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concrete(New composites)

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ABSTRACT

The objective of this study was to examine the effects of synergistic fillers on underwater construction, burning and mechanical properties of polymer portland cement concrete (PPCC).

Fine grains of hydrous calcium sulfate, Trihydrated alumina, Calcium carbonate and fibrous unhydrous calcium sulfate were examined in PPCC. It has been observed that these synergistic filler improves the mechanical property (stress) and reduce the average time of burning of PPCC. With fixed quantity of polymer, the deterioration of PPCC in water increases by replacing the sand with above stated fillers.

**SYNERGISTIC FILLERS IN POLYMER CONCRETE
(NEW COMPOSITES)**

BY

SYED HASSAN JAVED

Thesis submitted to the faculty of the Graduate School of
the New Jersey Institute of Technology in Partial
fulfillment of the requirements for the degree of
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CHAPTER 1

INTRODUCTION

1.1- CRITICAL REVIEW

Concrete is used in nearly all types of construction throughout the world because of its capacity to be formed into a variety of sizes and shapes, the ready availability of the raw material from which it is made, and its relatively low cost. Although concrete is an excellent building material, certain limitations to its use are recognized. These relate mainly to its relatively low tensile strength, its tendency to crack with changes in temperature and moisture, and its deterioration because of

permeability, absorption, and chemical attack under various conditions. Improvement in these properties could significantly extend the usefulness of concrete.

During the past few years, considerable research interests have been devoted to the development of concrete materials by utilizing polymers: polymer concrete is a premixed material formed by mixing monomer and aggregates of different sizes and then polymerized in the composite.

The development of Polymer/concrete composites is directed at both improved and new construction materials by combining the ancient technology of hydraulic-cement-concrete with the modern technology of polymers.

The need for such materials has always existed. since the traditional construction material portland-cement-concrete suffers the drawbacks of little or no resistance to Chemical attack, rapid deterioration under freeze-thaw conditions due to cyclic temperature changes, low tensile, shear and bond strengths, and inherent micro-structural menaces (voids, shrinkage-cracks, capillaries) which, individually or in combination with other, shorten the service of the structures.

Some polymers are very good binder for making concrete, since before its polymerization, the monomer is

in liquid form that can be easily mixed with aggregate or hydrated cement and then polymerized to form a solid.

Further, polymer concrete has high strength in tensile, compression and flexural, provides excellent bonding properties when formed in place and is waterproof, resistant to corrosion and generally chemically stable. Therefore it is conceivable that mixtures of polymers and cement or aggregate can develop such desirable properties.

There are generally three types of concrete materials with polymers to form composite materials.

1) Polymer-impregnated concrete(PIC), (2) Polymer-Portland- cement-concrete (PPCC), (3) Polymer concrete (PC). Details of all three types are given in chapter 2.

1.2- CONCEPT OF SYNERGISTIC FILLERS

As has been pointed out in sec 1.1 that concrete normally contains voids and gel pores which tends to reduce the strength. These voids can be filled up to some extent by low viscosity polymers such as PMMA. But in case of more viscous polymers such as unsaturated polyester resin, these voids and gel pores can not be filled up properly. Such voids also tend to increase when fibers

are used in excess. To improve the strength of normal or polymer concretes, fibrous fillers should not be used in excess amounts (not more than 9% by volume). Large and small aggregates also take part (depending upon the size) in this void formation phenomenon. In such situation synergistic fillers (fine) are useful to reduce these voids.

1.3- PRESENT STUDY

With this concept to reduce the voids present in polymer cement concrete, we choose different types of synergistic fillers such as CaCO_3 (140 mesh) , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (150 mesh) Trihydrated Alumina (325 mesh) and Franklin Fiber. Details of these materials are given in Chapter 3.

Chapter 2 describes the types of polymer concrete, which are in common use, and the chemistry of unsaturated polyester resin. These two topics are helpful to understand the subsequent part of the report.

Chapter 3 is the study of mechanical properties, falling through water test and time of burning of Polymer portland cement concrete with Synergistic fillers. It has been observed that these fillers improve the mechanical property (tensile stress) of the PPCC. In falling through water test, due to fine grains, these fillers require

more unsaturated polyester resin to become undispersable in water. In final section of this chapter average time of burning have been calculated.

Conclusion are drawn in chapter 4.

CHAPTER 2

THEORETICAL BACKGROUND

section one

CLASSES OF POLYMER CONCRETE MATERIALS

As shown in Fig.2.1, three principal classes of polymer- concrete materials exist: (1) Polymer-portland-cement concrete (PPCC); (2) polymer-impregnated concrete (PIC); (3) Polymer concrete (PC). The distinctions between these classes are important to the selection of materials and to design. With PPCC a monomer, pre-polymer, or dispersed polymer is incorporated into a portland cement mix and a polymer network formed in situ during curing of the concrete. With PIC previously formed concrete is

impregnated with a monomer which is subsequently polymerized in situ; here the polymer adds properties to those characteristics of the original concrete. With PC (or resin concrete), a polymer is used to bind an aggregate together.

2.1-1 POLYMER-IMPREGNATED CONCRETE (PIC)

The general principles required for impregnation and polymerization of monomers in situ are now reasonably well established, provided that most of the water ($\sim 90\%$) is removed by drying. Impregnation to level of, e.g. $\sim 15\%$ by volume of a wide variety of liquids (monomers, solutions, and even liquid sulfur) has been shown to be feasible. While there is still some disagreement about whether impregnation proceeds by a capillary-rise mechanism or a simple diffusion process, the impregnation follows a square-root-of-time rate law over most of its course. Consistent with a capillary-rise phenomenon, the rate of impregnation varies with the square-root of the ratio of surface tension to viscosity times the average pore radius, and with the applied pressure. The kinetics of polymerization may differ somewhat from that in bulk, but it is not difficult to achieve an adequate polymerization of many monomers by use of irradiation or thermocatalytic methods. In this way, one obtains an interpenetrating network

system comprising cement gel and a polymer that can confer useful properties.

Much emphasis has been given to acrylic monomer systems such as methyl methacrylate (MMA) or acrylonitrile mixtures because the use of these monomers has generally led to superior properties in the composite. Since such liquids have high surface tensions, low viscosities, good wetting properties, relatively low costs, and high reactivities, the empirical discovery of their virtues has a sound physico-chemical basis. Epoxies and other viscous monomers have also been used though the rate of impregnation is necessarily reduced.

With impregnation by an appropriate monomer, the principal effect of technological interest is the sealing of the continuous capillary pore system, resulting in exceptional decreases (to $\sim 99\%$) in the permeability to water and to salts such as sulfates and chlorides. The pore-sealing also minimizes changes in properties, e.g., dielectric constant and loss, that are sensitive to moisture content.

Dramatic improvements in abrasion resistance, Young's modulus and in compressive, tensile, and impact strengths (by factors up to about 5) have been noted by many investigators for impregnations with PMMA and other

glassy polymers, and related to the polymer loading. In general, impregnation with a glassy polymer yields a solid whose stress-strain behavior is linearly elastic almost to the point of failure. However, the stress-strain behavior can be modified from elastic and brittle to ductile by introducing plasticizing comonomers (1). Indeed, the state of the polymer in the pore is important; relaxation studies have shown that reinforcement requires that the polymer be in its glassy state (1).

A fracture-mechanics approach to strength has been used in a few cases to explain the improvement in strength. Using Griffith's equation it has been suggested that reinforcement improves strength by increasing both Young's modulus, E , and fracture energy, γ , but especially the latter(2).

In any case, the beneficial effects of impregnation may be due to the ability of the polymer: (i) to act as continuous, randomly-oriented reinforcing network; (ii) to increase the bond between the aggregate and cement paste; (iii) to absorb energy during deformation; (iv) to penetrate and reinforce the micropores; and (v) to bond with the hydrated or unhydrated cement.

As a result of the improvements in properties described above, PIC has long been considered as a potential material where properties such as high strength and stiffness, or resistance to corrosion of concrete or reinforced steel are important. Thus, from the beginning, end uses are such as in bridge decks, pipes, and structural elements have been examined, and a few large scale applications have been made, especially with bridge decks(3). The principal limitation is that of cost, for the process is complex, and monomer costs high if more than a surface impregnation is effected.

RESEARCH AND DEVELOPMENT

While the results of impregnations using various vinyl monomers and epoxies continue to appear, some attention has been given to other impregnants such as oligomeric isocyanates , ester acrylates, silicates and sulfur. In general, it seems likely that impregnation yields products having levels of properties not exceeding those of earlier MMA-based PICs. On the other hand, over the past few years, impressive improvement in mechanical properties have been attained by combining the use of autoclaved high strength

concrete with impregnation. The use of impregnated aggregates has also been studied recently(4). Earlier, work on the impregnation of other porous inorganic substrates such as gypsum ,had been reported. More recently, good results have been reported with pozzolan, lime and slag-based concretes . The impregnation of fiber-reinforced concrete has also continued to receive some attention.

An interesting spin-off from PIC research has been the adaptation of impregnation techniques to the case of non-polymeric sealants such linseed oil and silane-type materials. By eliminating the polymerization step, this approach can offer economies in process costs, and is currently being evaluated further for bridge-deck sealing.

Little research seems to be directed towards either the fundamental aspects of impregnation of process improvement, though the possibility of simplifying the impregnation process is being considered at least on paper. The occurrence of shrinkage during impregnation has been studied, and shown to be only slightly greater than that noted during the curing of concrete. An interesting approach to characterizing the polymerization

process in situ , based on dielectric measurement has been reported. This technique should be useful in process control.

The modeling of PIC as a composite material has recently been studied using a lower bound model proposed by others several years previously. Though the model has been questioned, it does seem to give reasonable predictions, after allowance is made for uncertainties in the values for modulus of the polymer actually in the pores. At the London Congress several investigators had discussed the question of the properties of the polymer(e.g., molecular weight, physical state and the polymeric-matrix interaction). Recent results suggest that acid-base interactions proposed earlier interactions between, e.g., Ca^{++} ions and ester groups may well explain the anomalously high softening point of PMMA in the pores of concrete.

The routine characterization of the depth of partial impregnation has often posed problems. Promising results using petrographic observations and resistivity measurements have been described. New techniques for predicting corrosion rates in reinforcing steel will also be useful in comparing PIC with other protective systems.

As mentioned above, the attainment of exceptionally high strength by the impregnation of autoclaved high-strength concrete has now been demonstrated in several laboratories in the U.S., Italy and most recently, in Japan. In fact the compressive-strength-to-density ratio of this material is nearly three times that of steel. Although Young's modulus is not much greater than that of ordinary PIC, the maximum strain at break is significantly increased.

Sulfur-impregnated concrete continues to be of interest, and earlier findings about this were confirmed by several groups. However, the deleterious effect of water is troublesome; attempts to inhibit the interaction between sulfur and $\text{CO}(\text{OH})_2$ have shown promise.

Surprisingly little has been done on design criteria with PIC. Two exceptions are the development of design criteria for post-tensioned PIC beams and analytical studies of ultimate strength and plastic ductility in PIC beams and columns compared with conventionally reinforced concrete beams and columns.

While carefully made PIC offers an unusual combination of excellent mechanical behavior and relative impermeability to deleterious salts, most applications involve "hard cases", in which the gain in service life is

believed to offset the high cost, or in which no other material or process appears to be more suitable.

Perhaps the most extensive programs continue to be concentrated on highway bridge decks, and an increasing number of impregnations are being conducted by contractors, in collaboration with the Federal Highway Administration (FHWA). Although most of these have involved the shallow impregnation of new decks to hinder the penetration of deicing salts.

Another major area of current interest is in hydraulic structures in which PIC's strength and abrasion resistance makes it an ideal candidates as a material for such applications as spillways and stilling basins . PIC is also being used, at least from time to time, in the restoration of structural elements and floors in deteriorated buildings. A program of research into PIC for such applications as pipes and storage tanks is being supported in India through the United Nations Development Program. PIC also shows considerable promise for marine applications(5).

2.1-2 POLYMER CONCRETE (PC)

With PC, a thermoplastic, or more commonly a crosslinked polymer, is used to replace portland cement as binder in a concrete mix. Since the polymer constitutes the continuous phase, behavior of the composite will clearly be determined by the polymer, whose properties, are of course, very dependent on time and temperature.

A wide variety of monomers, prepolymers and aggregates has been used. While epoxy resins are commonly used in PC, much attention has been focussed on the use of cheaper vinyl monomers such as unsaturated polyester resin, MMA, furane derivative and styrene, usually in conjunction with a crosslinking agent. Setting times and times for development of a high proportion of maximum strength can be readily varied from a few minutes to hours. Bond strengths to substrates are also usually high. In spite of high cost, PC is particularly useful for maintenance and repairs, especially when delay and inconvenience are important factors . Thus the cost/benefit ratio is favorable.

By carefully grading the aggregate it is possible to wet the aggregate and fill the interstices by the use of as little as 7-8 wt.% (\sim 14-16 vol. %) polymer . With high packing densities, high compressive strengths can be obtained. Flexural strengths, though much higher than those of concrete, are limited by the aggregate-matrix bond strength and by asperities in the aggregate, which can introduce stress concentrations. The use of silane coupling agents has been shown to improve compressive strength, presumably by improving bond strength. In general, as with glass-reinforced composites, strengths tend to be reduced by exposure to water, presumably because of deterioration of the aggregate-matrix bond. With proper selection of materials, the dielectric properties characteristic of good insulation can be achieved.

The deformation response of PC is highly variable with elastic moduli ranging up to about 35 GPa for a rigid matrix with a tensile failure strain of $< 1\%$; of course, moduli are much lower, and failure strain much higher, for rubbery matrices. It should be noted that shrinkage strains vary from polymer to polymer (high for polyesters, lower for epoxies), and must be considered in any application; such strains may, if not relieved by creep,

result in premature failure in a rigid PC. Since a polymer constitutes the continuous phase, it is not surprising that creep is generally higher than for concrete, and enhanced at high temperatures.

The versatility in formulation and in processing has led to many applications in the past, including flooring, cast articles of various kinds, patching, and overlays for highways bridge decks.

RESEARCH AND DEVELOPMENT

Of the three classes of polymer concrete systems, PC is currently attracting the most attention. A major reason for this is the realization that economies of scale can be achieved by continuous rather than batch processing. This fact has long been known in Europe, but is being appreciated in other countries. Thus while continuous processing of cultured-marble units has been practiced for some time, most other applications have involved batch operation, typically on-site. A second major development has been the rapid development of tailor-made PCs for various uses; indeed an increasing number of companies now offer a range of formulations, many in prepackaged forms. As these trends continue, and as the need for sophisticated product design and

development increases, we may expect to see more intensive basic research as well.

While new formulations continue to appear, and mix design has been studied systematically, both scientific and engineering research on PCs has been limited in scope. A notable exception has been research associated with the development of PCs for geothermal applications, where the extreme service conditions place exceptionally severe demands on the maintenance of properties at high temperature in an aggressive medium. Dental and bone cement materials constitute another example of an application posing severe materials problems. Still another example is the need for patching systems that can cure rapidly and bond to a wet substrate.

