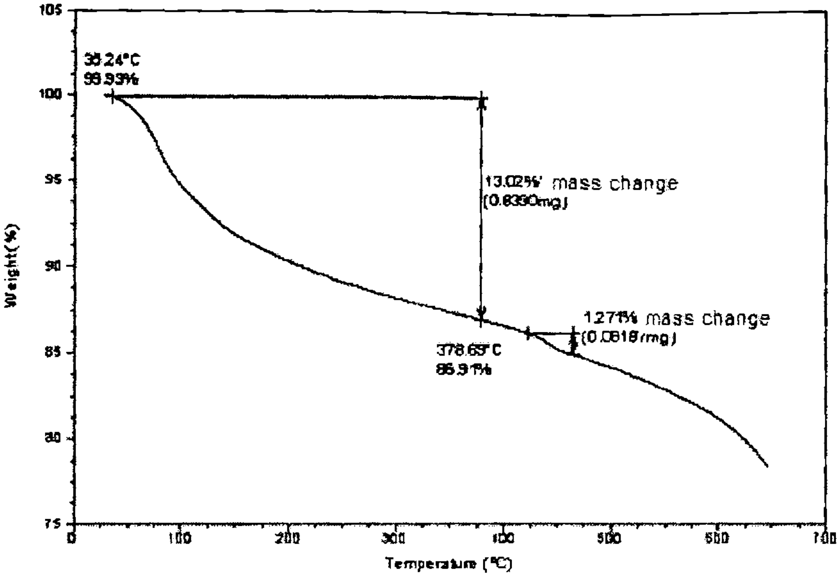


Fig.4.6 TGA of PVAL cement paste

As illustrated in Fig.4.6 some of the cement particles do undergo hydration which is represented in the percentage weight loss between 400° C and 460° C.

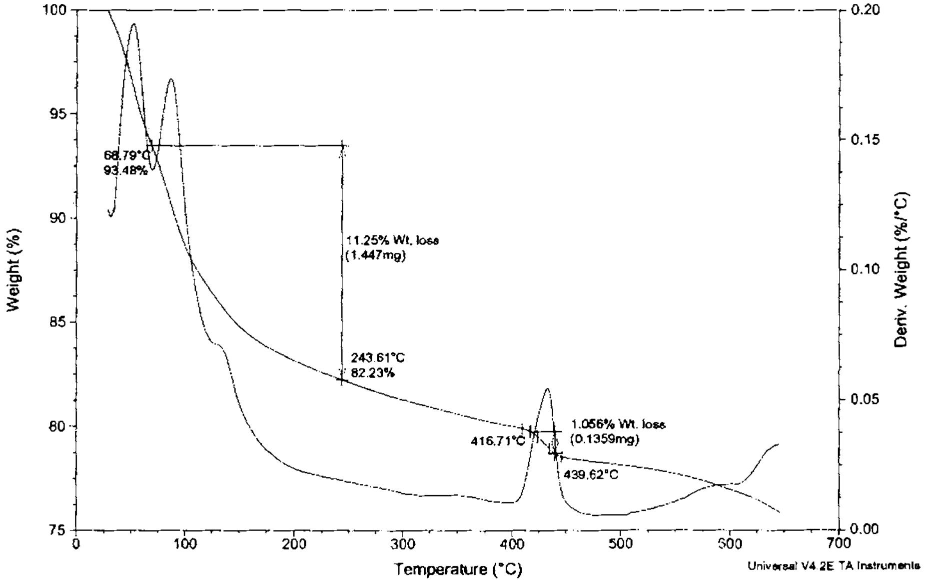


Fig.4.7 TGA of PVAL borax cement paste

The thermograph of PVAL borax cement paste in Fig.4.7 shows 11.25% weight loss between 50° C and 243° C. The initial loss of weight loss may be due to the degradation of water insoluble gel that is formed due to the reaction between PVAL and borax.

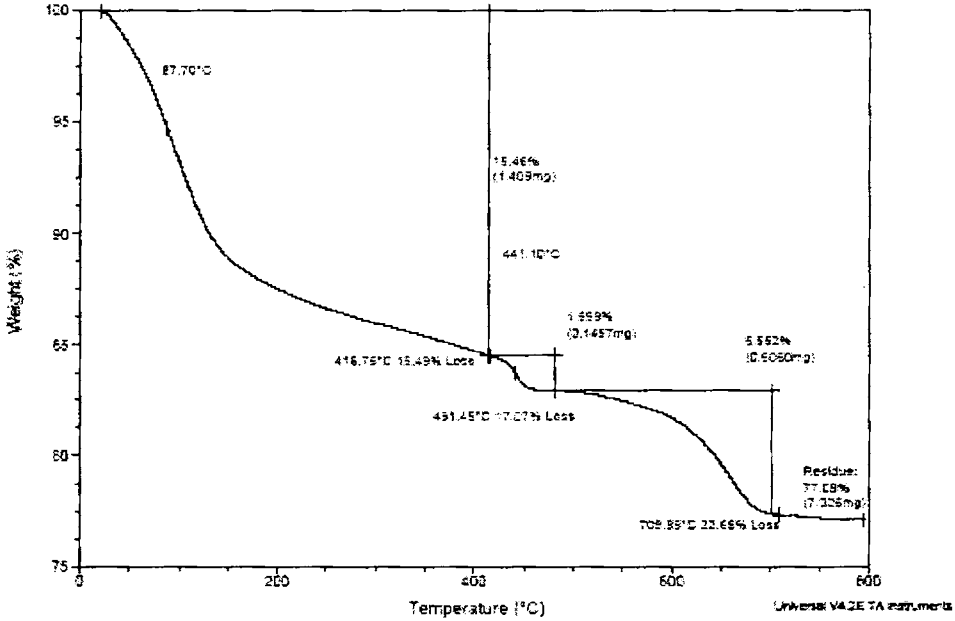


Fig.4.8 TGA of PF-PVAL cement paste

It is also found from Fig.4.8 that the mass loss in the range of 416°-482°C in the case of pastes of PF and cement is higher than similar losses of mass of cement pastes containing polyvinyl alcohol or polyvinyl alcohol with borax. This can be indicative of a higher extent of hydration of the cement when phenolic resin is added to the cement. The thermal loss above 600°C is due the degradation of PF resin [8].

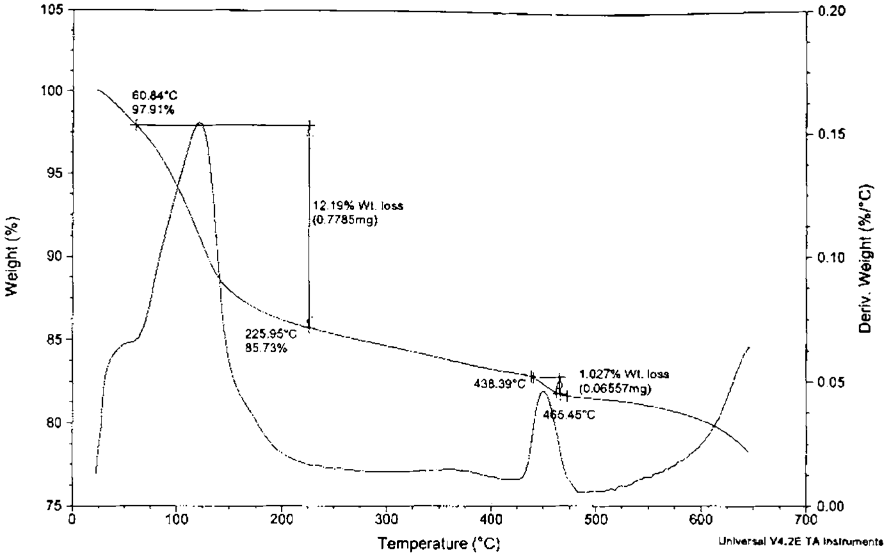


Fig.4.9 TGA of PEG cement paste

Fig.4.9 illustrates the weight loss of the PEG cement paste at different temperatures. Most of the weight loss is similar to that of virgin cement.

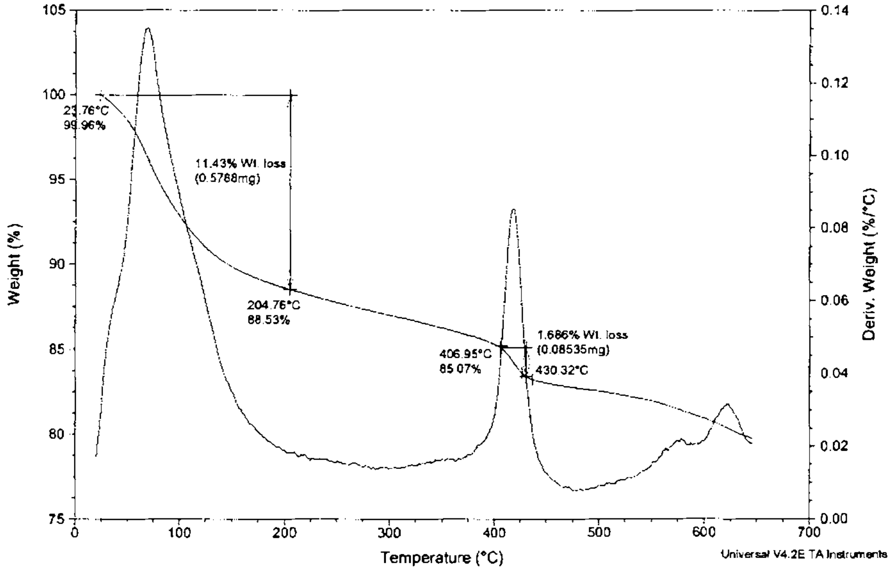


Fig.4.10 TGA of acrylic styrene polymer cement paste

The above figure (Fig.10) shows peaks of acrylic styrene polymer similar to virgin cement. There is very little interference in the hydration process by the polymer. The weight loss at around 600 C may be due to degradation of polymer and the decarbonation of $CaCO_3$ present in the cement matrix.

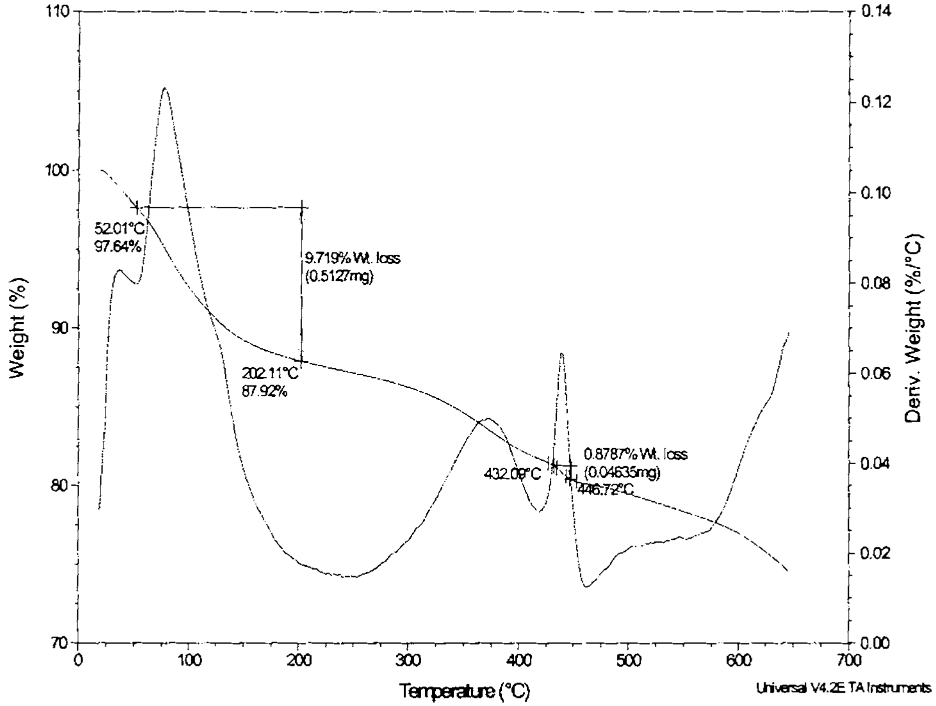


Fig.4.11 TGA of SBR latex cement paste

Apart from the initial of weight loss due to vaporisation of the moisture this thermograph in Fig.4.11 displays a decrease in the weight above 300°C. SBR undergoes thermal degradation at this temperature. Though it does not undergo reactions with cement the polymer forms a film around the cement particles during cement hydration. This is indicated by reduction in the percentage of weight between 400° C and 450° C.

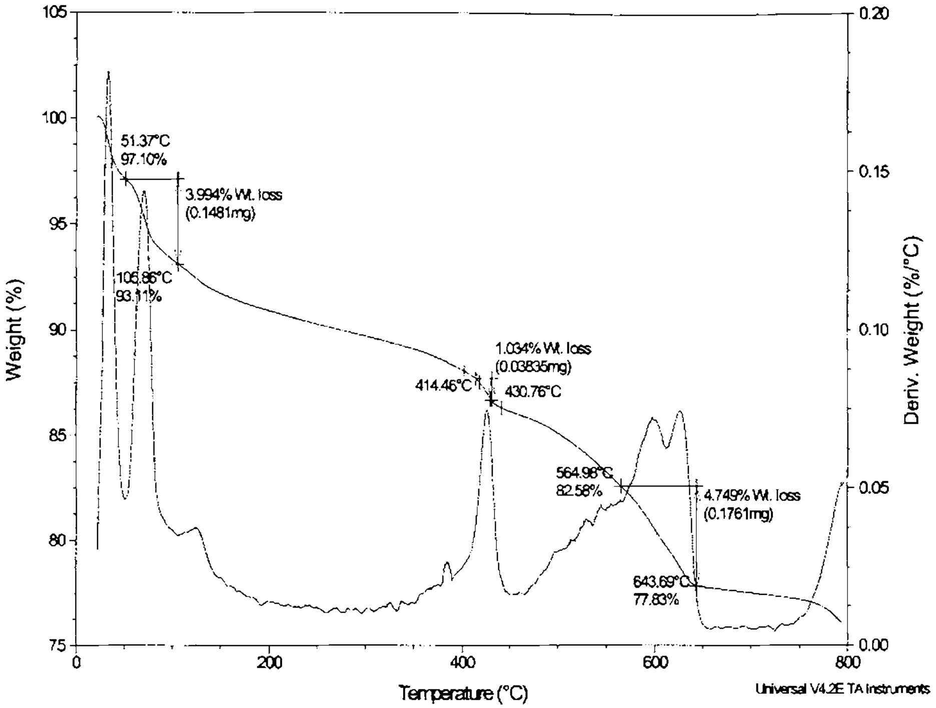


Fig.4.12 TGA of NBR latex cement paste

As seen in the thermal curve of NBR latex cement composite in Fig.4.12 there are two peaks indicating losses of weight below 200 C. The initial decrease indicates the moisture loss from the matrix and the second loss may be due to degradation of some emulsifiers present in the NBR latex. The reduction in weight at around 400°C indicates that hydration of cement has taken place. The degradation of the polymer has taken place at around 600°C.

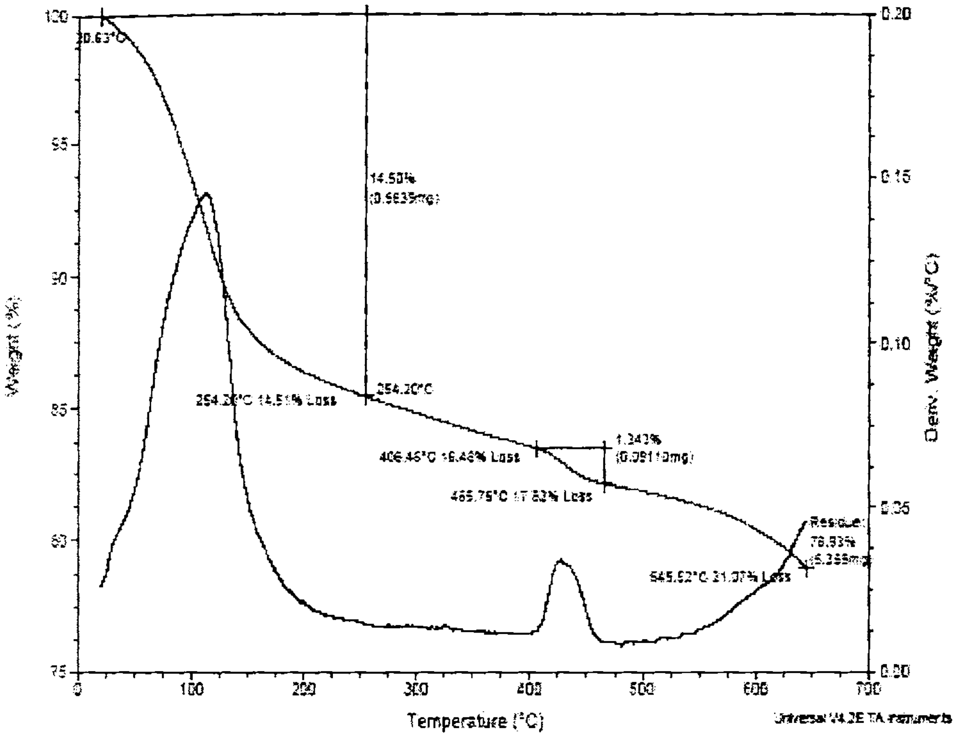


Fig.4.13 TGA curve of RF cement paste

As revealed in Fig.4.13 initial loss of weight is due to the vapourisation of pore and interlayer water present in the matrix which is similar to that of virgin cement. $Ca(OH)_2$ is usually formed as a byproduct during the hydration of cement particles. The negligible weight loss between 400°- 480°C indicates the absence of $Ca(OH)_2$ in the resin cement matrix. This may be due to the fact that the resorcinol formaldehyde resin prevents the complete hydration of the cement. The decomposition of the RF resin is indicated as a weight loss above 600°C.

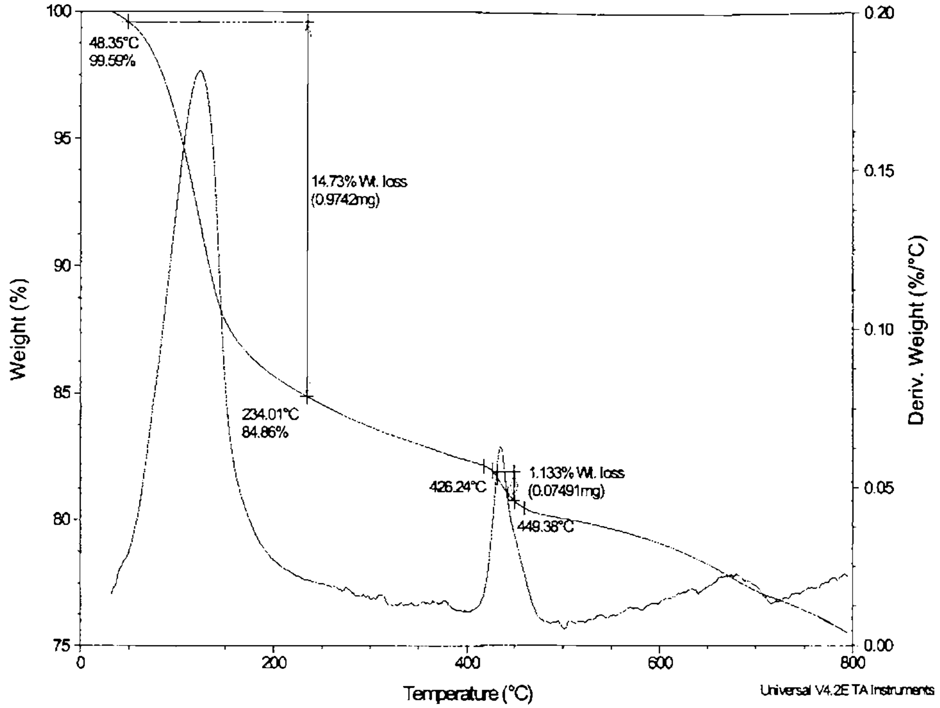


Fig.4.14 TGA of PF cement paste

In Fig.4.14 PF resin cement paste exhibits weight losses similar to that of virgin cement paste. Though PF resin does not undergo significant interaction with the cement particles, weight loss between 400°C and 450°C is less than that for virgin cement. This may be because the Ca^{2+} ions are embedded in the three-dimensional crosslinked network of the PF resin. The weight loss after 600°C may be due to degradation of the phenol formaldehyde resin [8] and the decarbonation of the $CaCO_3$.

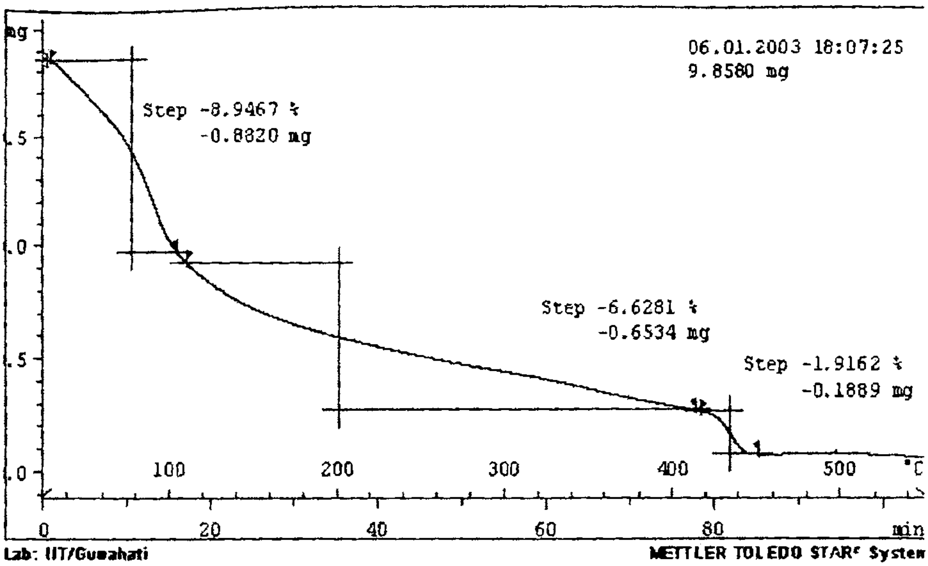


Fig.4.15 TGA of CF cement paste

From Fig.4.15 it is seen that m- cresol formaldehyde does not undergo any interaction with the cement particles unlike RF resin. There is a considerable loss of weight between 400°C and 450°C indicating that the resin does not hinder the cement hydration.

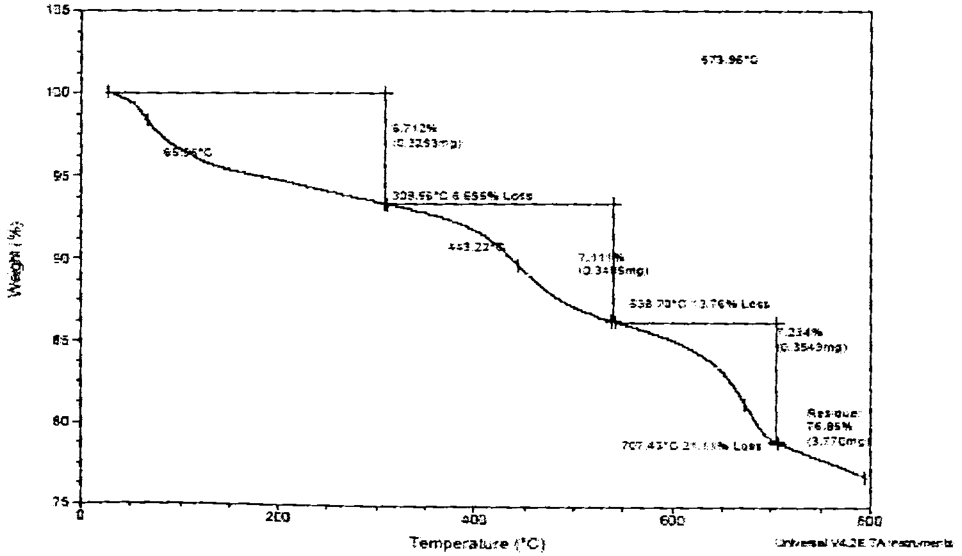


Fig.4.16 TGA of CNSL PF cement paste

CNSL PF resin is a hydrophobic thermosetting resin. When it is mixed with cement it does not mix with the cement uniformly and does not undergo interactions with the cement. As seen in Fig.4.16 the weight loss of 0.3419 indicates that it does not interfere with the cement hydration. The decomposition of resin takes place above 600°C.