Thus, much of the recent published research on new monomer systems and on properties and behavior has been simulated by the applications mentioned. (Presumably much proprietary research has gone on as well). In the BNL research on geothermal materials, many copolymer systems, both thermoplastic and thermosetting, have been, or are being, studied. Monomer systems include various combinations of divinylbenzene, triallyl cyanurate, siloxanes, various methacrylates, and acrylamides. While aggregates such as quartz, silica, fly-ash and

portland cement give composites serviceable up to 220 C, a combination of silica sand with portland cement is required for use at higher temperatures. The benefits obtained by including portland cement have been noted in other research as well.

Fundamental knowledge of the chemistry of the binder and aggregate and the surface chemistry involved in binder-aggregate interaction is required. While such knowledge is not necessary for PCs used in many structural applications, it is clearly important in more demanding cases. In addition to the examples mentioned, the use of PCs in load-bearing applications subject to a combination of high stress (static, cyclic or impact) and an aggressive environment (water, high temperature, chemicals) will require a sound base of research. Surface chemistry is also important to demolding. Research into both the physical and chemical factors that can cause failure in PCs has been very helpful in the case of polyester composites(2).

In spite of the knowledge that creep can be high in PCs, there have been few recent studies. However, at least for an epoxy-based PC it has been recently shown that the viscoelastic behavior was linear at low loads(21MPa). The effects of higher loads are under study.

Another important point to note is that in contrast to portland cement concrete, creep in PC is not reduced when the specimen size is increased. This reflects the difference in creep mechanism, that of the polymer involving molecular (segmental) motions. Interestingly, the creep of the PC at given load was only slightly higher (30%) than that of a typical polymer cement concrete.

The new technique developed by the FHWA (4) for prediction of corrosion rates will be helpful in comparing PCs with each other as well as with other protective systems. Dielectric behavior continues to be of interest, as PC is a candidate for the replacement of porcelain in high-voltage insulators. The combination of facile processing, good insulating qualities, and fracture toughness is indeed attractive.

As with PIC, highway applications have received much attention(2). Thus the FHWA implementation division has encouraged a large number of trials with PC overlays on bridge decks(4), and published a user's guide. Indeed, so far the overlays have performed well. Patching has been of interest for quite a few years, as mentioned above, one of the most recent applications is in the rapid repair of

runways(3). PC has been successfully applied to the renovation of structures, both buildings and dams, and is being evaluated in pilings(5). PC is also used in rehabilitating roadbeds of railway lines in the Northeastern corridor.

Miscellaneous applications include: various kinds of panels and tiles, cultured marble, pipes and liners, flooring, pilings and sanitary ware. Current potential applications in electric utilities include: tunnel segments, conduits, support structures, and as mentioned above, high-voltage insulators. Examples of other extremely demanding applications such as materials for dental and bone cements and geothermal applications have already been given.

2.1-3 POLYMER-PORTLAND CEMENT CONCRETE (PPCC)

From the standpoint of process technology, this most obvious approach is attractive.

Unfortunately, typical vinyl monomers such as MMA or styrene either interface with the hydration of the cement or degraded by the high alklinity present. Unsaturated polyester resin and epoxies can be effective,

though fairly high proportions are usually required if mechanical properties are to be improved. However, most attention has been given to the incorporation of a polymeric latex. In this case, the physical process of film formation is required rather than the chemical process of polymerization. Also, since the emulsion lubricates mix, less water is usually needed for workability, so that the optimum water content from the standpoint of final properties can be approached. In fact, polymer latexes-usually of acrylics, styrene-butadiene copolymers, poly(vinylidene chloride), epoxies, and poly(vinyl esters)-have been used in mortars and concrete for about 45 years. Polymer, if used 20 to 30 % is also recommended to use after hydration of cement but in this(5) situation water contents should be low i.e 20 to 30 % of cement.

Not surprisingly, the precise balance of properties depends on the nature of the polymer and its concentration. While flexural strength and toughness are usually increased, the modulus may or may not be increased; the more rubbery the polymer, the lower the modulus.

Several factors are apparently involved in improving properties of PPCC, the reduction in water-cement ratio and, hence, in the volume of capillary porosity; the entrainment of air as a fine dispersion; specific interactions with cement gel; and specific properties of the polymer, for example, toughness. More specifically, the following requirements for the polymer are believed to exist:

- 1) The polymer or latex must be able to form a film under ambient conditions, to coat cement grains and aggregate particales, and to form a strong bond between the cement matrix and the aggregates.
- 2) The polymer network must possess the capacity to intercept a growing microcrack and, by dissipating energy through microfibril formation (across a crack without separation from the crack walls), hinder crack propagation.

Actual bonding between Ca^{++} ions and polymer appears to exist. It has also been shown that the latex particles coat the cement gel and aggregate surfaces with a monolayer, which eventually coalesces as the various particles come into contact.

Thus, evidently some kind of composite action is involved, not just the reduction made possible in capillary porosity.

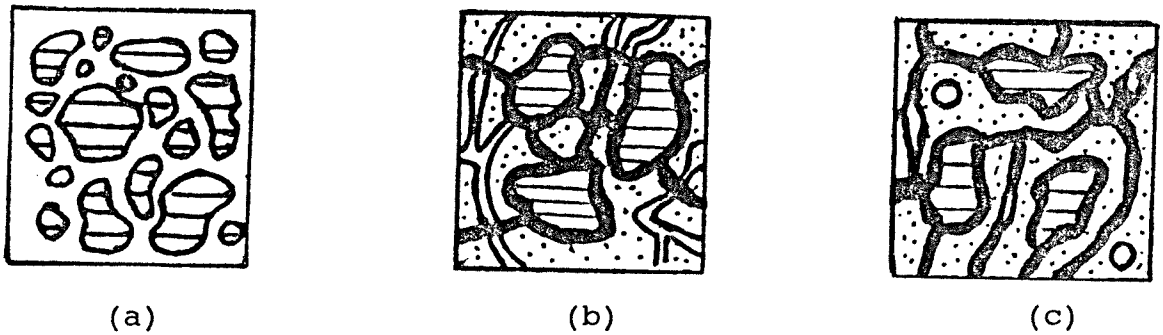
The most common applications have been in mortars, patching compounds, flooring, and overlays for bridge decks.

RESEARCH AND DEVELOPMENT

The most common systems have been based on copolymers of styrene-butadiene, vinylidene chloride, and acrylics. The use of self-emulsifying epoxies is also of current interest. Poly(vinyl acetate) is used to some extent, though the products are sensitive to moisture. Other systems described recently have been based on vinyl chloride copolymers, natural rubber(52), Polyester resin(1), and aldehyde-type resins. High strengths have been reported for systems based on PMMA emulsions. In a study of mortars and concrete incorporating a vinylidene-chloride-based emulsion system the effects on the aggregate-mortar interface were examined, as well as the effects of PMMA polymerized in situ and of a de-adhesion agent. Equations were developed to predict the strength and modulus of the concrete in terms of the mortar properties, adhesion and the friction angle. While

strength was effected by the adhesion, the property of the mortar itself was dominant. In another study of latex systems, it was found that the presence of the polymer results in a significant increase in the cracking stress and strain of the concrete, and an increase in creep. It was also noted that dry curing was especially favorable. Creep and shrinkage of a styrene-butadiene latex system has been recently measured; the values of 120% and 240% higher than for controls.(6).

Fig. 2.1



- (a) Polymer concrete.
- (b) Polymer-portland cement concrete.
- (c) Polymer-impregnated concrete.

Crosshatched areas represent aggregate particles; open and polymer-filled capillary pores are shown in (b) and (c); dots represent gel pores, some of which are polymer-filled in polymer-impregnated concrete.

section two

CHEMISTRY OF POLYESTER RESIN

2.2-1 HISTORICAL DEVELOPMENT

In 1847 the great Swedish chemist Berzelius treated tartaric acid with glycol and formed a resinous mass, Poly(glyceryl tartrate). Lorenzo reported a Poly(ethylene succinate) in 1863 and six years later Kraut advanced the first concept of a polyester chain structure.

The next landmark in the history of polyester resins was the publication by Vorlander in 1894 of his development of the first unsaturated polyester resins the

glycol maleates. This was followed by the work of W.J Smith in 1901 who reacted phthalic anhydrite with glycerol to produce Poly(glycerol phthalate) which led to the development of the alkyd resins by GEC and BTH from 1913 onwards. By modifying this resin with various vegetable oils an excellent base for paints was produced having outstanding durability, and the commercial of alkyd resins for surface coating took place over the following 20 years.

The modern history of unsaturated polyester resins began with the filing of a patent application in 1922 by Carleton Ellis and the subsequent publication of this patent in 1933. This covered the reaction products of dihydric alcohols and dibasic acid anhydrides for use as lacquers. Hundreds of publications followed in the succeeding 10 years, but the important development can be traced through several stages. First, the formation of interpolymers of esters of dibasic acid with vinyl compounds by Dykstra in 1934. Then followed the work by Bradley, Kropa and Johnson who prepared polymerizable compositions based on maleic anhydride.

This was followed by a further publication of Ellis who showed the copolymerization of maleic polyester resin with monomeric styrene in the presence of peroxide catalysts. This patent was primarily concerned with the

preparation of lacquers, and it is interesting to note that the benzoyl peroxide catalyst is referred to as a drier. Likewise the use of styrene is recommended to accelerate drying. This is an important patent since it is the first time these compositions are suggested for use as moulding materials. Muskat then showed that phthalic anhydride can be reacted with the maleic anhydric and glycol to reduce the tendency towards crystallization and so improve the compatibility of the final resin with styrene.

From this stage the present day polyester resins have not changed much in principle. The changes which have been made mainly concern the proportion of reactants used in the polyesterification, and the actual nature of the reactants. No account of the history of polyester resins would be complete, however, without mentioning the now classic work of Carothers on the theory of condensation polymers and polyesters in 1929 and Kienle's general theory of polymer formation based on polyester studies in the early nineteen thirties.

The commercial development of unsaturated polyester resin began in the United States in 1941. When an allyl casting resin was introduced for use as a glass substitute. Here unsaturation was obtained by using an unsaturated alcohol, allyl alcohol, instead of following

the more usual practice of using an unsaturated acid such as maleic or fumaric. This was followed in 1942 by an allyl low pressure laminating resin, allyl diglycol carbonate, which was used for the manufacture of some of the first glass-cloth reinforced resin radomes for aircraft.

By 1946 polyester resin were commercially available in the United States consisting of the polyester of diethylene glycol and maleic anhydride, and similar resin were soon manufactured in this country. These were soon replaced by polyesters of maleic anhydride and ethylene or propylene glycol with a saturated dibasic acid such as phthalic. They are usually supplied as solutions in monomeric styrene and they represent today the bulk of unsaturated polyester resin used throughout the world.

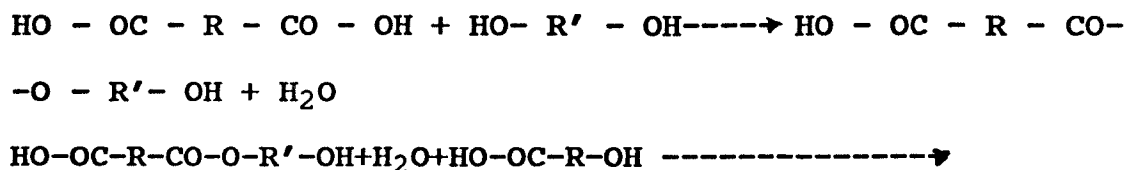
The earliest polyester resin could be cured only at a temperature of about 100 C, in the presence of benzol peroxide. By 1947, however, it was found that polyester could be 'cold cured' at normal room temperature by the use of a tertiary amine such as dimethyl aniline as a promoter in the presence of benzoyl peroxide. Many other cold-setting catalyst system have been developed subsequently, of which the most important are cobalt naphthenate with t-butyl hydroperoxide, cyclohexanone

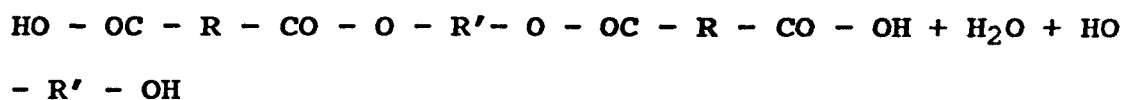
peroxide, or methyl ethyl ketone peroxide, first used commercially in 1947 and still widely used.

2.2-1 RESIN COMPOSITION

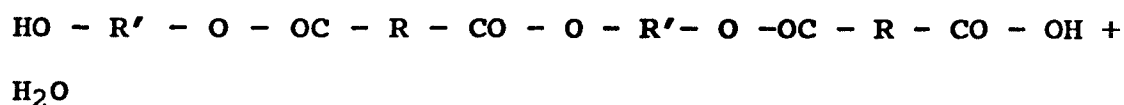
There are two stages in the manufacture of polyester resin: polycondensation and blending with a cross linking monomer. The base polyester is usually made by condensing phthalic and maleic anhydrides with propylene glycol. The polyesterification is a typical polycondensation reaction between stoichiometric proportions of the anhydrides and glycols with usually a slight excess of glycol to take account of any losses during reaction.

Since the glycols and anhydrides are both difunctional, each able to form two ester links, the esterification reaction continues step by step building up a linear chain molecules and splitting off a molecule of water as each link is formed.





----->



-----> etc.

Theoretically chains of indefinite length can be built up, but Whitehouse points out that in practice the reaction is only continued until some 10 to 30 links have been made giving polyesters With a molecular weight of about 1000-2000. The polycondensation is usually carried out without a catalyst at about 200 C under an inert atmosphere of nitrogen, the reaction being continued for several hours until an acid value of 30-40 mg KOH/g is achieved. A partially packed column is used to aid water removal and reduce any loss of glycol, half ester and so on. Alternatively, a small percentage of an azeotrope such as xylene may be added, facilitating the removal of the water and allowing lower reaction temperatures to be used. The azeotrope is then distilled off under vacume when the required acid value has been achieved.

After the linear polyester has been prepared it is blended with the polymerizable monomer, usually styrene, and stabilized against premature gelation by the addition of very small quantity of hydroquinone, t-butyl catechol or similar phenols, copper salts or other inhibitors.

Polyester resins having widely differing physical and chemical properties can be produced by changing the polycondensation conditions, by changes in the molar proportion of unsaturated to saturated acid, and by using different reactants.

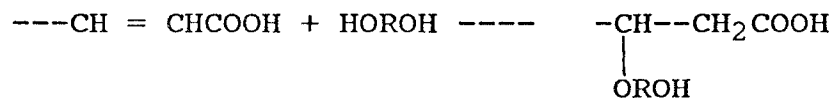
No polyester will consist of molecular chains of equal lengths. Nevertheless the properties of the final resin will depend on the correct weight-average number DP_w of maleate or fumarate double bonds per polyester chain. If, for example, Poly(ethylene maleate) is prepared from equimolar proportions of maleic anhydride and ethylene glycol and consists only of linear molecules, the statistical distribution of chain lengths follow Flory's equation:

$$W_x = x(1-p)^2 p^{x-1}$$

Where p is the fraction of carboxyl groups esterified and W_x the weight fraction of x -mer. The weight average DP_w and the number average DP_n for this distribution are given by the relationship:

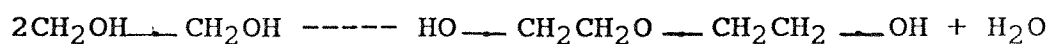
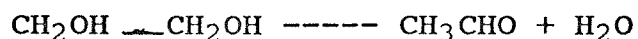
$$DP_w = (1+p)/(1-p) = 2DP_n - 1$$

Apart from variation in molar proportions, there are several possible ways in which the structure of condensation polymer may deviate from Flory's equation. Branched chains and ring structures can be formed by addition reactions between the unsaturated acid and the glycol, for example:



with possible further reaction to form lactones.

The glycol may decompose splitting off water to form aldehydes or ethers:



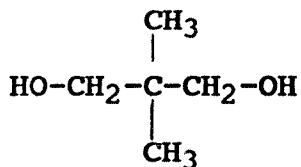
Or the unsaturated acid may decarboxylate forming an acrylic ester:



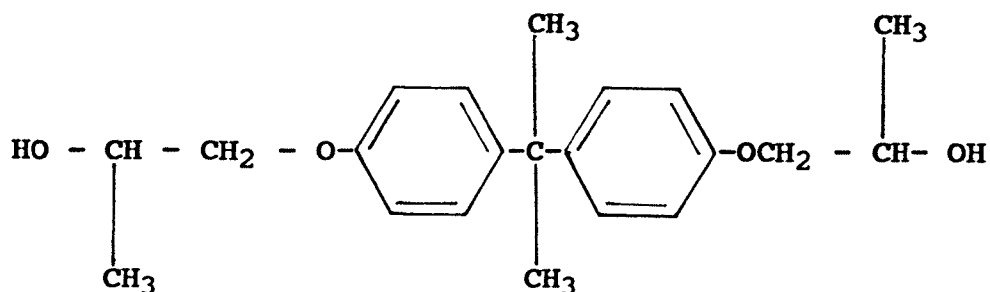
A further important secondary reaction is the cis-trans isomerization of maleic to fumaric in the presence of propylene glycol:



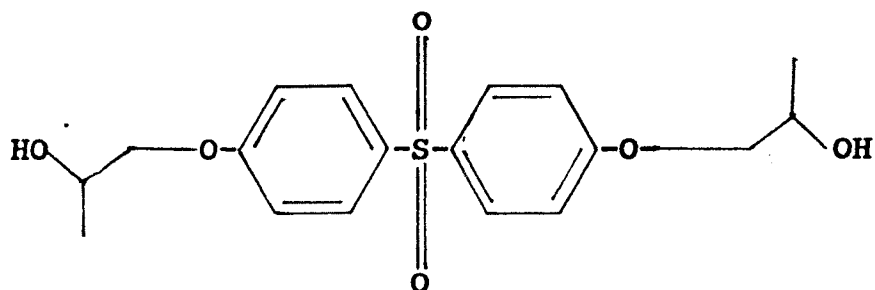
Although many commercial polyester resins are made from propylene glycol, maleic anhydride and phthalic anhydride, and blended with about 35% styrene, a number of alternative raw materials are also used. Other glycols widely used include ethylene glycol, diethylene glycol, neopentylene glycol,



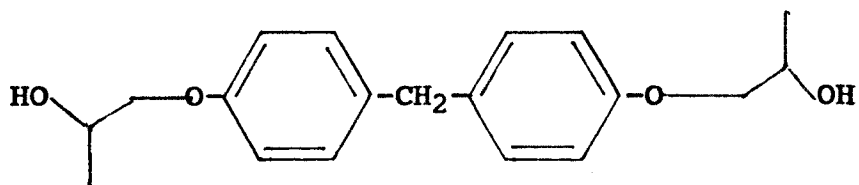
or alternatively high molecular weight dihydric alcohols based on bisphenol A such as:



Recently other high molecular weight dihydric alcohols have been developed from propoxylated Bisphenol S :



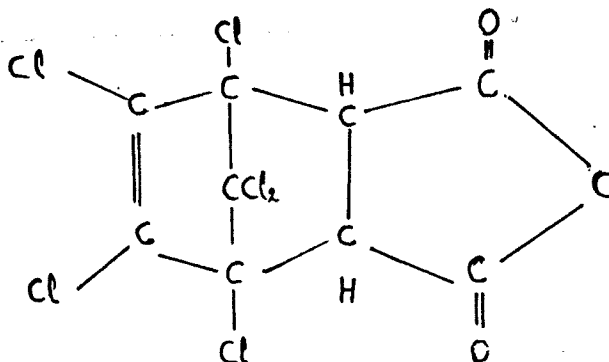
and from Bisphenol F:



Polyester resins based on glycols of this type have outstanding chemical resistance when fully cured.

Because of price and commercial availability there is less scope for varying the unsaturated acid component of the polyester. Apart from maleic anhydride, fumaric acid, the trans-isomer of maleic acid is widely used, yielding resins having a higher thermal softening point when fully cured than those based on maleic. In spite of the isomerization that takes place. Methacrylic acid and itaconic acid are also sometimes used.

Sometimes phthalic anhydride is replaced as the saturated acid component by its m-isomer isophthalic. Cured isophthalic polyesters are characterized by being tougher, and having a lower volatile loss when heated than those based on o-phthalic. Sebacic and adipic acids are widely used for producing flexible polyesters, and a number of acids containing chlorine or bromine are used for conferring a degree of fire resistance of the polyester. These include tetrachlorophthalic, tetrabromophthalic and the well known 'Het' acid. Hexachloro-endomethylene-tetrahydrophthalic:



Although styrene is by far the most important cross-linking monomer used with polyester resin, a number of others are used commercially. These include methyl methacrylate, -methyl styrene and diallyl phthalate.

It will be clear, however, that by variation of the raw materials used in the polyesterification reaction, as well as their molar proportions and the polycondensation conditions, a vast number of different polyesters can be produced. Each will have its own characteristics, and for further information on the structure and properties of polyester resins Boenig(8) book is particularly useful.

Much effort is being made at present to use propylene oxide and other alkylene oxides for direct esterification, thus obviating the need to remove water from the reaction. In this way it is possible to build a continuous process for polyester manufacture. As early as

1939 there was a publication relating to the production of high molecular weight substances by reacting anhydrides of polybasic acids with an alkylene oxide(8). More recent work has examined the role of certain esterification catalysts in this reaction, such as compounds based on titanium, cerium and zirconium(9).

2.2-3 CROSSLINKING

Polyester resins are usually supplied by tanker or in drums as stablized solutions of the linear polyester in a crosslinking monomer such as styrene. In this condition they are capable of further polymerization by crosslinking, since there are reactive groups still present in the form of unsaturations in, for example, the maleate or fumarate components of the molecular chain. This further reaction-curing is initiated by a catalyst system which will give free redicals at room temperature, and takes place in the mould when the resin has been reinforced with glass fiber. It is best illustrated by the crosslinking of linear chains of poly(ethylene glycol maleate) with styrene:

solution should contain about 35% by weight of styrene. Vaughan & Hayes has shown that if more than 39% of styrene is used some polystyrene chains will be found in the final cured polymer. On the other hand, it is unusual for only a single molecule of styrene to crosslink two polyester chains. For poly(propylene fumarate phthalate) the average crosslink appears to consist between one and three styrene units.

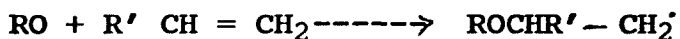
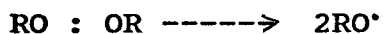
2.2-4 FREE RADICAL POLYMERIZATION

The solutions of linear polyester in the crosslinking agent, i.e. the polyester resin as supplied, is cured to a thermoset crosslinked polymer by a process of polyaddition with the aid of an initiator. Sometimes the initiator is actuated by a compound called activator. It is usual (though not strictly correct) to call the initiator a catalyst. Similarly the activator is called an 'accelerator'. The mechanism of this type of polymerization initiation has been the subject of much study(9). Dean, Weber and Crenshaw have shown that polymerization proceeds as the result of the free radical mechanism.

The various steps in polyaddition process (initiation, chain growth or propagation; termination) are typical of catalysed free-radical vinyl polymerization systems. It is first necessary to produce reactive free radicals in the resin medium, and the rate of production of these free radicals largely determines the rate at which polymerization proceeds. The problem of catalysing polyesters is thus resolved into providing the proper conditions in which free radicals can be supplied in situ at a predetermined temperature and rate. The thermal decomposition of an organic peroxide, or the decomposition of an organic peroxide by the reaction of other substances (accelerators) is the most usual method of achieving this(9).

When the peroxide link ruptures, two free radicals are formed. This link, like many chemical bonds, is made with a shared pair of electrons, but whereas many bonds when broken leave the electron pair on one fragment, so that the two fragments are oppositely charged, the two fragments from peroxide links each retain one electron. These free radicals with an odd electron are uncharged but impatient to revert to a paired state by capturing another electron from somewhere. This they do by abstracting one

from the vinyl monomer so forming a new free radical and initiating the rapid chain reaction whereby the crosslinked polymer is built up.



etc.

There are many free-radical initiators suitable for catalysing the polymerization of a polyester resin when heat can be applied, the most important being benzoyl peroxide and t-butyl perbenzoate. There are also many activators (accelerators) which will decompose these catalysts at room temperature, thus liberating free radicals and making it possible to cure the resin at room temperature. The most widely used cold setting system is methyl ethyl ketone peroxide or cyclohexanone peroxide-both in fact mixtures of hydroperoxides-with solutions of certain metal soaps such as cobalt or vanadium, which act as accelerator. Alternatively, tertiary amines such as dimethyl aniline can be used with benzoyl peroxide.

2.2-5 AIR INHIBITION

When a simple polyester resin is cured in the presence of air, the surface remains soft and tacky. There are two reasons for this air inhibition of the cure. Firstly, the cooling effect on the high surface-to-volume ratio of the surface film allows the exothermal heat to be rapidly dissipated, so that the temperature rise is insufficient to induce the accelerated generation of free radicals. Secondly, the free radicals react preferentially with oxygen so that at the surface the presence of air reduces the concentration of reactive free radicals so drastically that their primary function of initiating the copolymerization is seriously impaired.

Early polyester resins had to be cured under a Cellophane film to exclude the air, but since 1951 polyester resin became commercially available which are not air inhibited. There are several ways of achieving this, of which the most important is the incorporation of very small amount of paraffin wax in the resin(10). As the resin cures, the wax is thrown out of the solution forming a protective film on the surface. Another way of producing a non air-inhibited resin is to modify its chemical structure. Polyesters based on tetrahydrophthalic anhydride have excellent air drying properties, and can be used as lacquers(10).

CHAPTER 3

EXPERIMENTATION

section one

MECHANICAL PROPERTIES

3.1-1 FUNDAMENTALS OF FIBER REINFORCEMENT

It has been found that glass fiber improves the strength of concrete and Polymer concrete. There have been number of reports on microstructure of interfaces in Glass reinforced cement(GRC). Extensive studies of the morphology of interfaces formed between glass slides and Portland cement pastes have been reported by the group at Perdue University. It had shown the existance of intimate contact with glass of a 'duplex layer' about 1 m thick, consisting of portlandite,

oriented with c-axis perpendicular to the glass, backed with mainly rod-shaped particles of calcium silicate hydrate (CHS). As hydration proceeds, this duplex film eventually becomes tied to the bulk cement paste by deposition of additional calcium hydroxide, ettringite or other hydration products(11).

If we consider a very simple composite material containing ,say, glass fiber running in one direction right through the length of the sample; and if we further assume that fibers and matrix are bonded together so that, when a load is applied, they stretch equally; then it is easy to show that the stress in the composite is divided between fiber and matrix according to

$$\text{Stress} = (E_f V_f + E_m V_m) \epsilon_c \text{ -----} \quad (1)$$

E_f , E_m = Young's modulus of fiber and matrix

V_f , V_m = Volume fractions of fiber and matrix in the composite.

ϵ_c = Strain in the composite.

Equation (1) is one form of the law of mixtures-a fundamental equation governing the behaviour of fiber reinforced composite. Although this equation must be modified to take account of various factors in practical

composites (such as fiber of finite length laying in more than one direction, voids created by fiber, voids created by aggregates, voids in cement which appears during casting) it does already indicate two factors which are important in making effective use of fibers as reinforcement. These are that the fiber modulus, E_f , is large compared with the matrix stiffness, E_m , and that the fiber content, V_f , is as high as practicable. In the context of GRC, it is important to note that this is the fiber content by volume and not by weight as in usually measured.

Unreinforced cement pastes and mortars generally contain many voids together with cracks and microcracks due to differential shrinkage, aggregate boundaries and size etc. These propagate under an applied stress, join together, and cause fracture at very variable stress levels so that materials are not normally regarded as crack produces a localized region of much reduced stiffness and in GRC this load can be transferred to nearby fibers which play an important role in restraining early crack growth; this prevents very low stress matrix failure, and hence raises the average matrix failure stress. The fiber also distribute shrinkage stress more uniformly.

Romuadi, Aveston and Proctor (12) have argued on theoretical grounds that the presence of reinforced fibers actually raises the strength to failure of a cement or concrete mixture. There has been some dispute about to show clearly with the relatively low fiber contents used in practice.

In randomly reinforced concrete the stress/strain curves are generally divided into three regions. In the first region (which has normally high slope) shows a little contribution of fibers and all stress goes to cement or concrete. In the second region (very low slope or sometimes zero slope) the cracks develop and the load is transferred to the fibers and all further load is carried entirely by the bridging fibers, accompanied by opening of the existing cracks as the fibers stretch and perhaps begin to slip in the cement and at this stage slope of the stress/strain curves again become higher (lower or zero). This slope depends upon the stiffness, bond and fraction of the fiber.

MONOMER/POLYMER	COMPOSITES
MMA	PC, PIC
POLYESTER/STYRENE	PC, PIC, PPCC
ACRYLONITRILE	PIC
VINYL CHLORIDE	PIC
EPOXY RESINS	PC, PPCC
POLYVINYL ALCOHOL	PPCC
POLYVINYL ACETATE	PPCC
POLYVINYL CHLORIDE	PPCC
NATURAL RUBBER	PPCC
STYRENE/BUTADIENE RUBBER	PPCC
AMINO RESIN	PPCC
POLYESTERS	PPCC
POLYACRYLAMIDE	PPCC
POLYORGANO SILOXANES	PPCC

TABLE 3.1.1- Monomer and Polymer most commonly used in polymer concrete composites (19).

3.1-2 POLYMERS

As it has been mentioned in previous section that normal concrete contains voids and these voids increase when the percentage of fibrous filler or aggregate increases beyond certain limit (13).

To reduce these voids low viscosity polymers were found to be favorable. Table 3.1.1 shows the use of different kind of polymers in PC, PIC, PPCC. These polymers, when used upto 10-15% , forme fibrillated film, which not only fill up voids (up to some extent) but also give remarkable strength to the normal concrete.

As has been shown in Fig. 2.1 that all voids and pores are not filled up by polymers, especially when one uses high viscosity polymers these voids do not decrease appreciably (14). Another important factor which causes to increase these voids is size & shape of aggregates being used. For example aggregate of 50 mesh size will definately form more voids than that of 80 mesh sized aggregates.