Generally, cement composites of thermoplastics exhibit better mechanical behaviour than thermosets and rubbers but the properties are temperature dependent since they soften and melt at higher temperature and undergo degradation. Thermosets such as phenolic resins and melamine formaldehyde resin form a dense three-dimensional network in the cement matrix, which is impermeable to external chemicals and thereby increases the durability of the cement.

In Table 4.1 the thermal transitions at various temperatures (°C) and the corresponding percentage weight losses are summarized. The I.TEMP in the table indicates the initial temperature when the sharp decrease in weight was observed and F.TEMP shows the final temperature.

Table 4.1 Weight loss at various thermal transitions for cement composites of polymers

POLYMER	I.TEMP-1	F.TEMP-1	WT. LOSS	I.TEMP-2	F.TEMP-2	WT.LOSS	I.TEMP-3	F.TEMP-3	WT.LOSS
PF-PVAL	51.37	276.39	12.01	433.39	453.80	1.092	585.16	698.17	4.596
AS	23.76	204.76	11.43	406.95	430.32	1.686	--	--	--
PVAC	59.08	238.78	11.46	438.66	459.76	.9756	--	--	--
CEMENT	58.43	149.14	6.391	428.71	443.67	1.205	--	--	--
PEG	60.84	225.95	12.19	438.39	465.45	1.027	--	--	--
NBR	51.37	105.86	3.994	414.46	430.76	1.034	564.98	643.69	4.749
PVAL-B	68.79	243.61	11.25	416.71	439.62	1.056	--	--	--
SBR	52.01	202.11	9.719	432.09	446.72	.08787	--	--	--
L-NBR	37.26	135.17	9.8267	336.68	525.99	1.257	--	--	--
PVAL	36.24	378.68	13.02	425	470	1.271	--	--	--
RFC	20.63	254.20	14.50	406.46	465.75	.0911	--	--	--
PFC	35	234.01	14.73	426.24	449.38	0.0749	--	--	--

4.3.2 Soxhlet Extraction

The percentage extractable matter was determined by Soxhlet extraction studies carried out for 24h with hot water. The results are given in Table 4.2.

Table 4.2 Percentage of hot water soluble extractables in polymer cement composites

S.No	Polymer	% extracted
1.	NBR	7.725
2.	SBR	11.093
3.	PFVA	5.581
4.	PVAB	5.2975
5.	PVAL	20.03
6.	PEG	16.34
7.	PEG-A	7.412
8.	PVAC	12.524
9.	Cement	17.87
10.	RFC	1.433
11.	PFC	1.715
12.	MFC	16.129
13.	AS	7.663

a) Rubbers

This study revealed that the extractable matter is less in the case of rubber latex cement pastes compared to the virgin cement. This may be due to the polymer film formed around the cement particles, which prevents water-soluble matter from leaching. Hence, leachability of cement paste is reduced by the presence of polymer particles, which is a positive contribution of the polymer latex.

b) Thermoplastics

Among the thermoplastics used in this study, the leachability of PVAL composites was found to be the maximum. PVAL does not undergo any interactions with cement and therefore gets extracted by hot water. When PF or borax is added to PVAL-cement pastes this behaviour is remarkably reduced.

As explained in Section 2.3.3 (b) borax forms a water insoluble gel with PVAL in the alkaline cement medium [10].

When PF resin is added to PVAL-cement, PVAL may undergo reactions (Fig. 4.17) with any residual formaldehyde present in the resin forming polyvinyl acetal polymer [11]. This polymer is insoluble in water and has little leachability. This forms a barrier preventing any soluble matter from leaching.

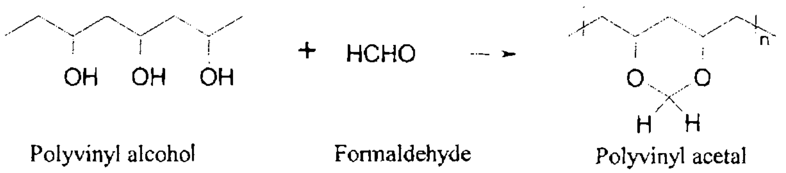


Fig.4.17 Reaction between polyvinyl alcohol and formaldehyde

Polyethylene glycol having low molecular weight undergoes interactions with the Ca ions whereas those with molecular weights higher than 6000 act as nucleating agents for crystallisation of calcite [12]. Therefore, the PEG with lower molecular weight exhibit 7.41% of water soluble extractables during the Soxhlet extraction compared to the polymer of higher molecular weight.

From the above table the water soluble extractables in PVAC is 12.5% which is lesser than virgin cement paste. As mentioned earlier in Section 4.3.1 (1) the PVAC undergoes saponification reactions in the presence of alkaline cement environment.

Acrylic styrene polymer undergoes self crosslinking reactions at room temperature thereby reducing the porosity of its composites with the cement paste and reducing the leaching of the water soluble components.

c) Thermosets

The phenolic resins reduce the extraction of water-soluble components. This may be due to the formation of a dense three-dimensional network, in which the cement particles are embedded which prevents leaching.

Moreover, in the case of RF it undergoes interactions with cement and further reduces the extractability of water soluble components [14].

4.3.3 EDTA titrations

From the above analysis, it was found that some polymers such as resorcinol formaldehyde resin reacted with the Ca ions and chelated them. Only such reactions were studied by this method. However, though some of the other polymers also form reaction products with Ca ions they do not chelate the calcium ions. The hydroxyl groups in the resorcinol are very reactive and form compounds with the Ca ions that are embedded in the three dimensional cross-linked network.

4.3.4 Scanning Electron Micrographs

Fig. 4.19 to 4.47 reveals the scanning electron micrographs of the thermoplastics, thermosets and rubbers used for the present study. These reveal the porosity, microcracks, extent of hydration of the cement and the distribution of the polymer in the cement matrix.

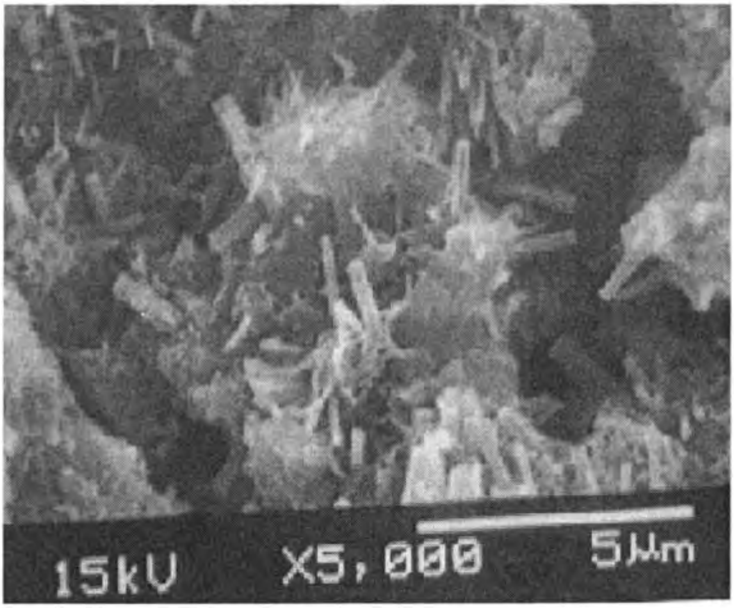


Fig.4.18 SEM of cement

In Fig.4.18, the SEM of cement, the internal structure of the cement reveals needle like crystals of cement gel, calcium hydroxide plates and the elongated ettringite crystals, all of which are products of cement hydration. Due to these crystallized forms, cleavage sites are developed on the surfaces. The calcium hydroxide undergoes reaction with external chemicals forming soluble salts thereby decreasing the strength and durability of the structure.

a) Rubbers

The micrographs shown below depict the morphology of the NBR latex cement composite before and after etching.

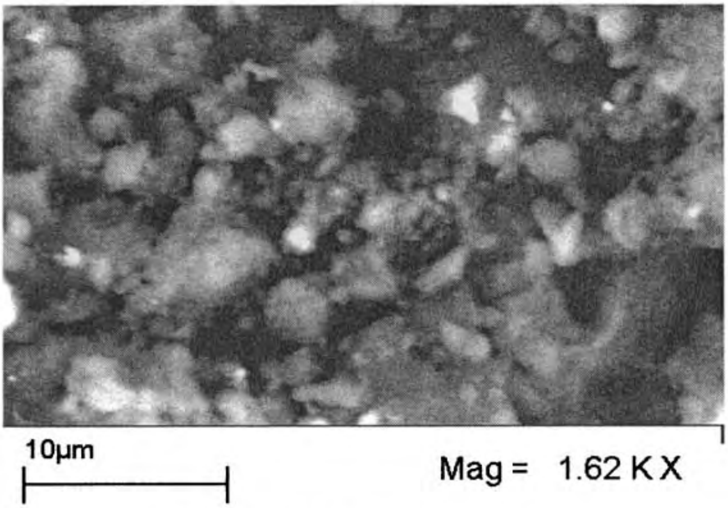


Fig.4.19 SEM of NBR cement composite

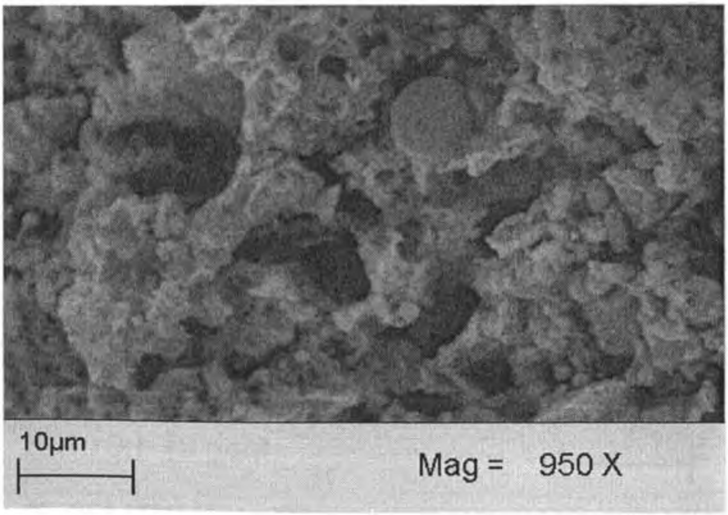


Fig.4.20 SEM of NBR cement composite- acid etched

From Fig. 4.19 it is seen that there are no needle like crystals of ettringite formed in the polymer cement matrix (found in the virgin cement paste) in the presence of NBR latex. Since the minimum film forming temperature of rubbers is below room temperature the latex forms a film around the cement particles as seen in Fig.4.20. This film prevents the movement of water to the cement particles thereby retarding the hydration of cement.