3.1-3 MATERIALS AND THEIR SPECIFICATIONS

Material used has the following specifications:

FILLERS

1) TERRA ALBA

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (97%) , CaSO_4 (3%)

Average mesh size : 150

2) TRIHYDRATED ALUMINA (100%)

Average mesh size : 325

3) CALCIUM CARBONATE

CaCO_3 (95%) , Ca(OH)_2 (5%)

Average mesh size : 140

4) FRANKLIN FIBER (Whisker Fiber)

CaSO_4 (60%) , $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ (38%) , CaCO_3 (2%)

Average fiber length : 4mm

Average fiber diameter: 5 micron

5) CEMENT

Keystone Portland cement

6) PLAY SAND

Obtained from local market.

7) UNSATURATED POLYESTER RESIN

Viscoisity, brookfield	:	300 - 400 cp
Specific gravity	:	1.1 - 1.11
Weight per gallon	:	9.2 - 9.3 lbs

3.1-4 MIXING AND CASTING

Mixing was done before casting the specimens. Cement, sand and fiber glass were mixed throughly and then 6 % water was added, fillers were added into the mixture and finally unsaturated polyester resin, containing 2 % benzoyl peroxide and two drops of DMA, was added.

Catalyst was added in unsaturated polyester resin 60 second perior to addition of cement mixture. Total mixing time with UP was 7 minutes for each specimen. All specimen were casted in Briquit grand mold.

3.1-5 TESTING PROCEDURE

All samples after casting were kept at the room atmosphere for about 28 days. The Tensile strength vs strain of the various samples is given in the section of test results. For these tests Instron machine was used. The deflection speed was 0.02 in/min and chart speed was set to be 0.5 in/min. Stress strain curves were obtained from time vs Stress graphs.

4.6- COMPOSITES

Number of samples having various compositions were casted and tested, formulation of some of these samples are being included and the test results are included in subsequent section.

FRANKLIN FIBER(WHISKER FIBER)

(PERCENT BY WT.)

	SAMPLE 1	SAMPLE 2	SAMPLE 3
CEMENT	25%	25%	25%
PLAYSAND	0	23%	28%
FIBER GLASS	6%	6%	6%
WATER	6%	6%	6%
FRANKLIN FIBER	43%	20%	15%
UNSAT. POLYE. RESIN	20%	20%	20%

TRIHYDRATED ALUMINA

(PERCENT BY WT.)

	SAMPLE 1	SAMPLE 2	SAMPLE 3
CEMENT	25%	25%	25%
PLAYSAND	0	14%	19%
FIBER GLASS	6%	6%	6%
WATER	6%	6%	6%
TRI HYD. ALU.	44%	30%	25%
UNSAT. POLYE. RESIN	20%	20%	20%

TERRA ALBA

(PERCENT BY WT.)

	SAMPLE 1	SAMPLE 2	SAMPLE 3
CEMENT	25%	25%	25%
PLAY SAND	29%	24%	19%
FIBER GLASS	6%	6%	6%
WATER	6%	6%	6%
TERRA ALBA	15%	20%	25%
UNSAT. POLYE. RESIN	20%	20%	20%

CALCIUM CARBONATE

(PERCENT BY WT.)

	SAMPLE 1	SAMPLE 2	SAMPLE 3
CEMENT	25%	25%	25%
PLAY SAND	28%	23%	18%
FIBER GLASS	6%	6%	6%
WATER	6%	6%	6%
CaCo ₃	15%	20%	25%
UNSAT. POLYE. RESIN	20%	20%	20%

CONTROL SAMPLES

(percent by wt.)

	SAMPLE 1	SAMPLE 2	SAMPLE 3
CEMENT	0%	25%	25%
PLAY SAND	80%	49%	49%
FIBER GLASS	0%	0%	6%
WATER	0%	6%	20%
UNSAT. POLYE. RESIN	20%	20%	0%

3.1-6 TEST RESULTS

Test results of the samples i.e. tensile stress vs strain were obtained after 28 days. Following Tables shows the modulus of elasticity & ultimate tensile stress of the samples tested. Figs. 3.1 to 3.7 shows the stress vs strain of the same samples.

FRANKLIN FIBER (WHISKER FIBER)

SAMPLE NO.	ULT. TENSILE STRESS(Psi)	MODU.OF ELAST.(Psi)
1	720	1.22×10^4
2	1750	0.84×10^4
3	2600	1.37×10^4

TRI HYDRATED ALUMINA

SAMPLE NO.	ULT. TENSILE STRESS(Psi)	MODU.OF ELAST.(Psi)
1	1300	3.37×10^4
2	2250	2.25×10^4
3	1780	2.68×10^4

TERRA ALBA

SAMPLE NO.	ULT. TENSILE STRESS(Psi)	MODU.OF ELAST.(Psi)
1	1570	5×10^4
2	1890	6×10^4
3	2100	6.75×10^4

CALCIUM CARBONATE

SAMPLE NO.	ULT. TENSILE STRESS(Psi)	MODU.OF ELAST.(Psi)
1	910	$5 \cdot 10^4$
2	1150	$6 \cdot 10^4$
3	1250	$7.5 \cdot 10^4$

CONTROL SAMPLES

SAMPLE NO.	ULT. TENSILE STRESS(Psi)	MODU.OF ELAST.(Psi)
1	1475	$2.28 \cdot 10^4$
2	1000	$4.4 \cdot 10^4$
3	460	$0.5 \cdot 10^4$

The stress/strain curves of these samples are shown in Figs. 2.1 to 2.7. Figs 2.1 to 2.4 shows the trend of stress/strain curves when various amounts of fillers were added in PPCC.

Franklin fiber(whisker fiber) having fiber length 4mm improves not only the tensile strength of PPCC but also the modulus of elasticity which is an indication that these fibers are elastic in nature. Sample number one of Franklin fiber shows very low ultimate tensile stress, because of excess amount of fiber. The excess amount of this fiber increases the voids and therefore, reduces ultimate tensile stress.

Trihydrated alumina also indicates lower strength at higher percentage. Modulus of elasticity decreases as the percentage increases, but compared to Franklin fiber the modulus of elasticity of this composite is higher.

Terra alba and calcium carbonate shows same modulus of elasticity upto 20% with different ultimate tensile stress.

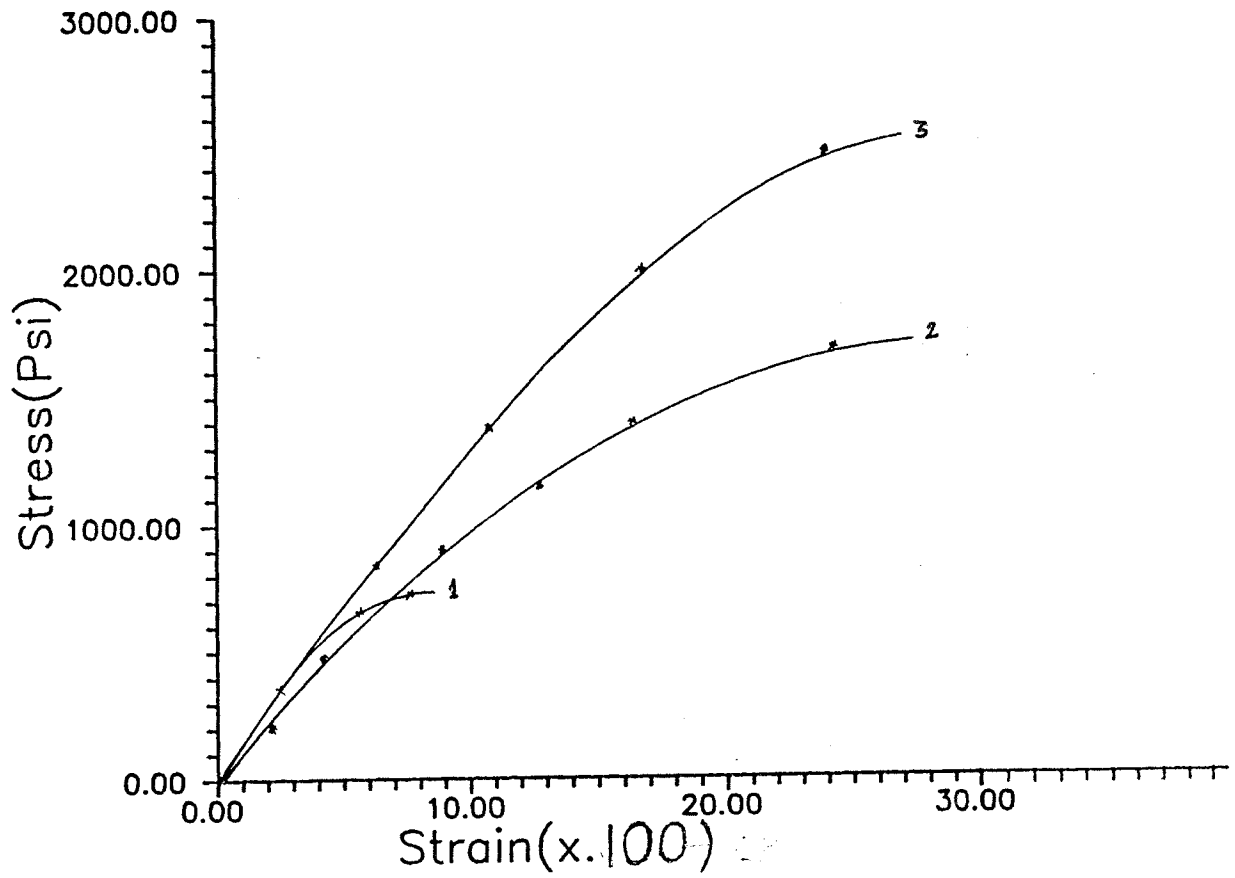


Fig.3.1 Stress(Psi) vs Strain (in/in) for Franklin fiber (Whisker fiber) (1) 43%, (2) 20% and (3) 15%.

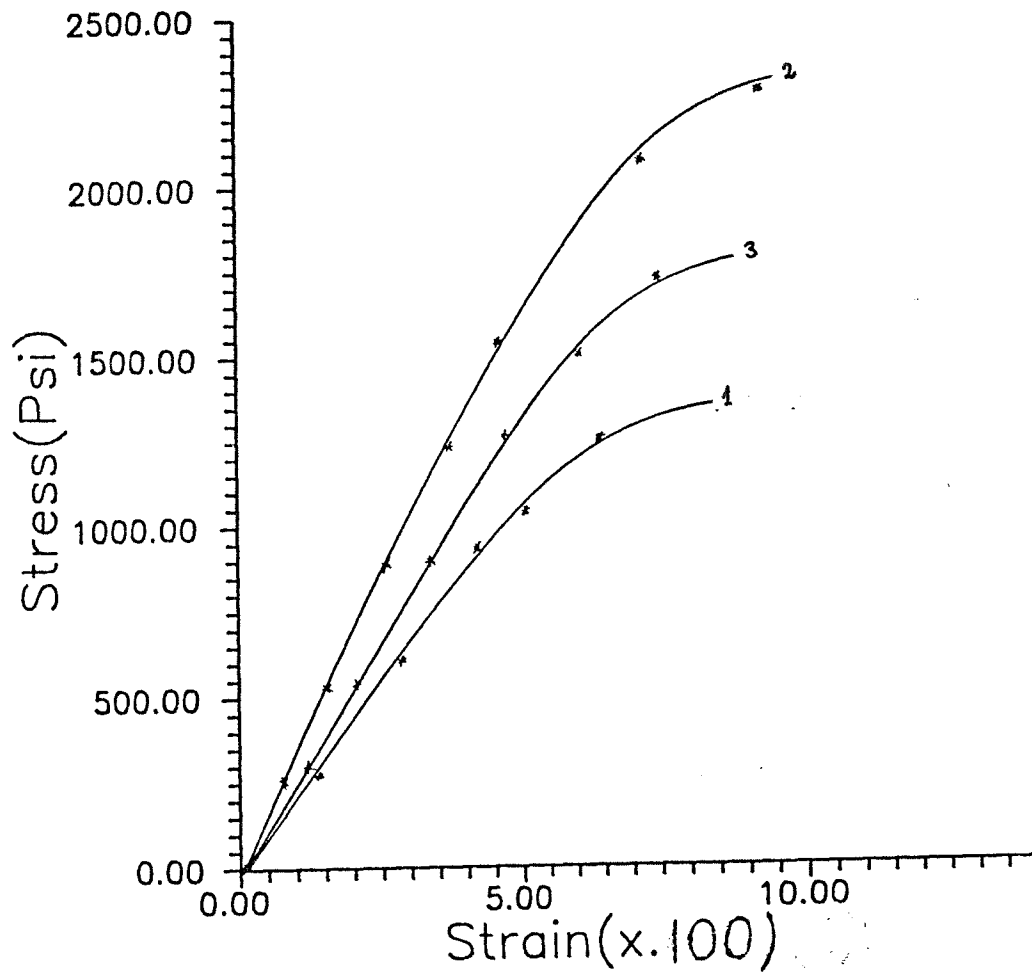


Fig.3.2 Stress(Psi) vs Strain (in/in) for Trihydrated alumina (1) 44%, (2) 30% and (3) 25%

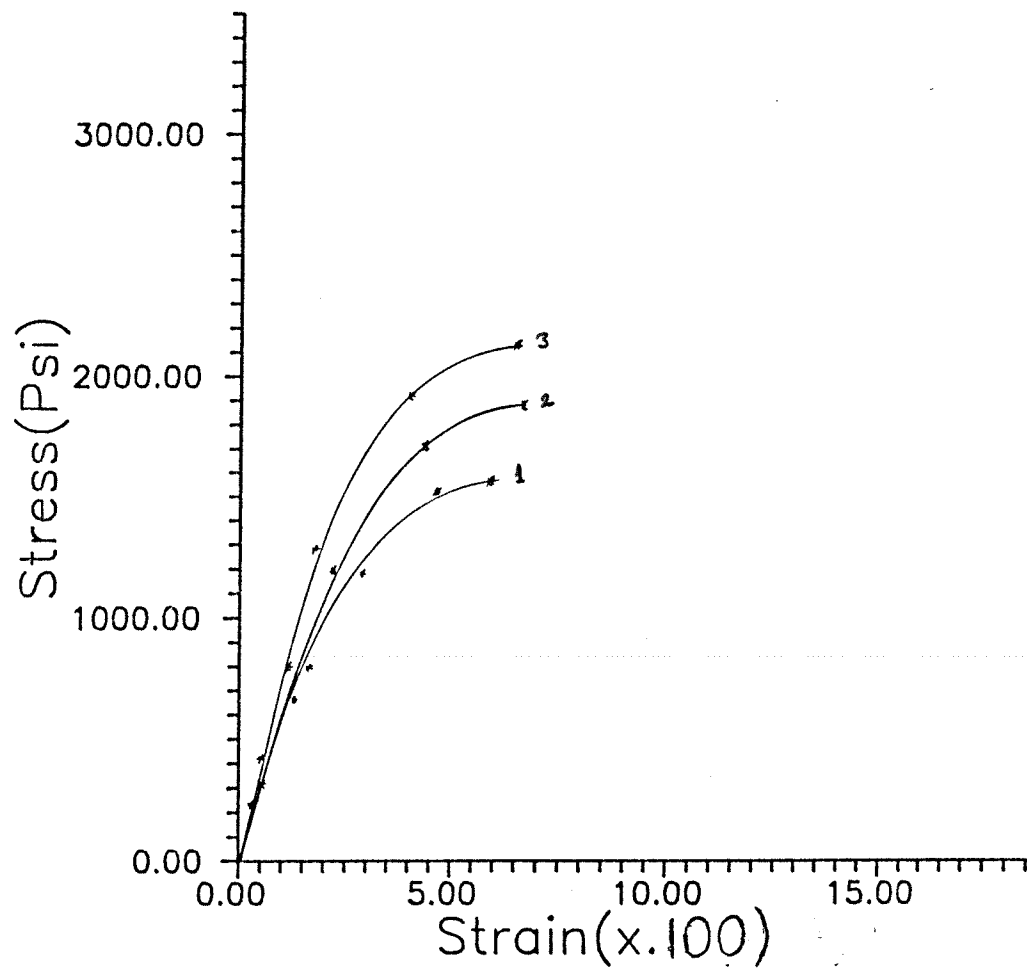


Fig.3.3 Stress(Psi) vs Strain (in/in) for Terra alba (1) 15%, (2) 20% and (3) 25%

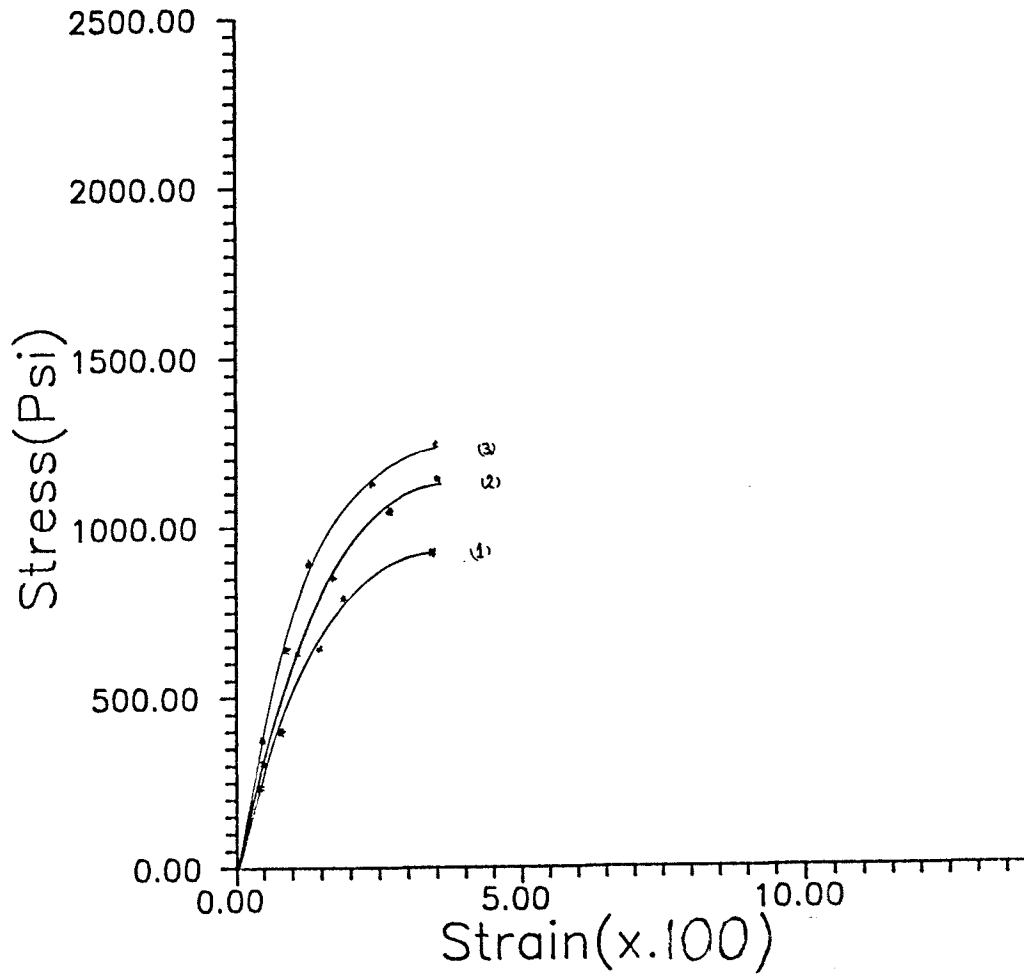


Fig.3.4 Strss(Psi) vs Strain (in/in) for Calcium carbonate (1) 15%, (2) 20% and (3) 25%.

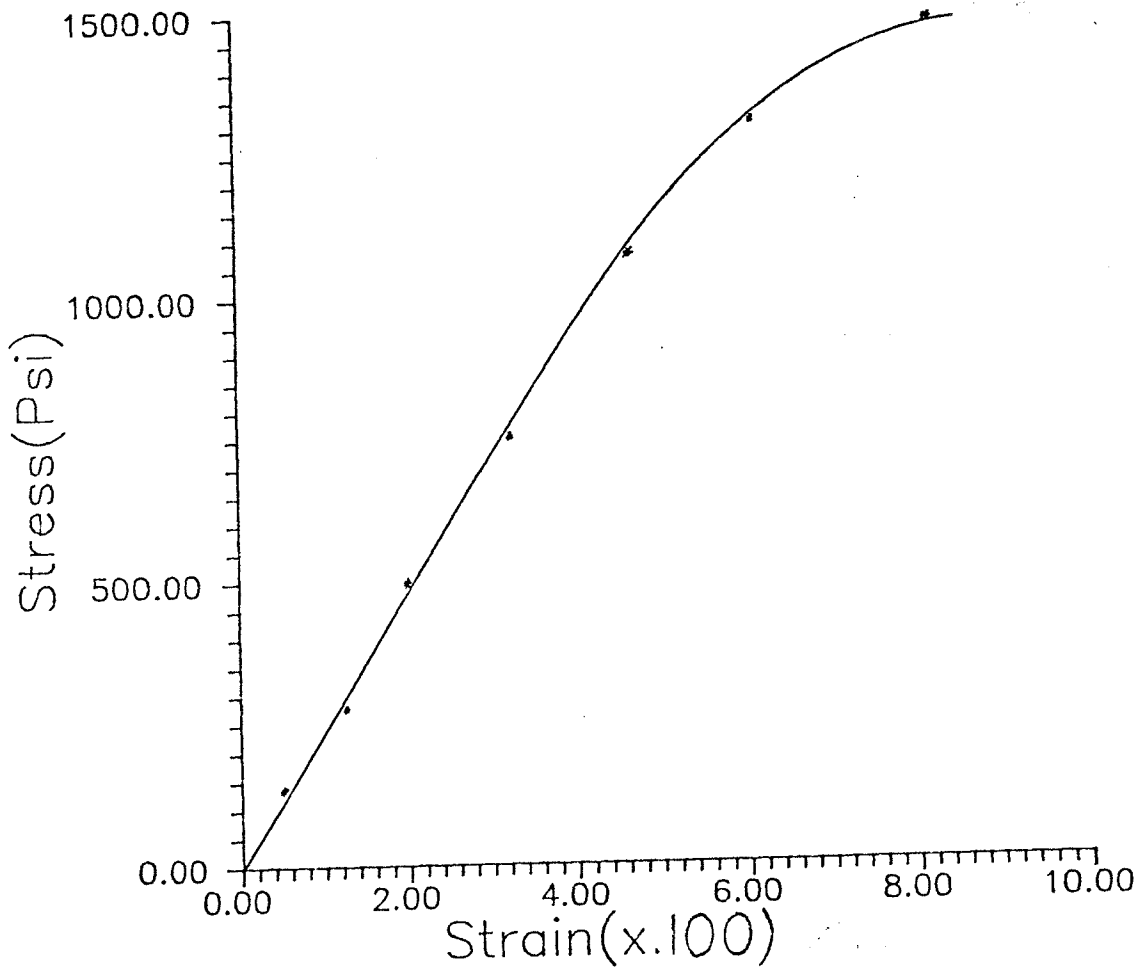


Fig.3.5 Stress(Psi) vs Strain (in/in) for Control sample 1.

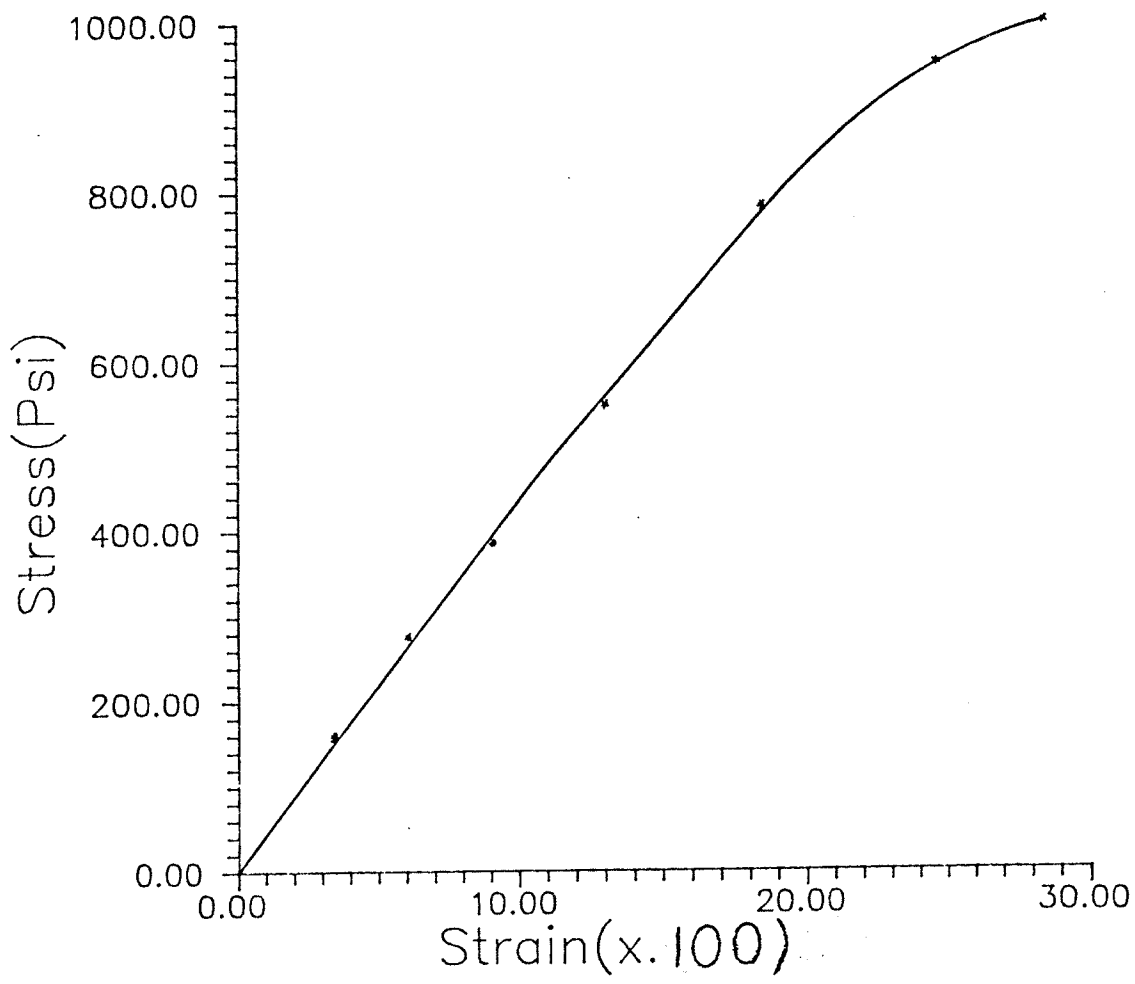


Fig.3.6 Stress(Psi) vs Strain (in/in) for Control sample 2.

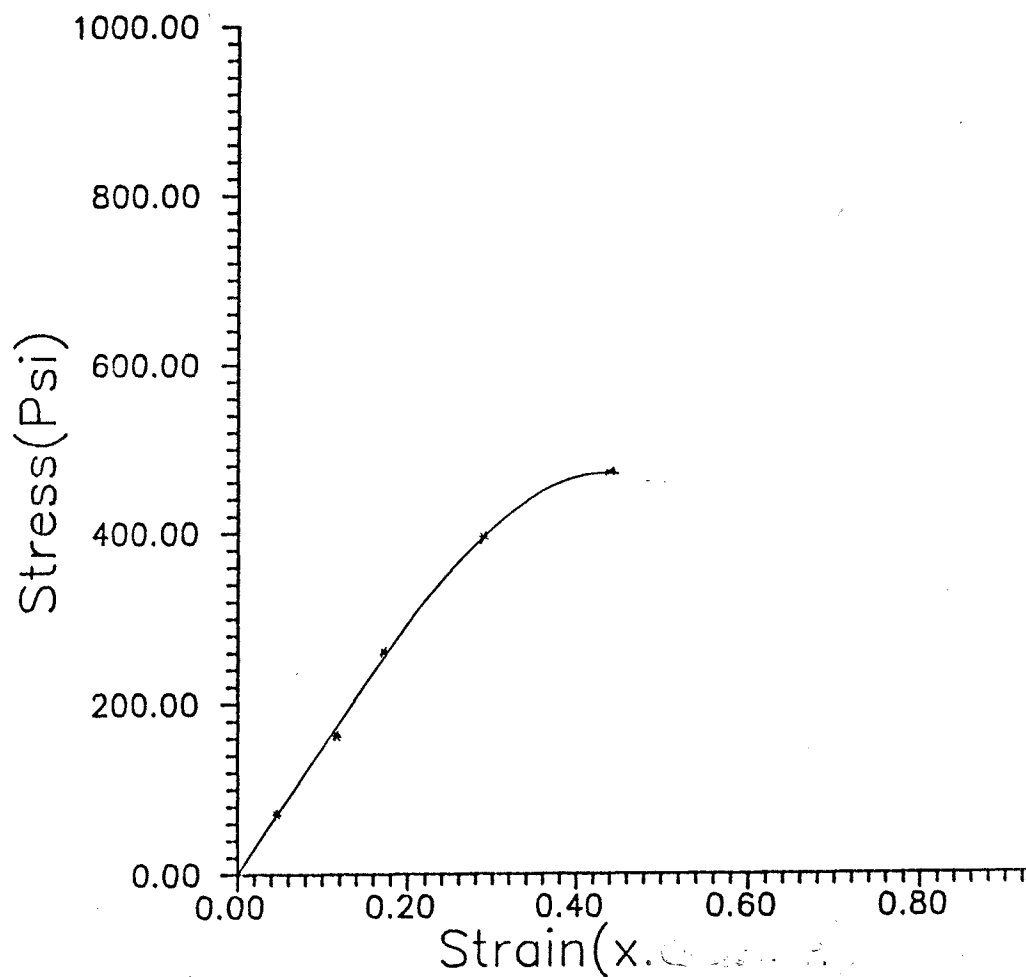


Fig.3.7 Stress(Psi) vs Strain (in/in) for Control sample 3.

section two

FALLING THROUGH WATER TEST

3.2-1 INTRODUCTION

Water deteriorates the concrete. The rate of deterioration depends upon the conditions of water i.e. rate of flow, temperature, composition etc. and upon the composition of concrete and type of construction. Some additives improve the strength of polymer concrete but on the other hand may facilitate deterioration of concrete when brought into contact with water. To protect concrete from water, different kinds of polymer can be used. There are two important methods which can be used to protect concrete from water.