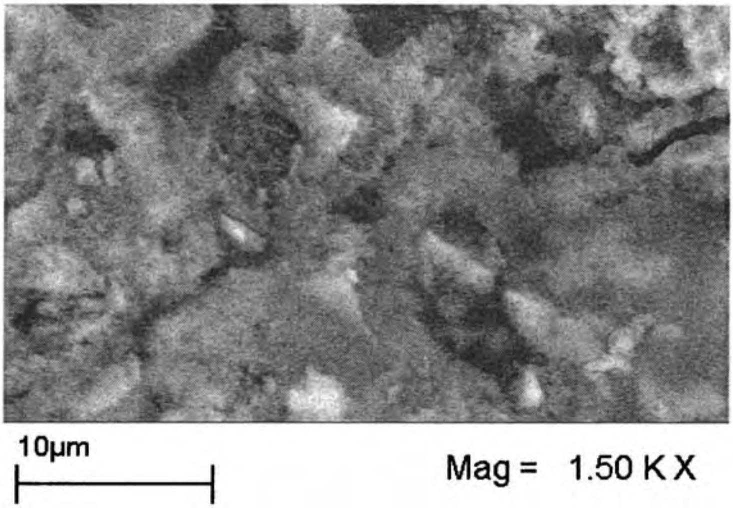


Fig. 4.21. SEM of SBR cement composite

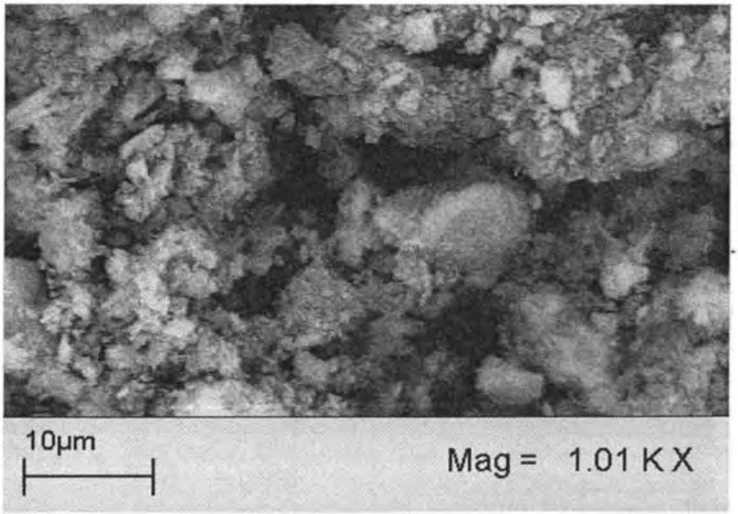


Fig. 4.22 SEM of SBR cement composite- acid etched

The microstructure of the fracture surface of SBR cement composite in Fig. 4.21 depicts a reduction in the size of the hydrated cement crystals. This has resulted in a more compact structure than virgin cement paste and absence of microvoids in the polymer cement matrix. In Fig. 4.22 layers of the polymer are seen on the cement particles and these stretch and bridge the gap between the voids and cracks.

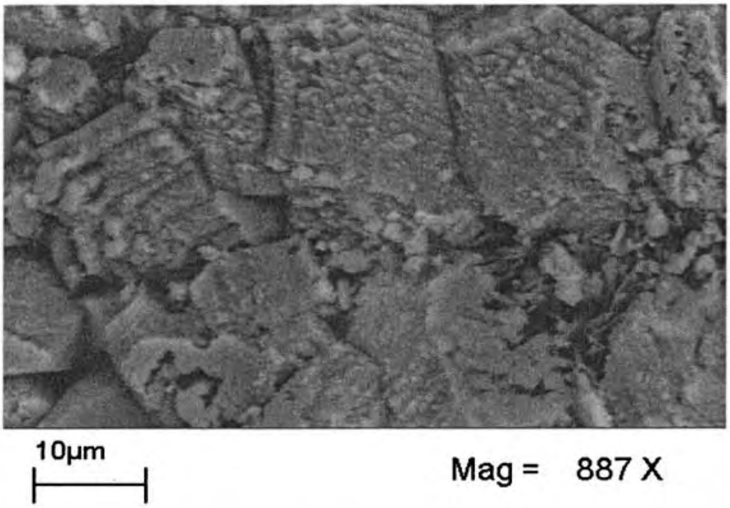


Fig.4.23. SEM of linear NBR spheres cement composite

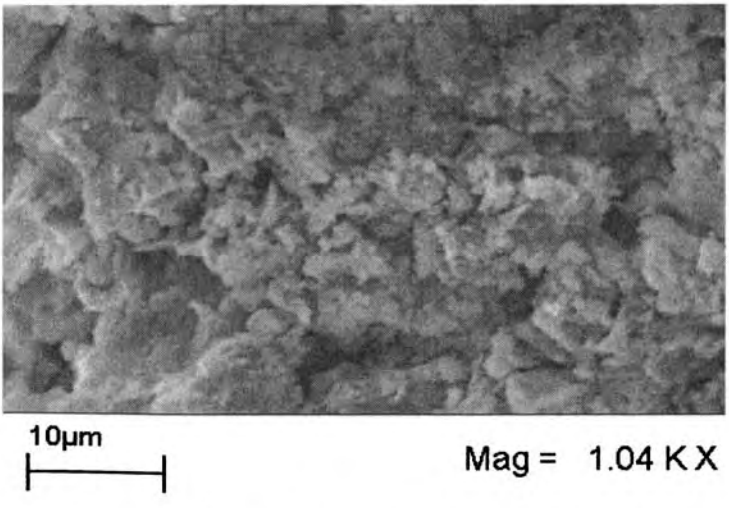


Fig.4.24. SEM of Linear NBR spheres cement composite- acid etched

Since the linear NBR spheres do not form a film around the cement particles they do not hinder the cement hydration. This is evident from the presence of hydrated crystals of the cement particles in Fig. 4.23. The acid etched micrograph in Fig.4.24 reveals the bridges formed by the NBR spheres over the microcracks though they do not form a film around the cement particles.

b) Thermoplastics

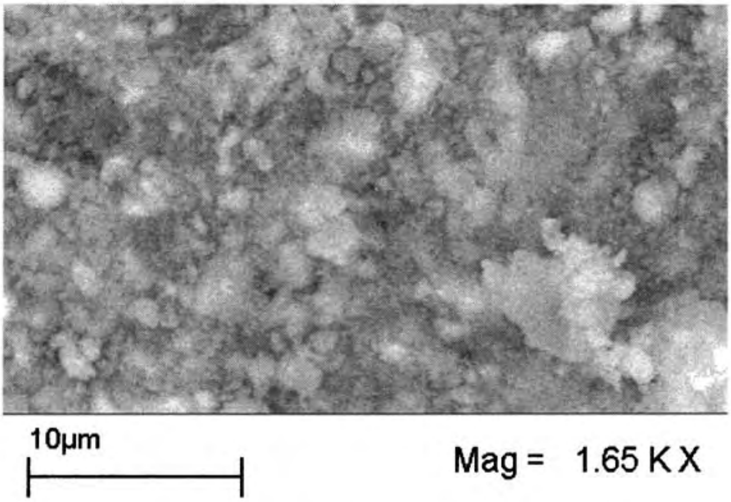


Fig.4.25. SEM of Poly vinyl acetate cement composite

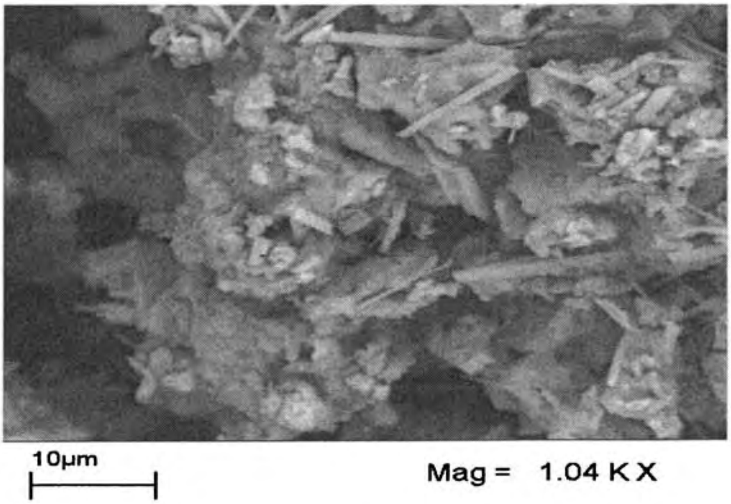


Fig.4.26. SEM of PVAC cement composite acid- etched

In the cement composites of PVAC the microstructure seems more homogenous with less microcracks and voids than virgin cement. The crystallized rods of ettringite in PVAC in Fig. 4.25 are an indication of its gradual formation due to the consumption of Ca ions by the acetate groups in the PVAC. This consumption retards the nucleation and growth of the ettringite crystals [7]. This also shows that the addition of the polymer decreases the hydration of cement by consuming the Ca ions present in the aqueous phase. PVAC are seen as fibrils in Fig.4.26 in the cement matrix.

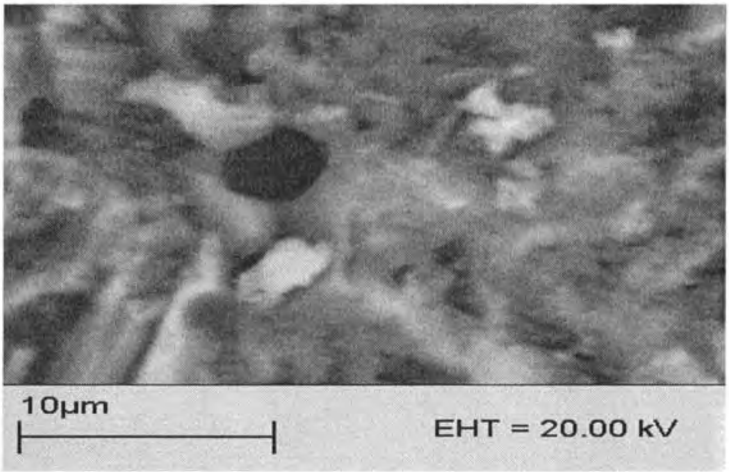


Fig.4.27. SEM of Poly vinyl alcohol cement composite

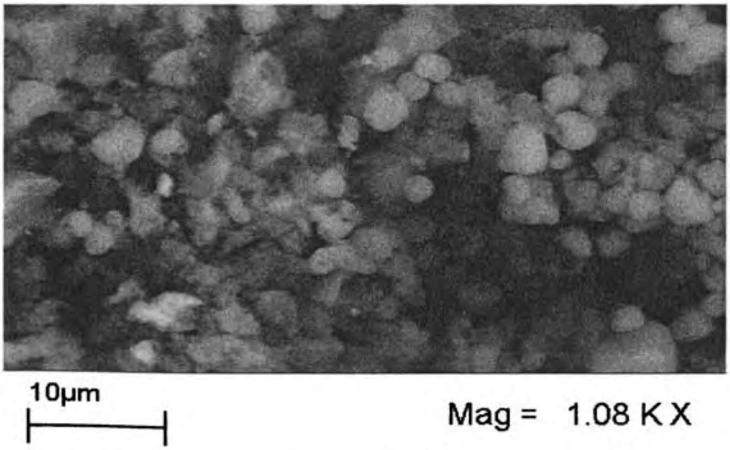


Fig.4.28 SEM of Poly vinyl alcohol cement composite- acid etched

In cement composites of PVAL in Fig.4.28 PVAL is seen as globules in the polymer cement matrix. Some of these globules can be observed between the cement hydrates while others around the non-hydrated cement grains. This clearly indicates that the polymer reduces the porosity of cement matrix by sealing the major pores. The polymer also prevents the percolation of water into the cement particles reducing the hydration rate. PVAL acts as a rheological additive and forms a film at lower P/C ratios [14]. This reduction in porosity prevents movement of external chemicals into the cement matrix thereby enhancing chemical resistance of the composites. This also slows down the penetration of gases and water in to cement matrix [15].