- 1) Coating of polymer
- 2) Addition and polymerization of monomer.

Coating of polymer is a useful technique for floor protection where water is not supposed to be in contact for a long time and weather changes are not remarkable. The coefficient of expansion for polymers is higher than that of normal concrete, specifically the coefficient of expansion of unsaturated polymer resin is three times that of normal concrete(15). Therefore, if concrete is coated with polymer, large variation in temperatures may cause the polymers to be flaked off. For floor coatings it has been suggested that coating should be not more than 6 mm(16). For underwater concretes it is also difficult to do coating frequently as a part of maintenance. Second method, i.e. addition of polymer, has been suggested in most of the underwater constructions(17) The percentage of polymer which is being used depends upon the type of concrete, and the ultimate requirements.

Organic polymers when introduced in cement concrete forms fiber but this fiber formation depends upon the quality of polymer and method of mixing. When polymers are mixed in the form of latex they form more regular

texture and are more helpful in increasing the strength. For low percentages of water it is better to mix water before mixing polymer. This method of mixing of polymers in cement or concrete is known as impregnation.

In underwater construction the objective is not only to improve the strength but also to protect concrete from water attack. In this situation percentage of polymer must be higher so that it can form a film around the particles or lump of particles or on aggregates to make the concrete long life. Normally the bond strength between unsaturated polyester resin and cement is higher than that of cement-filler bond (if the filler is not synergistic). In case of using large percentages of polymer, the water/cement ratio should not be high because excess water weakens the bond strength of unsaturated polyester resin and cement.

The quality of deterioration of underwater concrete may be caused mainly by the washout of cement from concrete because cement in the concrete is a binding agent. By increasing the polymer contents, the resistance of the concrete to be separated in water improves. Care must be taken in introducing polymer so that polymer should not effect the hydration of the cement.

With the increasing use of offshore concrete structures it has become essential to establish a technology to obtain reliable concrete quality underwater. This technology is also likely to be useful for preventing failures in the concreting operations at ordinary underwater structures such as slabs for bridge piers and breakwaters. As concrete is being placed under water, the cement may become separated or washed away from a part of the aggregates or fillers upon contact with the water, either as the concrete mix is falling through the water or the concrete mix is spreading in the widthwise direction underwater. The part of the concrete from which the cement has been separated subsequently deteriorates. This behavior of concrete has been the most serious problem in the construction of underwater concrete structures. In order to prevent the cement or filler from becoming separated from the concrete mix in water, a viscosity building agents such as a cellulose derivatives could be useful(18). Different kind of polymers has been suggested to improve the viscosity of cement-concrete. Our objective was to use unsaturated polyester resin and industrial fillers.

In the previous section we have pointed out that how industrial fillers such as Franklin fiber, Hydrated alumina, Terra alba and Calcium carbonate effects the strength of polymer concrete.

In the subsequent section we have searched out that what is the effect of these industrial fillers in polymer concrete in underwater construction. To find out the deterioration of cement and fillers the method we adopted is entirely relative i.e. falling through water test.

3.2-2 PROCEDURE

Since the cement or filler washout was thought to be the main cause of quality deterioration, the loss of cement or filler from the concrete could be a measure of the resistance of concrete to be separated in water, when a constant volume of concrete travels in water at a constant speed and distance. Based upon this concept the falling through water test was introduced. The specimen of concrete mix for the test was put into a 0.2 cup. Also a cylindrical container having a diameter 100mm and containing water therein to a depth of 250mm was prepared. The falling through water test was conducted by placing

the cup with the specimen concrete mix at a height of 75mm above the water surface in the container, and then pouring the specimen concrete mix so as to allow it to fall by gravity into the water. The test results was obtained by measuring the turbidity of the water by transmittance at a wavelength of 600 m with a spectrophotometer.

The extent of the deterioration in underwater concrete depend not only upon the resistance of the concrete, but also upon the relative velocity between the concrete and water. This extent, therefore, is influenced by the method of concrete placing, the condition of the water, the dimensions of the structure to be constructed, and many other factors. Nevertheless the results obtained by the falling through water test could be a measure for relative comparision of the resistance of the concrete mix to be separated underwater. In this test a higher transmittance corresponds to a stronger resistance.

When only ordinary portland cement or the filler under consideration was dispersed in water, the relationship between the cement concentration or filler concentration in terms of transmittance was obtained as shown in Fig.3.8. From this relationship the content of the cement and filler separated from the concrete in the falling through water test could be known under the

assumption that deterioration of the cement causes dispersion of filler and cement in the water.

For each test the ratio of cement/water was 4/1 and the variable quantity was the fillers and adopted same procedure as stated above. It has been observed that about 5% unsaturated polyester resin makes cement undispersable in water upon performing same procedure. The following table shows the unsaturated polyester resin required to make filler and cement undispersable.

Table 3.2.1 Minimum amount of U.P. required.

U. P. %	MATERIALS
6.00	Terra alba
7.50	Hydrated alumina
8.50	Franklin fiber
9.00	Calcium carbonate
5.00	Cement

3.2-3 TEST RESULT

The amount of unsaturated polyester resin required to make concrete undispersable in water depends upon the type of filler used in concrete. Since cement and most of the fillers usable in concrete are not 100% soluble in water, disperse and then settle down in water. Therefore, to find out exact relationship between transmittance and material dispersed in water, it is necessary to shake the cell before inserting in spectrophotometer.

Figs.3.9 to 3.12 indicates the effect of fillers in polymer concrete. In this study the cement/water ratio was 4/1 with 5% polymer. As has been indicated in previous section that 5% unsaturated polyester resin makes the cement undispersable. These figures show effects of fillers compositions if one make unsaturated polyester resin(5%of cement) constant. Terra alba increases the turbidity of water by increasing its percentage in polymer cement. Trends of Hydrated alumina and Terra alba are almost the same both gradually increases the turbidity of water. Therefore in using these fillers one may use relatively low percentages of polymer. On the other hand Franklin fiber and Calcium

carbonate both increases the turbidity of water more efficiently. Franklin fiber is most suitable for concrete if used in lower percentages; upto 10% Franklin fiber does not indicate adverse effects on dispersion of concrete in water but after 10% the dispersivity due to this filler in water increases rapidly, whereas dispersivity due to the calcium carbonate is more severe than the Franklin fiber up to 10% but in the range of 25% to 30% the effect of Calcium carbonate and Franklin fiber is almost the same. This is due to the fact that as the surface area of filler increases more polymer is needed . In fact by increasing the percentage of fine fillers one should increase the quantity of polymer. It is apparent that Terra alba and Hydrated alumina shows better results as compared to Calcium carbonate and Franklin fiber.

Graphs are drawn between transmittance and time of polymerization of U.P. at different percentages of fillers added. In unsaturated polyester resin D.M.A has been added as an acclerator to reduce the polymerization time. Each graph indicates that after 20 minutes the polymerization effect become constant.

Cement containing 25% water shows 70%

transmittance in spectrophotometer. It is also important to understand the effect of filler in concrete with out polymer. Once we have relationship between (cement-filler) and turbidity then it become easier to predict the quantity of unsaturated polyester resin required in the composition. For example Figs.3.13 to 3.16 shows the fillers/cement vs transmittance relationship. Now in case of Terra alba 40% Terra alba and 60% cement (where cement/water ratio is 4/1) shows 35% transmittance, to enhance the transmittance up to 100% i.e. to make undispersable about 5.4% of unsaturated polyester resin is required. With the help of Figs.3.13 to 3.17 and Fig.3.8 it is easier to find out approximate amount of filler and cement dispersed in water, but not exactly.

It is quite difficult to find out exact relationship between weight of filler dispersed in water verses transmittance, because cement and even most of the fillers does not give linear relationship and therefore, it is advisable to study the behaviour of filler in water and then to study its behaviour in water with cement.

It has been emphasised that all this study is relative by adopting falling through water technique; the relative relationship was obtained to understand the effect of fillers. For Terra alba at low percentages the

dispersivity is lower and in the range of 25% to 60% the dispersivity become high. Hyrated alumina, calcium carbonate and Franklin fiber increases the dispersivity of the cement in water by increasing their percentages(20, 21).

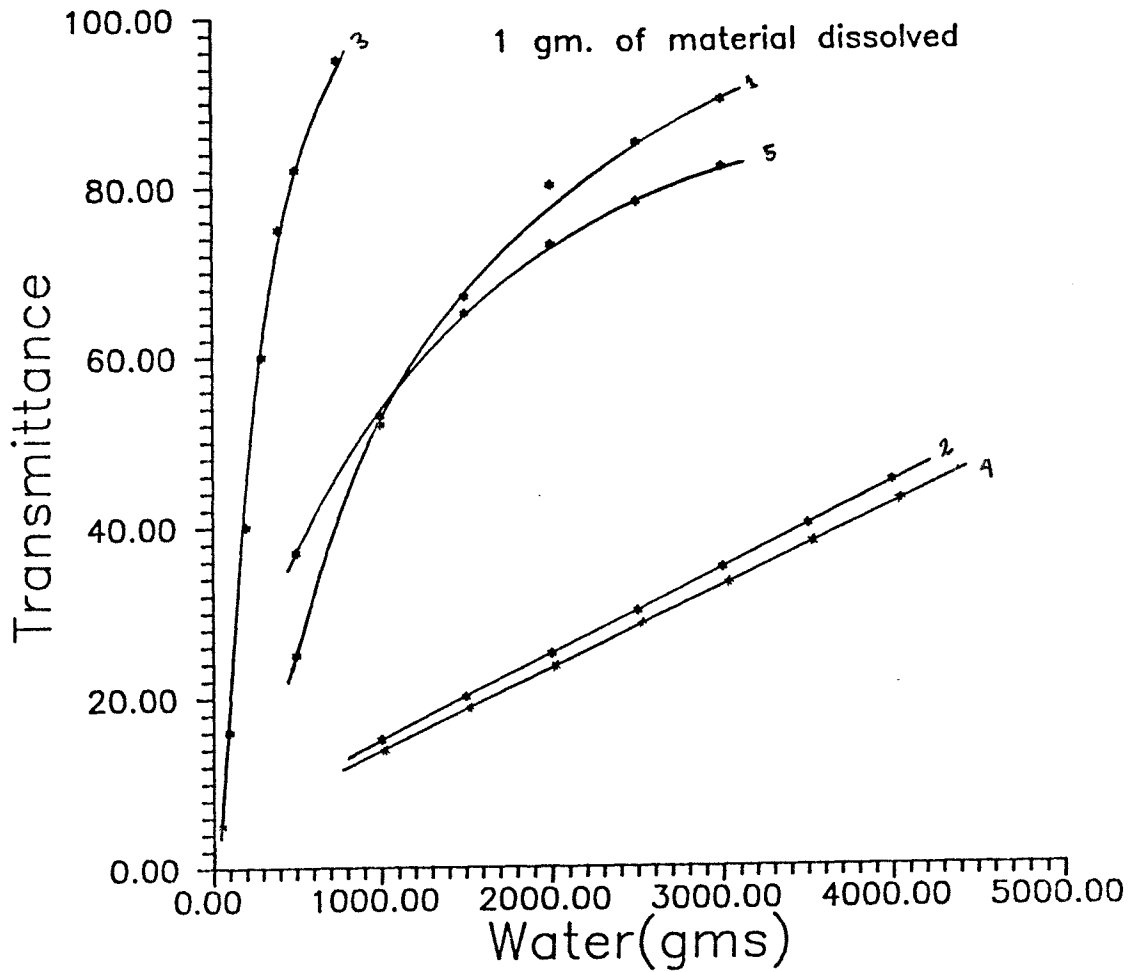


Fig.3.8 Transmittance for (1) Franklinfiber (2) Trihydrated Alumina (3) Terra Alba (4) Calcium Carbonate (5) Portland cement, when added (1 gram) in various amounts of water.

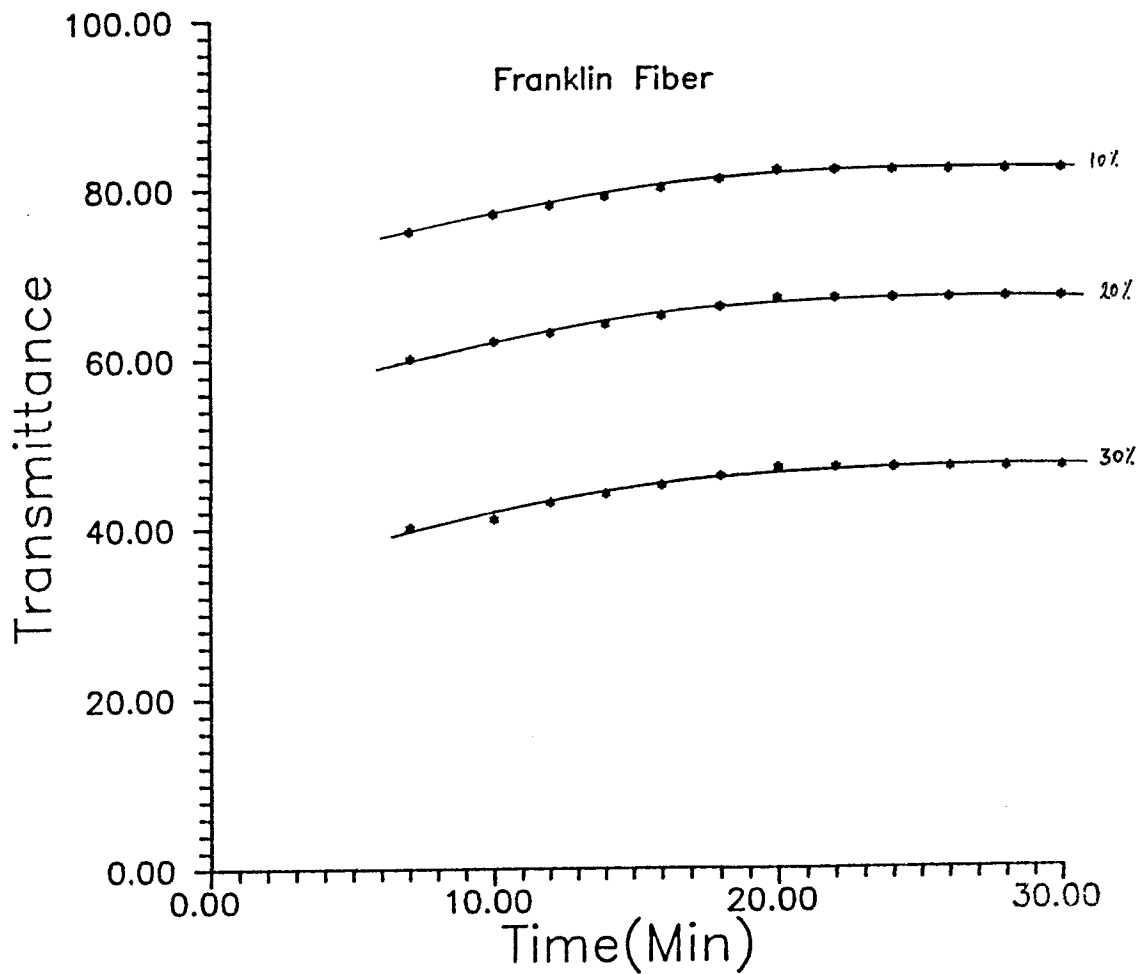


Fig.3.9 Trend of deterioration of PPCC during the course of polymerization of U.P, when (1) 10%, (2) 20% and (3) 30% Franklin fibers were added.

U.P=5%

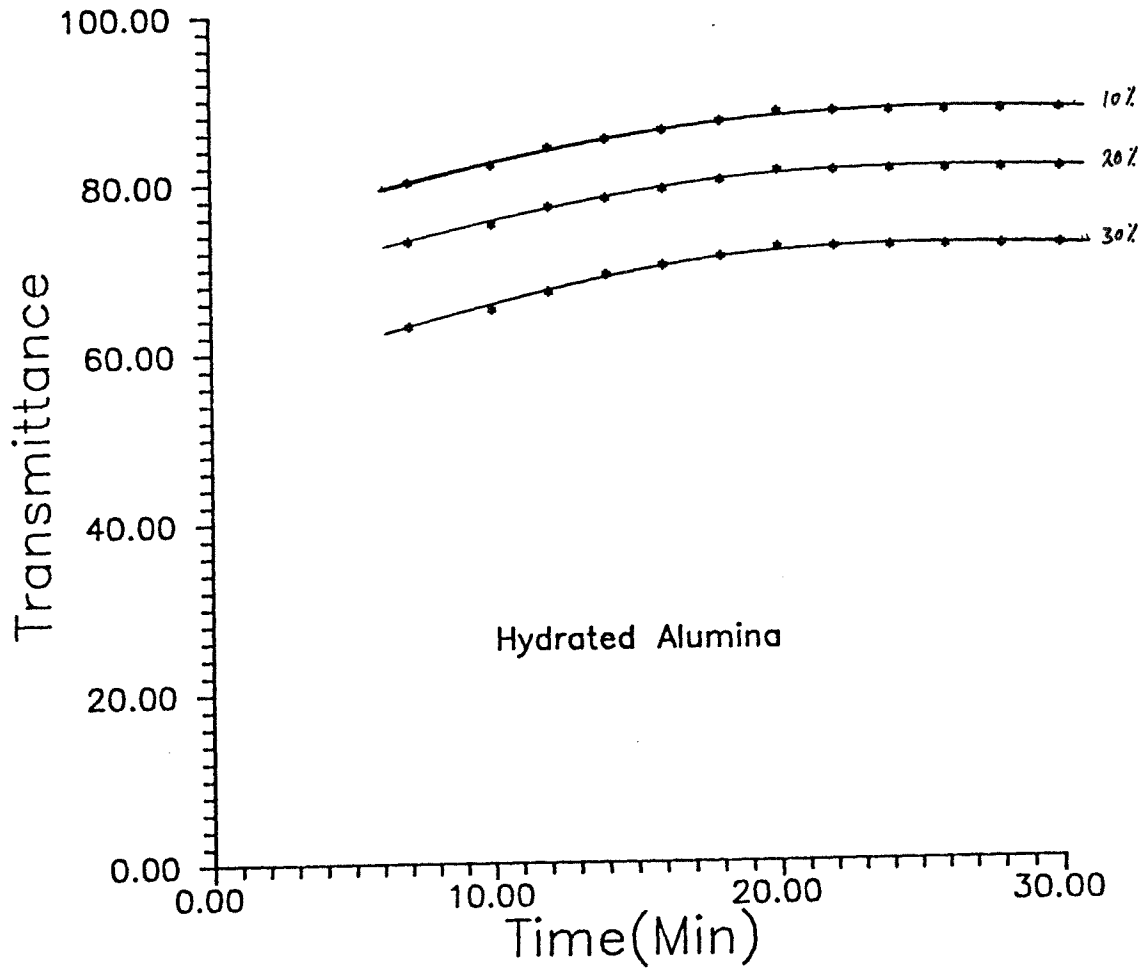


Fig.3.10 Trend of deterioration of PPCC during the course of polymerization of U.P, when (1) 10%, (2) 20% and (3) 30% Trihydrated Alumina was added.

U.P=5%

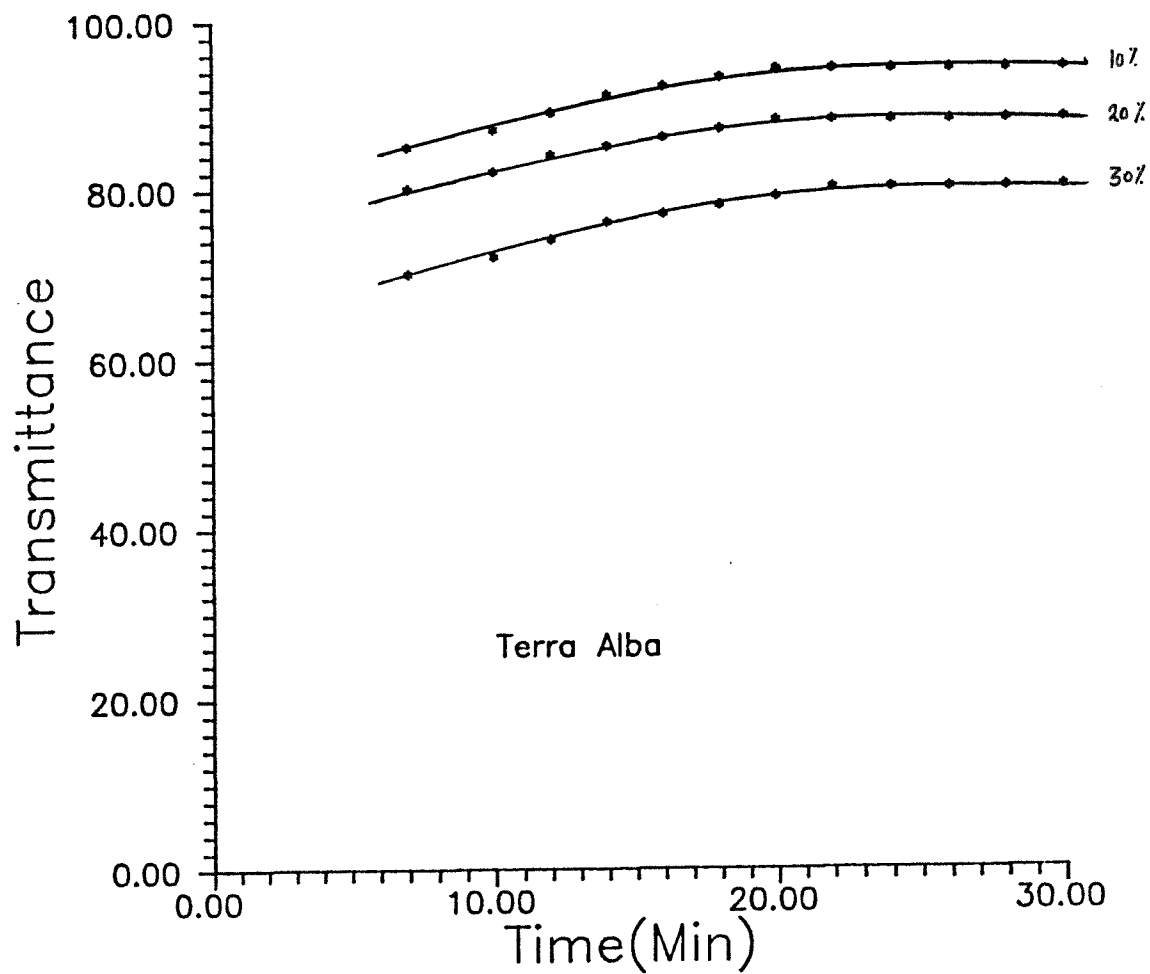


Fig.3.11 Trend of deterioration of PPCC during the course of polymerization of U.P, when (1) 10%, (2) 20% and (3) 30% Terra Alba was added.

U.P=5%

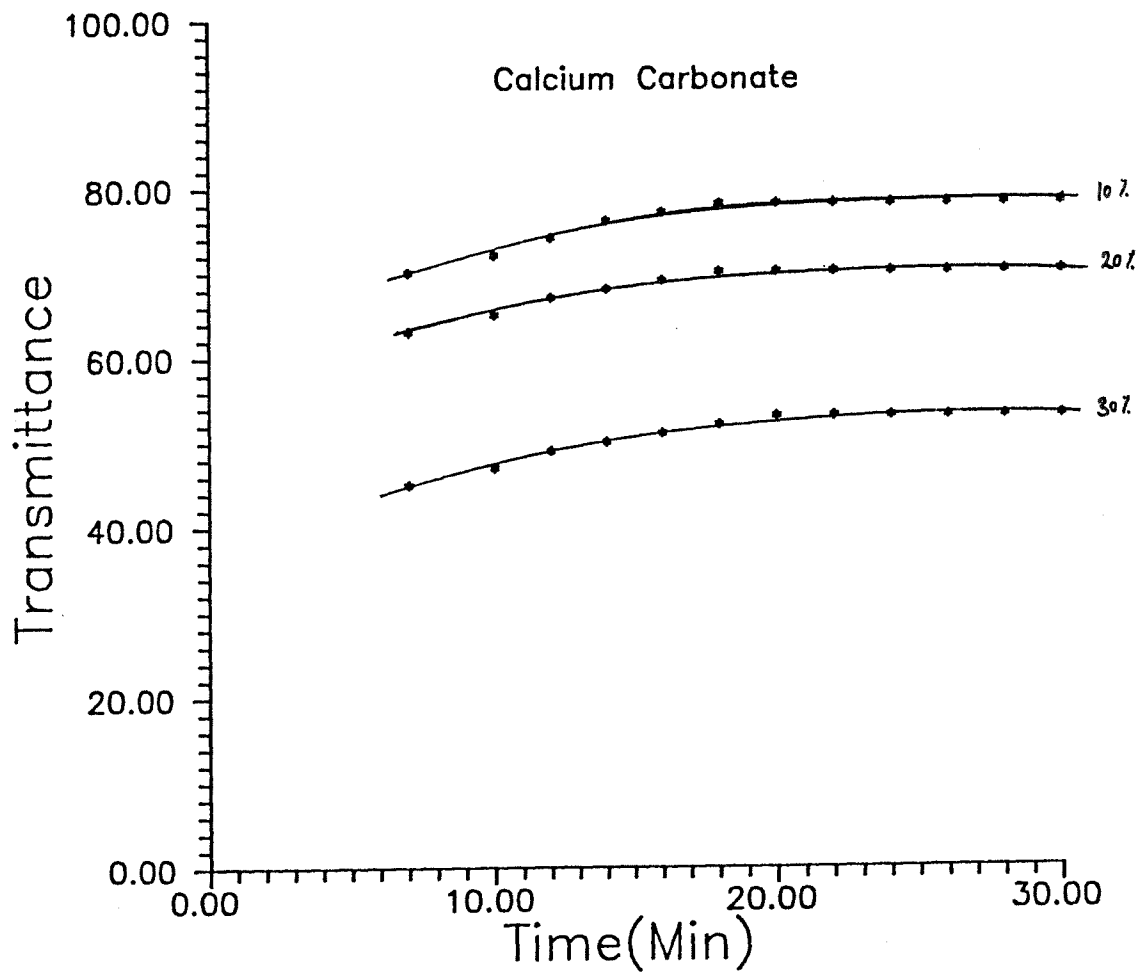


Fig.3.12 Trend of deterioration of PPCC during the course of polymerization of U.P, when (1) 10%, (2) 20% (3) 30% Calcium Carbonate was added.

U.P=5%

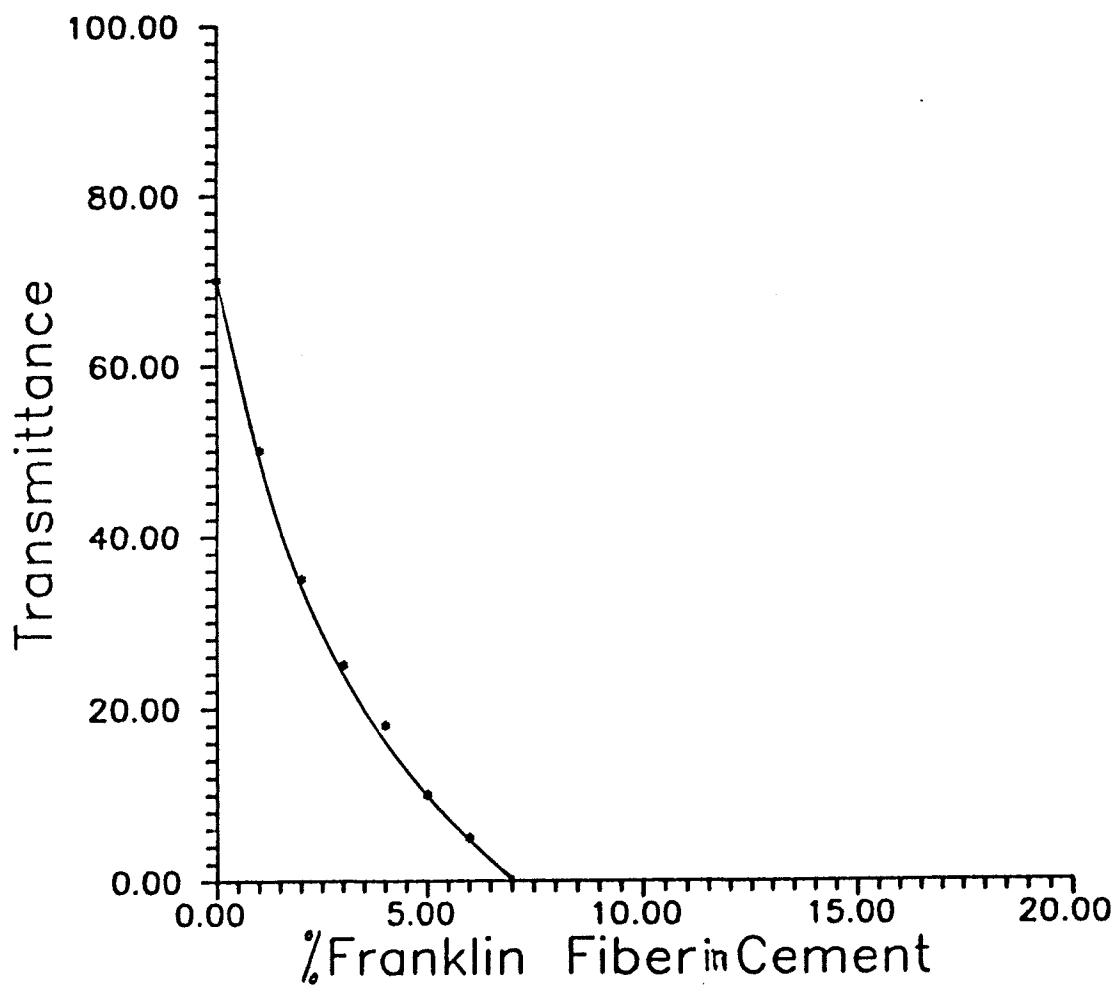


Fig.3.13 Deterioration of Portland cement by increasing the percentage of Franklin fiber (Cement:Water ratio is 4:1).