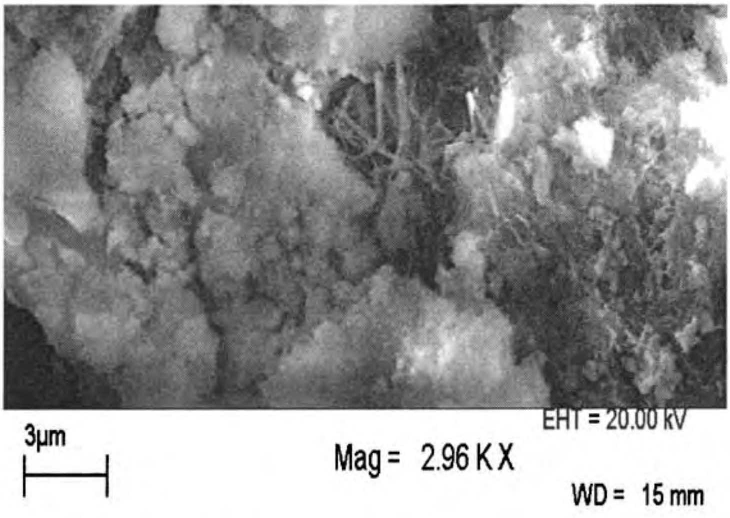


Fig.4.29 SEM of Poly vinyl alcohol borax cement composite

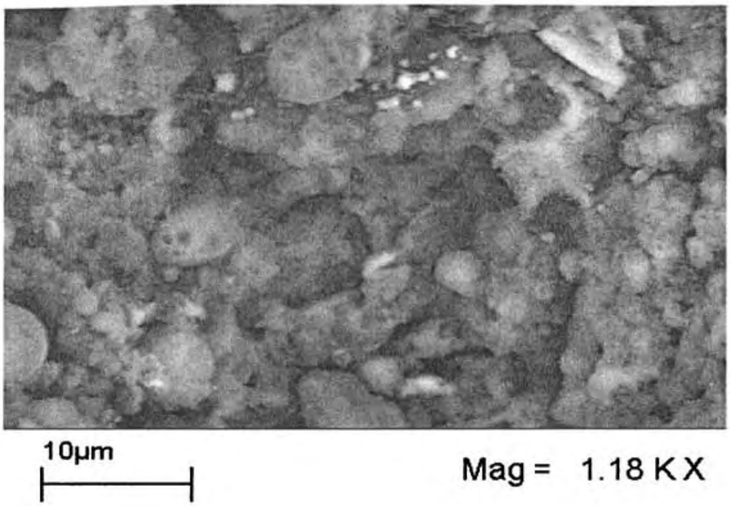


Fig.4.30. SEM of Poly vinyl alcohol borax cement composite- acid etched

The microstructure of the polyvinyl alcohol borax cement composite as seen in Fig.4.29 reveals a compact uniform matrix and absence of large crystals that usually form during cement hydration. In Fig.4.30 a decrease in the amount of PVAL globules and gel formation due to reaction between the PVAL and borax is observed. This gel prevents the leaching of the polymer and the water soluble components when exposed to moisture.

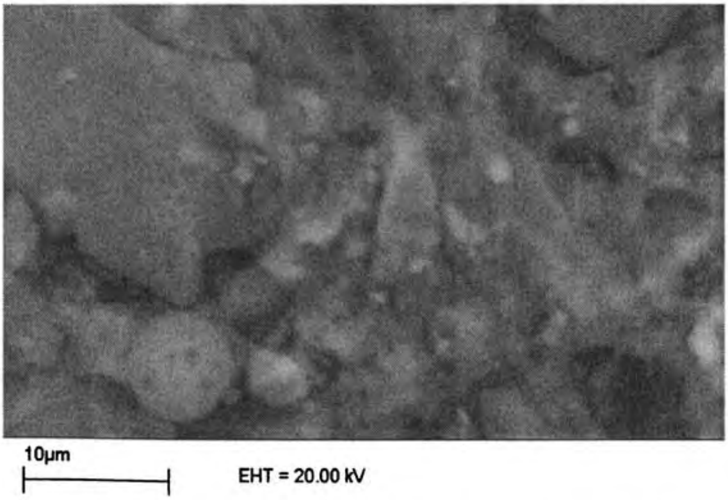


Fig.4.31 SEM of PF poly vinyl alcohol cement composite

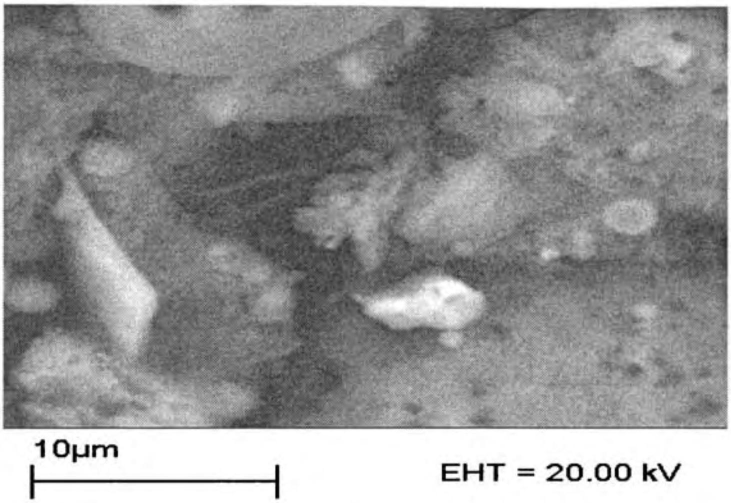


Fig.4.32 SEM of PF poly vinyl alcohol cement composite –acid etching

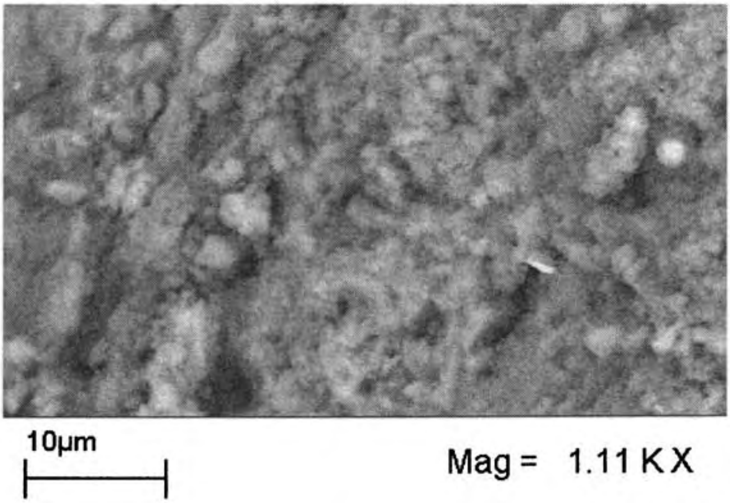


Fig.4.33. SEM of Poly ethylene glycol cement composite

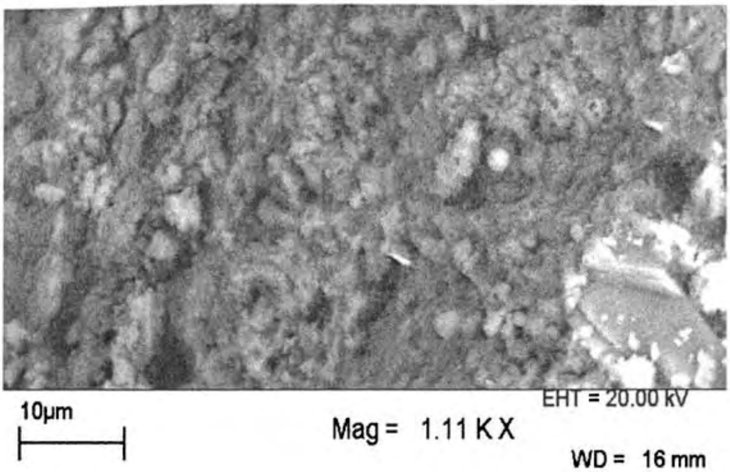


Fig.4.34. SEM of PEG cement composite- acid etched

In the cement composites of PEG, the microstructure seems more homogenous with less microcracks and voids than virgin cement. In the case of water soluble polymers like PEG (as indicated in Fig. 4.34) they act as rheological additives and form a film at lower polymer/cement ratios [14]. This coherent network of the polymer in the cement matrix as in Fig.4.35 prevents the dissolution of cement grains when exposed to external chemicals leading to enhanced chemical resistance of the composites and slows down the permeation of gases and water in to the cement matrix [15].

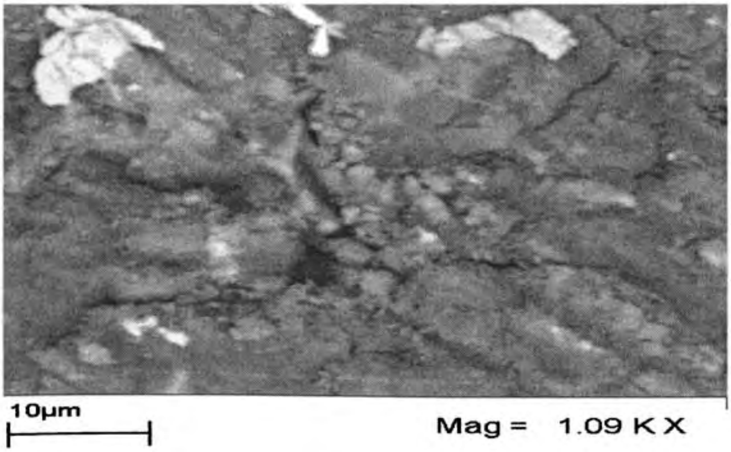


Fig.4.35. SEM of Acrylic styrene polymer cement composite

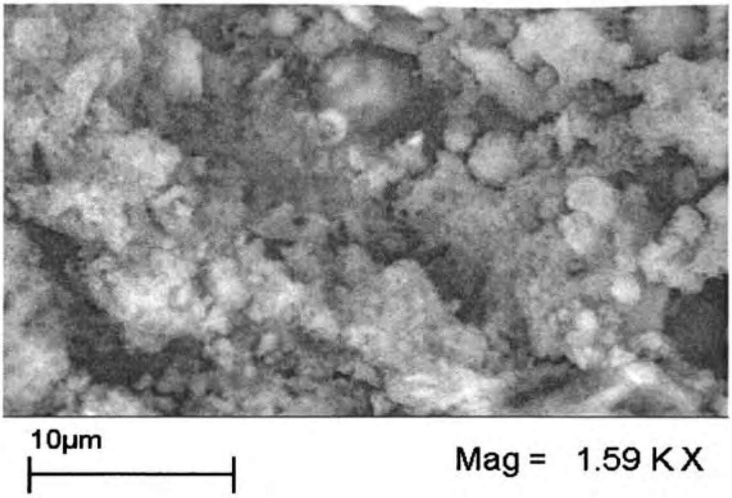


Fig.4.36 SEM of Acrylic styrene polymer cement composite- acid etched

The micrograph of unetched acrylic styrene polymer cement composite in Fig.4.35 reveals a matrix without voids and cracks. The dispersion of the acrylic styrene in the cement matrix is evident from the micrograph, Fig.4.36 of the polymer cement composite. It is also evident from the micrographs that there is no film formation due to the high MFT of the polymer.

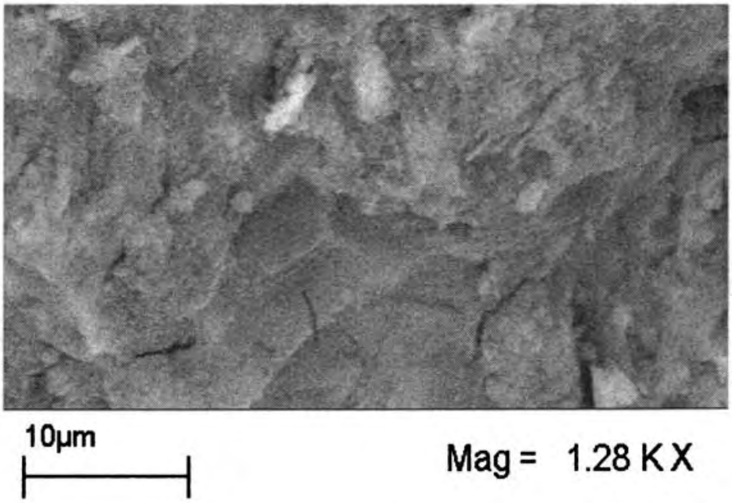


Fig.4.37 SEM of Acrylic polymer cement composite

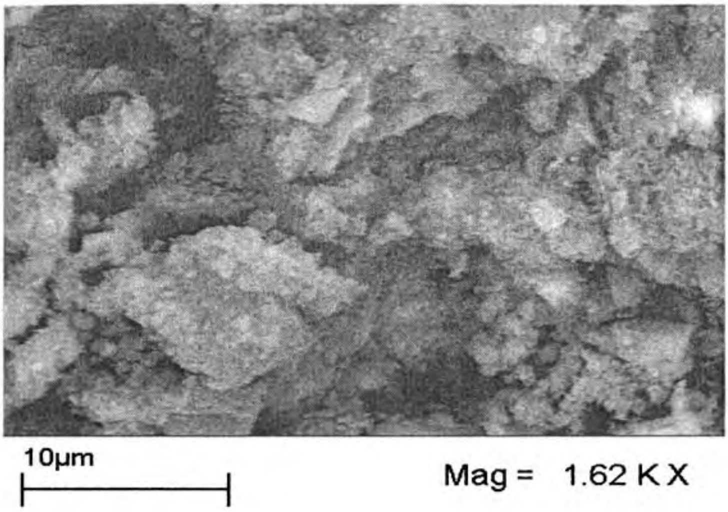


Fig.4.38 SEM of Acrylic polymer cement composite- acid etched

The unetched acrylic polymer cement composite in Fig. 4.37 shows a compact structure without micropores and voids in the polymer cement matrix. The polymer retards hydration of cement particles which is indicated by the absence of needle like crystals of ettringite. The microstructure of the etched composite in Fig. 4.38 exposes the polymer network within the cement matrix.

c) Thermosetting polymers

These polymers form a dense three dimensional network when crosslinked and enclose the cement particles in the network. In the case of most of the cement composites of phenolic resins employed in this study most of the cement hydration takes place in first 24 hours after mixing. During the crosslinking of the resin the excess of formaldehyde evaporates creating microvoids in the composites as revealed in the micrographs of the unetched samples.

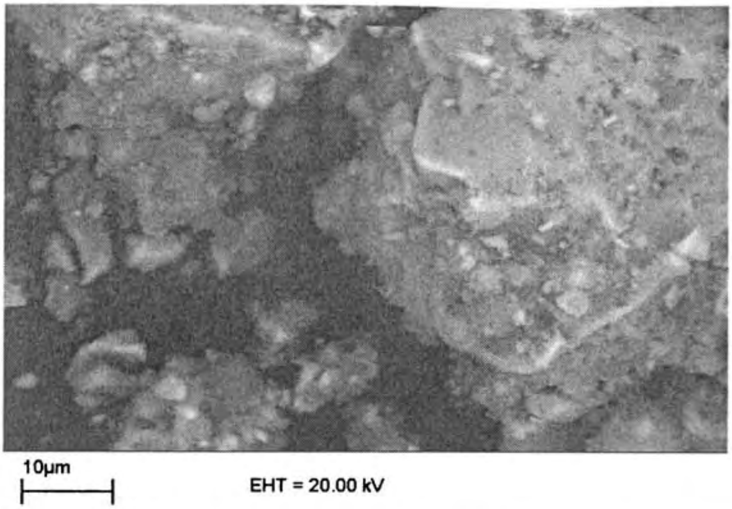


Fig.4.39 SEM of PF cement composite

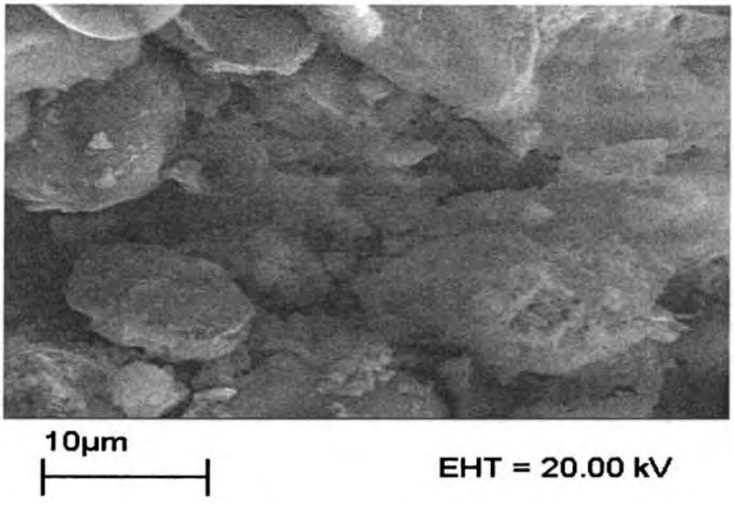


Fig.4.40. SEM of PF cement composite- acid etched

The PF resin cement composite was examined under the SEM after the resin crosslinked to form a three-dimensional network and after hydration of cement particles. When the resin gets crosslinked some of the cement particles get embedded in it. Therefore, the hydration of these cement particles does not go to completion. This is evident from the absence of hydrated crystals in the micrograph of unetched PF resin cement composite Fig. 4.39. The etched samples in Fig. 4.40 reveal the polymer network in the cement and the presence of hydrated and unhydrated cement particles in this network.

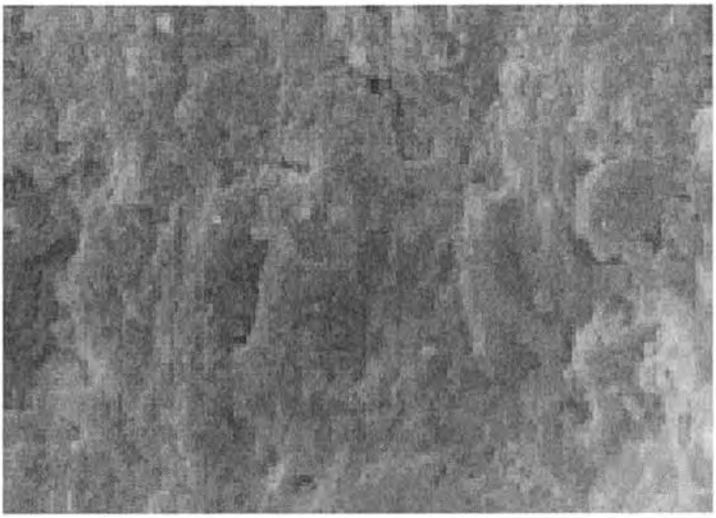


Fig.4.41 SEM of unetched RF resin cement composite

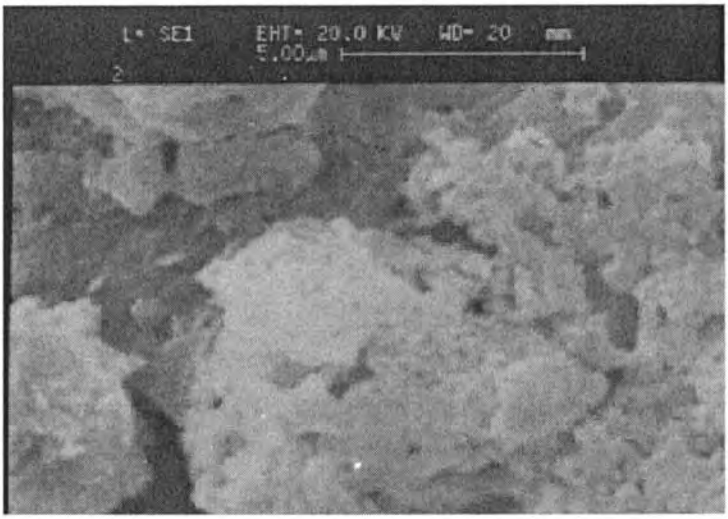


Fig.4.42 SEM of etched RF resin cement composite

The reduction in the crystal structures in Fig.4.41 results in a denser microstructure than that of conventional virgin cement. The porosity of the resin cement composite is much less than virgin cement paste resulting in a more compact structure. This decrease in the porosity results in improved chemical resistance of the composite. The above observations were confirmed from the results obtained from the pulse velocity measurements. Since the pores are occupied by the phenolic resin the possibility of external fluid permeation is less thereby increasing the durability of the RF resin cement. It is observed in Fig. 4.42 that the polymer has interwoven into the cement matrix resulting in a interpenetrating polymer network.

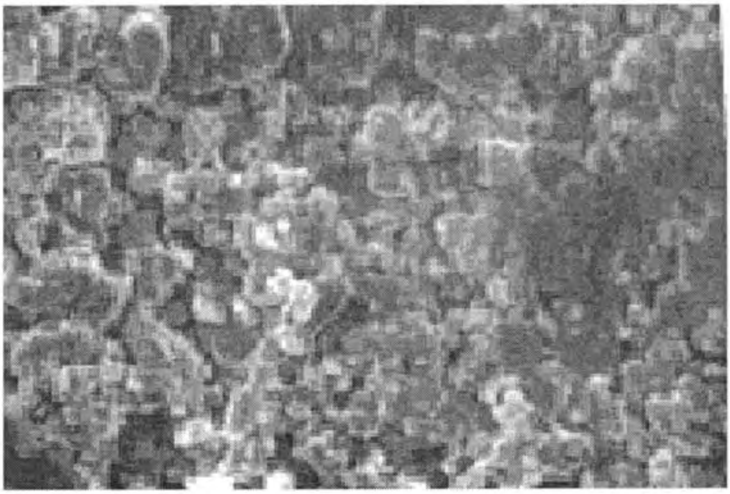


Fig. 4.43 SEM of unetched CF resin cement composite

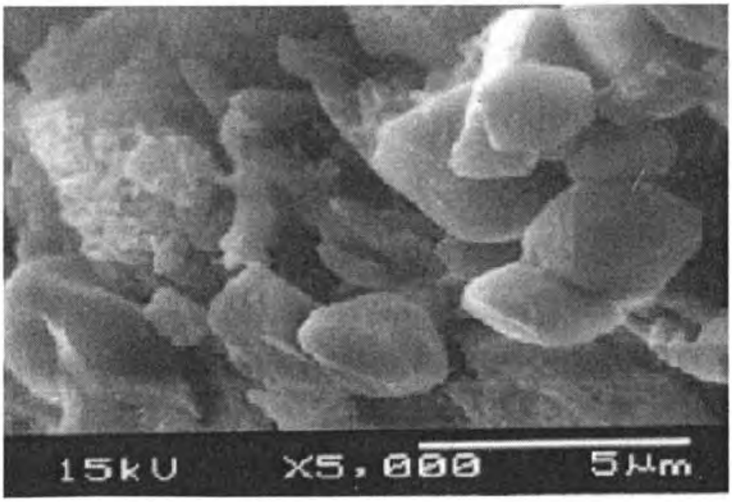


Fig. 4.44 SEM of etched CF resin cement composite

As seen in Fig.4.43 the CF resin forms a uniform matrix though it does not undergo any interaction with cement particles. In the micrograph of etched resin cement as seen in Fig.4.44 the resin is seen as globules in which the hydrated and unhydrated cement particles are embedded. This may be because the resin forms a dense network after crosslinking.

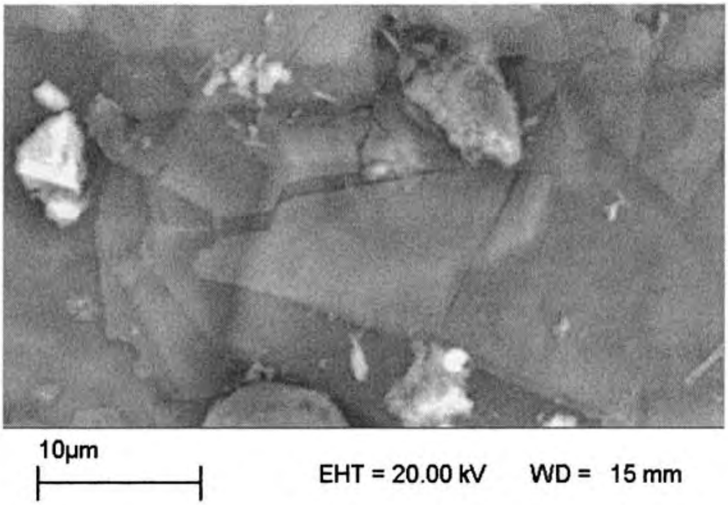


Fig.4.45. SEM of CNSL phenol formaldehyde resin cement composite –unetched

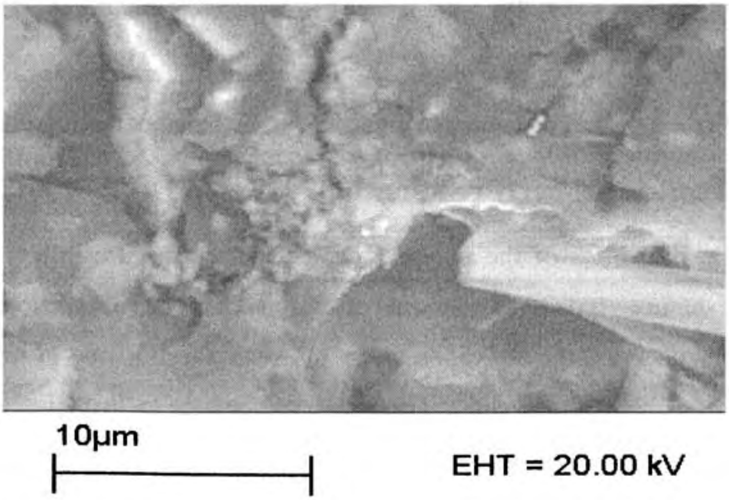


Fig.4.46. SEM of CNSL phenol formaldehyde resin cement composite –etched

CNSL-PF resin is a hydrophobic resin and therefore does not form a good composite with the hydrophilic cement. This resin is seen as a separate phase in Fig.4.46. This explains the poor mechanical and chemical resistance properties of the composite. Since the resin does not mix with the cement particles hydration takes place unhindered.

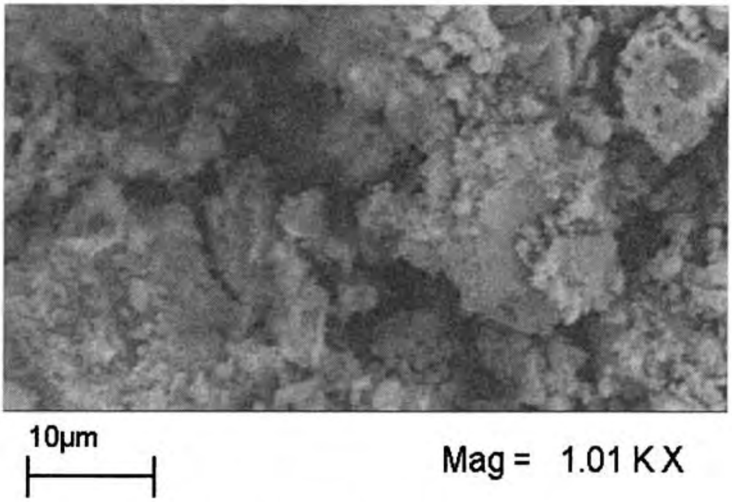


Fig.4.47. SEM of MF - acid etched

Studies on the microstructure of MF resin cement composite after acid etching (Fig.4.47) shows a network similar to that of the other thermosetting resins.

4.4 Structure property relationship

The properties of the polymer cement composite are influenced by the chemical nature, type and amount of polymers. The interactions vary for polymers with the same backbone chain but with varying side groups and also with varying molecular weight. This section attempts to investigate the above factors with respect to the polymers used.

4.4.1 Polyvinyl alcohol and polyvinyl acetate

It is evident from Fig.4.48 that these monomers differ in the side groups attached to the backbone—in case of PVAL it is OH and it is $OCOCH_3$ for PVAC.

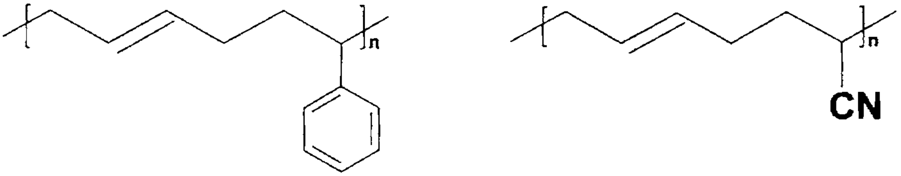
Fig. 4.48 Structures of PVAL and PVAC

In the case of acrylates and PVAC, the polymer undergoes saponification reaction in the presence of an alkaline cement medium. First, Ca ions present in the pore solution during the hydration of the cement initiates the reaction with some of the free carboxylic groups present in the polymer. Later, the reaction between the carboxylate group and the OH^- ions is initiated. This results in a more compact matrix with a bond formed between the Ca ions of the $Ca(OH)_2$ and the acetate ions of the polymer. $Ca(OH)_2$, a byproduct of cement hydration is responsible for leaching on exposure to moisture which affects the durability of the building structure. This is the reason why the compressive strength and the chemical resistance of PVAC is superior to PVAL. The acid resistance and leachability of the poly vinyl alcohol-cement composites improves when borax and PF resin are added.

4.4.2 Rubbers

The rubber latexes used for this study differ in the comonomer attached to the butadiene molecule (Fig.4.49). In the case of SBR, styrene is attached to the butadiene while for NBR, it is the acrylonitrile molecule. Though NBR is a polar rubber the compressive strength and the chemical resistance of the SBR composite are found to be better than the former.

Both SBR and NBR apparently did not undergo any chemical interactions with the cement.



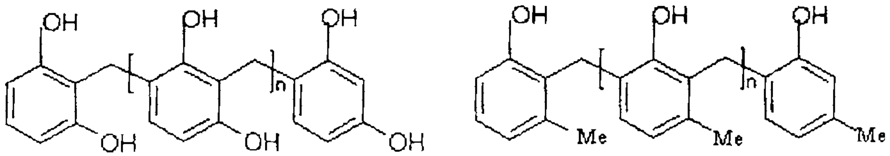
Styrene butadiene rubber- SBR **Acrylonitrile butadiene rubber- NBR**

Fig.4.49 Structures of SBR and NBR

4.4.3 Phenolic resins

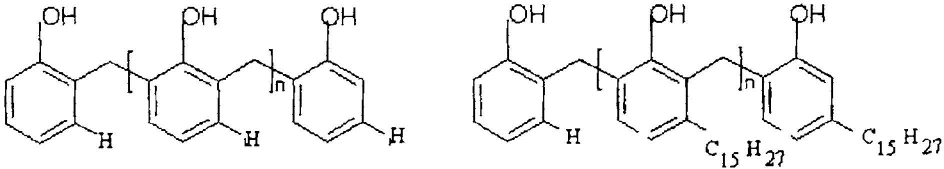
From the Fig.4.50 the phenolic resins used in this study viz. PFC, CFC, RFC differ in the side group attached at the meta position of the phenolic compound. In the case of phenol the side group is H, CH_3 for m-cresol and OH for resorcinol. The rate of formation of the phenolic resin is fast in the order resorcinol > m-cresol > phenol. Resorcinol formaldehyde forms a crosslinked network during synthesis due to the high heat of formation and reactivity. In the case of m-cresol formaldehyde, the prepolymer had to be added to the cement within 48 hours of synthesis before it formed a three-dimensional network. The interactions of the phenolic resins with cement are also different.

Though resorcinol formaldehyde prevents the completion of cement hydration (as evident from the TGA graphs), it forms a bond with the Ca ions present in the cement and improves the properties of the composite. The chemical resistance properties of phenol formaldehyde resin cement composite increases on addition of poly vinyl alcohol due to the formation of the acetal structure. The properties of the CNSL phenol formaldehyde resin are very poor may be due to the bulky unsaturated side chain in the case of the CNSL compound.



Resorcinol formaldehyde resin

M-cresol formaldehyde resin



Phenol formaldehyde resin

Cardanol PF resin

Fig.4.50 Structures of phenolic resins

4.4.4 Molecular weight of PEG

The influence of the molecular weight of the polymer on the properties of the polymer cement concrete has been investigated for many polymers such as poly acrylic acid [16] and PVAL [17]. The above studies reveal that the molecular weight of the polymer in case of PVAL has an influence on the flexural properties of the composite and in the case of poly acrylic acid it has an influence on the chemical reaction with the cement.

In this study, two different molecular weights of PEG were used to prepare polymer cement composites. Though there was no significant change in the compressive strength of the composites the extraction of the water soluble components was more in the case of PEG of higher molecular weight than the polymer with lower molecular weight. This may be due to the formation of the bond between the Ca ions and OH— and -O—groups in the low molecular weight PEG (below 5000) molecule. As the molecular weight of the PEG increases the viscosity of its solution in water also increases. Therefore the polymer induces the nucleation of the calcite crystal [12] encouraging the formation of hydration crystals.

It was also observed that the phenol formaldehyde resin of lower molecular weight forms cement composites of comparatively inferior properties.

4.5 Conclusions

Microstructural studies of the samples of cement composites of different rubbers, thermoplastics and thermosets were carried out based on scanning electron micrographs, thermographs, EDTA titrations and Soxhlet extraction data. It was observed that the addition of polymer to cement changes the microstructure and morphology of the cement. SEM observations show that the polymer modified cement microstructure is characterized by the presence of polymer networks encapsulating hydrated cement particles, polymer granule beads and unhydrated cement grains.

Some of the broad conclusions arrived at by the addition of the polymer are cited below:

a. The polymer retards and interferes with the hydration of cement particles as evidenced by the absence of hydrated cement crystals in most of the micrographs of the composites.

b. The polymer seals the pores and microvoids preventing the leachability of water-soluble components thereby enhancing the durability of the composite when exposed to external chemicals.

c. Some of the polymers such as RF and PVAC undergo interactions with the cement particles which result in the formation of bonds between the cement and polymer phases.

d. Depending on the minimum film formation temperature of the polymer and the P/C ratio, the polymer coalesces to form a film around the cement particles. This takes place during the hydration of cement. At higher values of P/C the polymer forms a thick film which prevents the percolation of water into the cement particles. Though this film retards the hydration of cement it serves to act as a barrier to external chemical environments.

e. Among the cement composites of the polymers prepared, the ones that used thermoplastics and rubber latexes exhibit film formation while those that used thermosets had cement particles embedded in a dense 3-dimensional network formed by the thermoset.

f. The properties of the polyvinyl alcohol cement composites are improved by the addition of borax. Borax decreases the leachability of water soluble components by forming a water insoluble gel with PVAL.

Among the rubbers and latexes used linear NBR spheres form bridges over cracks formed in the cement matrix enhancing the load bearing capacity of the composite.

Higher molecular weights of polyethylene glycol do not interfere with the hydration of cement. They also reduce the leachability of water-soluble components to form better composites.

RF forms better cement composites among the thermosets employed in this study by forming a bond between the Ca ions in the cement and OH groups in the resin. This resin also reduces the leachability of the water-soluble components in the cement matrix.

References

[1] Larbi, J.A. and Bijen, J.M.J.M.; *Proc. of the 6th ICPIC*, Sept. 24-27, 1990, pp. 185-192.

[2] Janotka, J. Madejová, L. Stevula and D.M. Frt'alová; *Cem. Conc. Res.*, Vol.26, No.11, 1996, pp. 1727–1735.

[3] Jeewoong Kim and Vipulanandan C.; *Cem. Conc. Res.*, Vol. 33, No.5, 2003, pp. 621-627.

[4] Jeffery G. H., Bassett J., Mendham J., Denney R.C.; *Vogel's textbook of Quantitative chemical analysis*, Fifth edition, Published by Longman Scientific & Technical and co published by John Wiley and Sons, USA, 1989, pp. 325.

[5] Jae-Ho Kim, Richard E. Robertson and Antoine E. Naaman; *Cem. Conc. Res.*, Vol.29, No.3, March 1999, pp. 407-415.

[6] Lucia Alarcon-Ruiz, Gerard Platret, Etienne Massieu and Alain Ehrlacher; *Cem. Conc. Res.*, Vol.35, No.3, 2005, pp. 609-613.

[7] Silva, D.A. et al; *Cem. Conc. Res.*, Vol. 32, No.9, 2002, pp. 1383-1390.

[8] Knop, A. and Scheib, W.; *Chemistry and application of phenolic resins*, Chapter 7, Springer Verlag Publishers, New York 1979.

[9] Priya Nair and Paul A.; *Proceedings of the 25th Conference on Cement Microscopy and Symposium on Rietveld Techniques, ICMA*, Richmond, U.S.A., 6-10th April 2003.

[10] Vinyl alcohol polymers; *Encyclopedia of polymer science and engineering,* Vol.17, John Wiley and Sons, pp. 175.

[11] Charles E. Carraher Jr.; *Seymour-Carraher's Polymer Chemistry,* Marcel Dekker Inc. Publishers, USA, 6th Edition, 2003, pp.127.

[12] An-Jian Xie, Chun-Yan Zhang, Yu-Hua Shen, Ling-Guang Qiu, Pei-Pei Xiao and Zhao-Yang Hu, *Cryst. Res. Technol.*, Vol.41, No. 10, 2006, pp. 967 – 971.

[13] Takata et al.; *Proc. of the Second East Asia Symposium on Polymers in Concrete (II-EASPIC)*, China, 1997, pp. 503-510.

[14] Knapen, E. and Gemert, D.V.; *Proc. of International Symposium Polymers in concrete,* Portugal, 2-4 April 2006, pp. 85-95.

[15] J. Mirza, M. S. Mirza and R. Lapointe; *Construction and Building Materials,* Vol. 16, No.6, September 2002, pp. 365-374.

[16] Huizhong, W. et al; *Proc. of 6th ICPIC*, Shanghai, China, 1990, pp. 204-209.

[17] McHugh, A.J. and Tan, L.S.; *Journal of Materials Science*, Vol. 31, 1996, pp. 3701-3701.

Chapter 5

CONCLUSION OF THE WORK

From the above studies the following conclusions were made:

- Polymers in general have three effects on the PMC:
    - They partially obstruct the fine pores in the network formed by the cement hydrates,
    - They fill the larger pores and bridge the microcracks in the cement matrix
    - They tend to form films that encapsulate the cement grains.
- Addition of a polymer to the cement-water blend results in the reduction of the water to cement ratio of the PMC which leads to the formation of a compact structure with lesser imperfections than that formed in virgin cement matrix.
- The addition of a polymer also results in higher air entrainment, improved workability and a decrease in cement hydration.
- Though the load bearing capacity reduces due to addition of a polymer, the degree of retention of compressive strength of the PMC on exposure to external chemical environments is far superior to that of virgin cement.
- Properties of the composites are dependent on the chemical nature and percentage of polymer in the PMC.
- Thermoplastics form better composites with cement than rubbers and thermosetting polymers in terms of compressive strength. Among the

thermoplastics, cement composites of poly vinyl acetate and poly ethylene glycol exhibit higher load bearing capacities.

- Thermosets form a dense three-dimensional brittle network in the cement matrix. This network prevents the percolation of external chemicals into the matrix preventing their interactions with the cement particles. This leads to improved resistance towards various chemical environments. However the compressive strengths of thermoset based PMCs were found to be less than that of virgin cement.
- Thermal analysis of the PMCs indicates interactions between some of the polymer molecules and cement particles.
- The leachability of the hot water soluble components reduces when polymers are added to cement which increases its durability. The percentage of water soluble components of poly vinyl alcohol modified cement paste is less when borax or phenol formaldehyde resin is added to it.
- Polymers form a film around the cement particles during the formation of a PMC. While this results in the reduction in the extent of hydration of the cement particles, it increases the chemical resistance properties of the overall composite. The formation of the film depends on the proportion of the polymer added to the cement and their minimum film forming temperature.
- Polymers modify the microstructure of the hydration products of cement and form a dense matrix. This also contributes to the increase in chemical resistance.
- Unlike styrene butadiene rubber, nitrile rubber and poly vinyl alcohol, the polymers RF, PEG and PVAC undergo interactions with cement. Interactions like these enhance the durability of PMC in different chemical environments.

LIST OF ABBREVIATIONS

Abbreviations	Expanded form
AS	Acrylic styrene polymer
ASC	Acrylic styrene polymer cement paste
ASTM	American standard of testing methods
BIS	Bureau of Indian standards
BSI	British standards institute
C_2S	Di calcium silicate, belite
C_3 AF	Tetra calcium aluminoferrite, Felite
C_3A	Tri calcium aluminate, celite
C_3S	Tri calcium silicate, Alite
CF	m- cresol formaldehyde resin
CFC	m- cresol formaldehyde resin cement paste
EDTA	Ethylene diamine tetra acetic acid
EN	European standards
LH	Low heat cement
L-NBR	Linear Acrylonitrile butadiene rubber
L-NBRC	Linear Acrylonitrile butadiene rubber cement paste
MF	Melamine formaldehyde resin
MFC	Melamine formaldehyde resin cement paste
MFT	Minimum film forming temperature
NBR	Acrylonitrile butadiene rubber
NBRC	Acrylonitrile butadiene rubber cement paste
NR	Natural rubber
PA	Acrylic polymer
PAC	Acrylic polymer cement paste
PAN	Polyacrylonitrile
PC	Portland cement

PCC	Polymer cement concrete
PEG	Poly ethylene glycol
PEGC	Poly ethylene glycol cement paste
PF	Phenol formaldehyde resin
PFC	Phenol formaldehyde resin cement paste
PIC	Polymer impregnated concrete
PMC	Polymer modified concrete
PMMA	Poly methyl methacrylate
PTFE	Poly tetrafluoroethylene
PVAC	Polyvinyl acetate
PVAC-C	Polyvinyl acetate cement paste
PVAL	Poly vinyl alcohol
PVAL-B	Poly vinyl alcohol borax
PVAL-B-C	Poly vinyl alcohol borax cement paste
PVALC	Poly vinyl alcohol cement paste
PVC	Poly vinyl chloride
RF	Resorcinol formaldehyde resin
RFC	Resorcinol formaldehyde resin cement paste
SBR	Styrene butadiene rubber
SBRC	Styrene butadiene rubber cement paste
SEM	Scanning electron microscope
SR	Sulphate resistance
Tg	Glass transition temperature
TGA	Thermo gravimetric analysis
Tm	Melting temperature

GLOSSARY OF TERMS

Aggregate:	Sand and gravel mixed with cement and water to make concrete.
Bogue calculation:	Calculation to give the approximate proportions of four main clinker minerals in Portland cement.
Bleeding:	A form of segregation in which some of the water in a mix tends to rise to the surface of freshly placed concrete.
C_2S:	Dicalcium silicate
C_3A:	Tricalcium silicate
C_3S:	Tricalcium silicate
C_4AF:	Tetracalcium aluminiferrite
Cement clinker:	Portland cement clinker is unground (unmilled) nodular product from the Kiln.
Cement hydration:	Process of reaction of cement with water.
Cement:	Hydraulic powder which reacts with water to form a solid mass
Cis arrangement:	The *cis* configuration arises when substituent groups are on the same side of a carbon-carbon double bond.
Concrete:	A synthetic rock containing sand and gravel aggregate bonded in a cementious matrix.
Creep:	Time-dependent deformation of polymers or concrete due to a sustained load.
C-S-H:	Calcium silicate hydrate
Drying shrinkage:	When excess of water is added to cement than needed to hydrate the cement, much of the remaining water evaporates, causing the concrete to shrink.
Efflorescence:	Efflorescence is a deposit of white salts left on a surface when a solution containing the salts leaches from concrete or masonry and then evaporates.
Ettringite:	Needle like crystalline compound produced by the reaction of C3A, gypsum, and water within a portland cement concrete. Formula is $C_3A.3CaSO_4.32H_2O$

Flash set:	This occurs when excess of soluble sulphate is available in the mix water during the mixing process.
Freeze thaw:	When water freezes, it expands about 9%. As the water in moist concrete freezes, it produces pressure in the pores of the concrete. If the pressure exceeds the tensile strength of the paste or aggregate, the cavity will dilate and rupture. The accumulative effect of successive freeze-thaw cycles and disruption of paste and aggregate eventually causes significant expansion and deterioration of the concrete.
Fresh concrete:	This is concrete that has been recently mixed and is still workable and plastic.
Grout:	Mixture of cementitious material with or without aggregate or admixtures to which sufficient water is added to produce a pouring or pumping consistency without segregation of the constituent materials.
Leachability:	The percolation of matter on exposure to various environments.
Mortar:	This is a mixture of sand, cement and water.
Portlandite:	$Ca(OH)_2$ this is formed in regions in concrete initially occupied by water on mixing. It is denoted by CH.
Pozzolana:	These are predominantly silicaeous and do not react with water alone but react with lime and water to produce calcium silicate hydrate.
Spalling:	This is the breaking of layers or pieces of concrete from the surface of a structural element when it is exposed to the high and rapidly rising temperatures experienced in fires.
Water/cement ratio:	This is defined as the weight of water in a mix divided by the weight of cement. It is denoted by W/C.
Workability:	This is the property of freshly mixed concrete, mortar or paste which determines the ease and homogeneity with which it can be mixed, placed consolidated and finished.

PUBLICATIONS

International Journals:

1. **Priya Viswanath, E.T.Thachil**, "Properties of polyvinyl alcohol cement composites", Materials and Structures, Springer, ISSN:1359-5997 (Print) 1871-6873, 2007 (Online).

   (DOI: 10.1617/s11527-007-9224-2).

2. **Priya Nair, E.T.Thachil, A. Paul**, "Properties of phenolic resin cement concrete", Journal of Advances in Cement Research, Thomas Telford Publications, Vol. 19, No. 3, 2007, pp. 101-108

   (DOI: 10.1680/adcr.2007.19.3.101).

International Conferences:

1. **Priya Viswanath, Eby Thomas Thachil**, *"Evaluation of Compressive Strength and Chemical Resistance Of NBR And SBR Latex-Modified Concrete"*, Proceedings of the 5th Asian Symposium on Polymer Concrete, 11-12th September 2006, Chennai, Allied Publishers, Vol. 1, pp. 125-132.

2. **Priya Viswanath, Eby Thomas Thachil**, *"Chemical Resistant Properties Of Phenolic Resin Cement Concrete"*, XIX Symposium On Nordic Concrete Research & Development – A Meeting Place For Research And Practice, Rica Park Hotel, Sandefjord, Norway, 13-15th June 20.

3. **Priya Nair,** A.Paul, "*Effect of interactions between Phenolic Resin and Cement in Phenolic Resin Cement Concrete*", International Congress of Polymers in Concrete, Berlin, Germany, 2-4th June, 2004, (Accepted).

4. **Invited Paper**: **Priya Nair**, "*Microstructure and Chemical Resistant properties of Resorcinol formaldehyde Resin sand Cement concrete*", Proceedings of the 26th International Conference on Cement Microscopy, 2004, pp. 139-146. CODEN: PIMIE5 ISSN: 1068-8242.

5. **Priya Nair,** A. Paul, "*Effect of Sand On The Properties Of Polymer Cement Mortars*", 9th International Conference on Mechanical Behaviour of Materials, Geneva, Switzerland, May 2003, (Accepted).

6. **Priya Nair** and A. Paul, "*Microstructure Of Phenolic Resin Cement Concrete*", Proceedings of the 25th Conference on Cement Microscopy and Symposium on Rietveld Techniques, ICMA, Richmond, U.S.A. , 6-10th April 2003, (on CD).

7. **Priya Nair** and A. Paul, "*Investigations Into The Preparation And Properties of Phenolic Resin Cement Concrete*", Advances in Polymer Technology '02, Kochi, India, December 2002, pp.74-81.

8. **Priya Nair** and A. Paul, "*Preparation and Evaluation of Properties of Phenolic Resin Cement Concrete*", Proceedings of the International Symposium on Bond in Concrete – From research to standards, Budapest, Hungary, November, 2002, pp. 404 -411.

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Research Publications	10 (Two in International journals and eight in International Conferences)