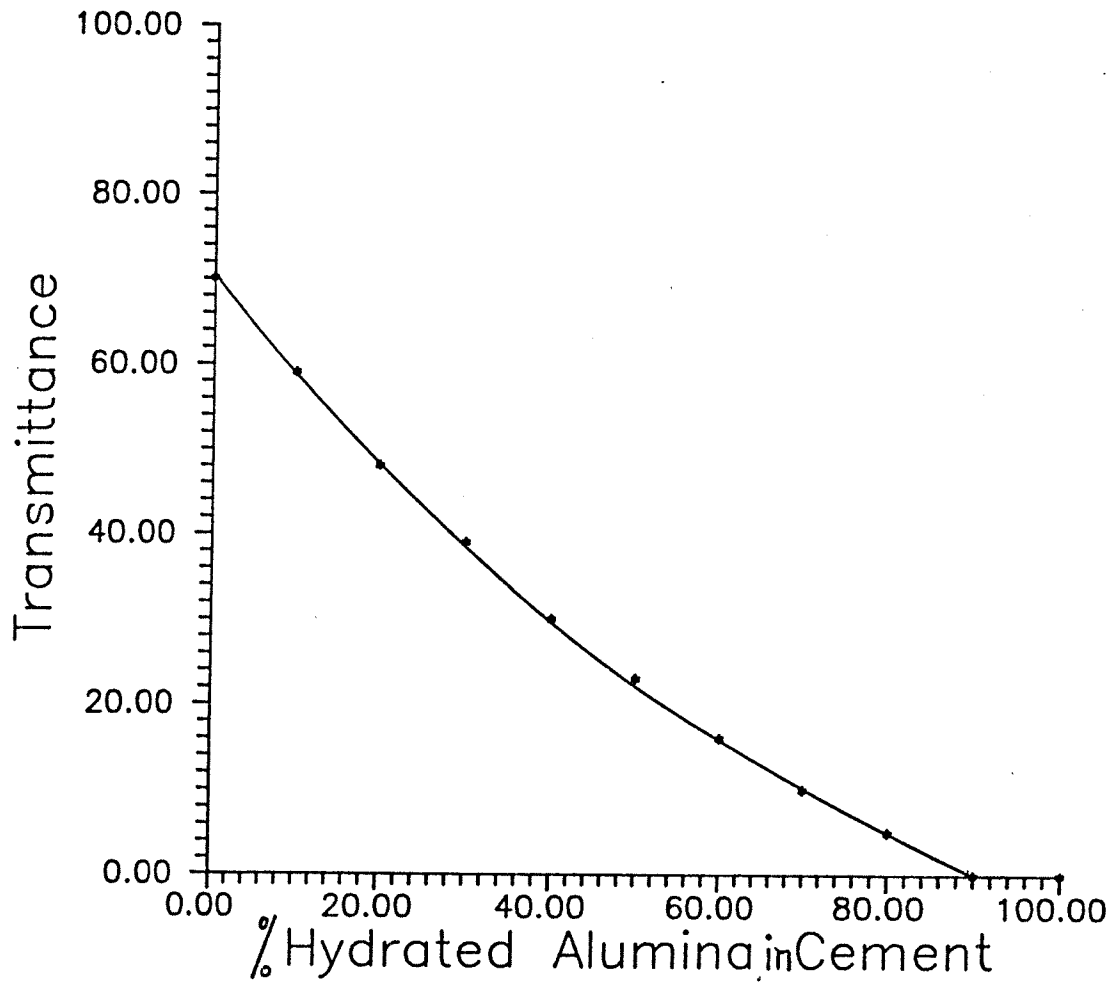


Fig.3.14. Deterioration of Portland cement by increasing the percentage of Trihydrated Alumina . (Cement:Water ratio is 4:1)

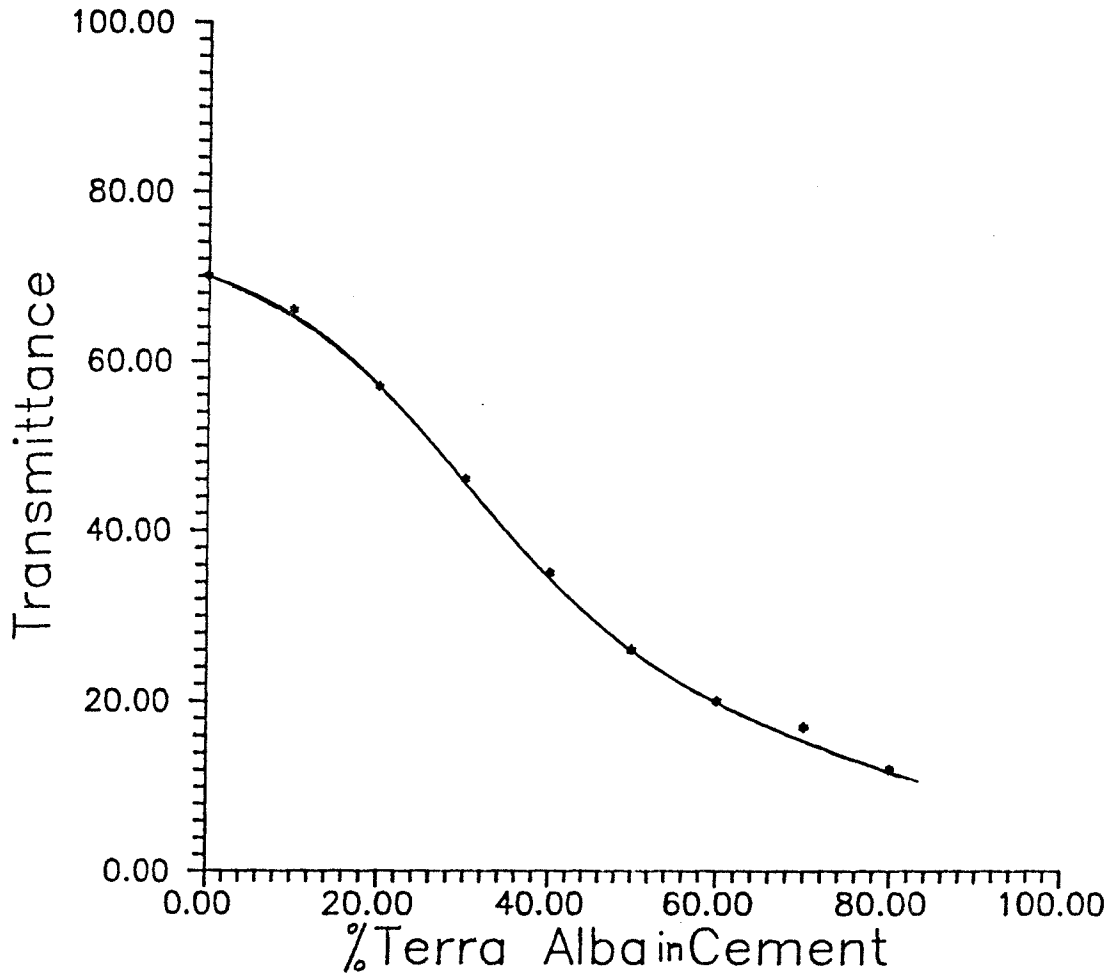


Fig.3.15. Deterioration of Portland cement by increasing the percentage of Terra Alba . (Cement:Water ratio is 4:1)

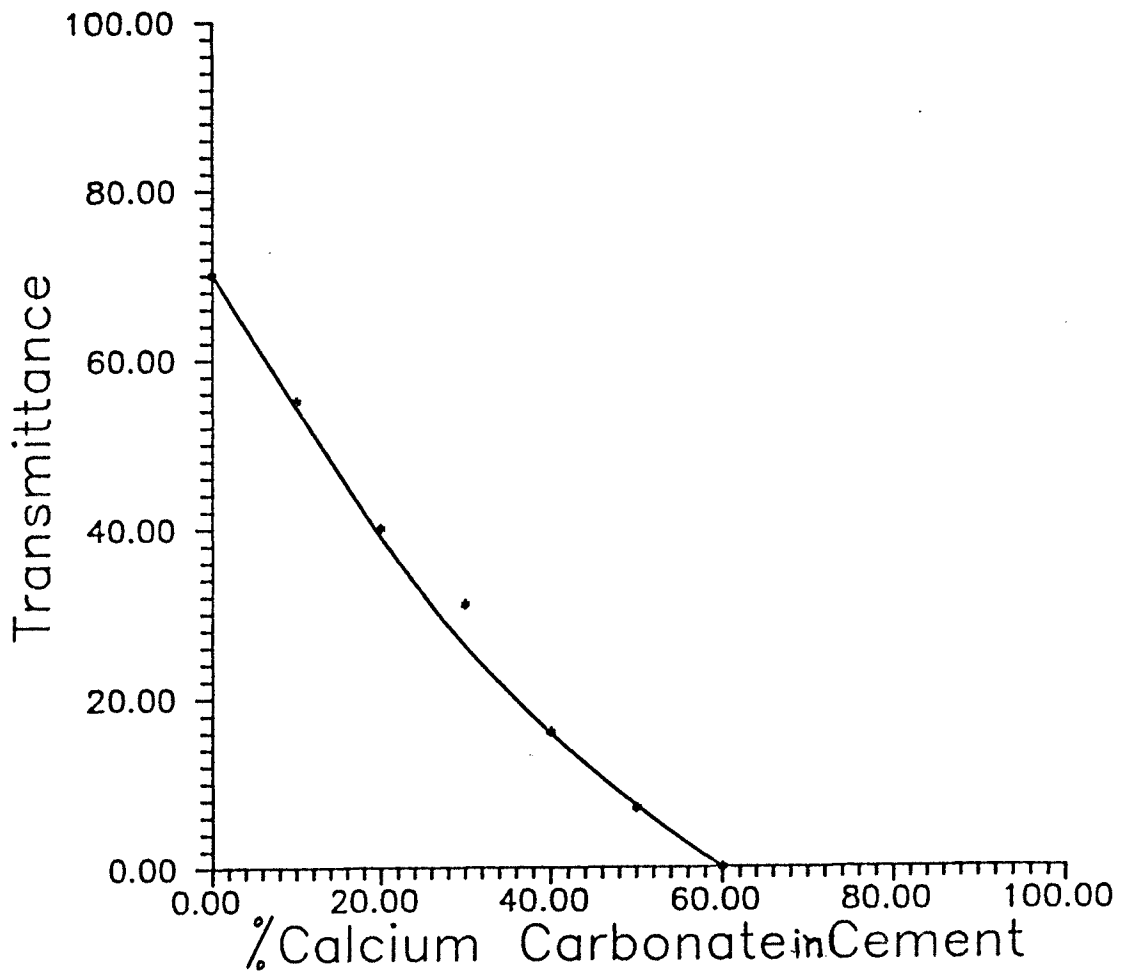


Fig.3.16. Deterioration of Portland cement by increasing the percentage of Calcium carbonate. (Cement:Water ratio is 4:1)

section three

BURNING TEST

Purpose of this section is , not to make the polymer cement concrete fire retardant, but to find out how fire affects the polymer cement concrete when synergistic fillers were added.

3.3-1 SOME DEFINITIONS

A number of terms in use today are confusing to some. For example, what do we mean by fire

retardant, fire resistant and fireproof. What is the difference, if any, between a flame retardant and a fire retardant. More often than not the meaning is not clear from the context. Occasionally the author himself has not defined in his own mind exactly what he wishes the term to convey.

Several of the foregoing terms have been used interchangeably just to avoid monotony in the writing and, it is hoped, in the reading. Thus fire retardant, fire resistant, and flame resistant are used interchangeably in many sections. Fireproof is not used loosely; indeed it is rarely used, because there are few substances that are fire or flameproof. Thereby, a definition arises: a material that is fireproof is totally unaffected in its properties by fire. Materials which do not contribute to the fire or propagate it are known as inerts. On the other hand, fire-retardant or fire-resistant materials are much reduced in flammability, burn slowly, and do not propagate fire rapidly, but they are substantially altered and eventually are consumed by a fire.

An example or two may help. Steel is not fireproof; it softens near 540 C and yields under stress at higher temperatures. It is not necessarily consumed in a fire but important properties are altered. Similarly,

concrete may crack and break up under the thermal stresses of a fire. One has to define the intensity and duration of the fire before the terms have real meaning. A substance that withstands completely an oil fire may be totally consumed in an oxy-acetylene.

"Fire retardant" is used as a modifying phrase to describe the property of resisting fire; it is also used in the nominative sense to describe a chemical species. Thus we talk of "fire-retardant lumber", meaning lumber which resists fire; but we say that ammonium phosphates are "fire retardants", that is, they are chemicals useful for retarding fire in a given system.

The words "resist" and "retard" imply a partial but not complete barrier to fire, whereas "proof" is an absolute term.

3.3-2 THEORIES OF FLAME RETARDANCY

The five generally accepted mechanisms by which flame retardants function under combustion conditions are.

1) The Gas Theory

Large volumes of noncombustible gases are produced

which dilute the oxygen supply to the flame and/or dilute the fuel concentration needed to sustain the flame.

2) The Thermal Theory

The endothermic degradation of the flame retardant lowers the polymer surface temperature and retards pyrolysis of the polymer. Also the degradation products of the agent can react endothermically with flame species and lower the temperature of the flame.

3) The Chemical Theory

The flame retardant dissociates into free radical acceptors which compete with the chain-propagating steps of the combustion process.

4) The Coating Theory

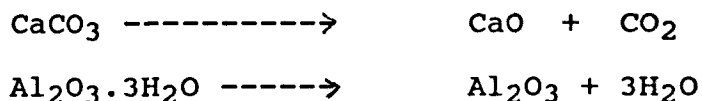
The pyrolyzing flame retardant forms a protective liquid or char barrier which minimizes transpiration of polymer degradation products to the flame front and/or acts as an insulating layer to reduce the heat transfer from the flame to the polymer surface.

5) The Physical Theory.

The flame retardant acts as a thermal sink to increase the heat capacity of the combustion system or to reduce the fuel content to a level below the lower limit of flammability. Either or both mechanisms will inhibit

the combustion and extinguish the flame.

The flame-inhibiting effects of CaCO_3 and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ are examples of the gas theory in action as agents dissociate to noncombustible gases which dilute the flame reactions.



Most of the polymers are fire sensitive and a lot of work have been devoted to make such polymers fire resistant by using different additives such as halogens, phosphorus, antimony and by using the mixtures of these materials. Following table shows the phosphorus and halogen requirements for self-extinguishing properties of various polymers:

Table 3.3.1

Polymer type	%P alone	%X alone	%P+%X additive	%P+%X actual
Polyurethane	1.5	18%-20%Cl 12-14%Br	1%P+6-7%Cl .5%P+9%Br	1%P+10-15%Cl .5%P+4-7%Br
Polyester	5%	25%Cl 12-15%Br	1%P+20%Cl 2%P+7-9%Br	1%P+15-20%Cl 2%P+6%Br
Epoxies	5-6%	26-30%Cl 13-15%Br	2%P+18%Cl 2%P+9%Br	2%P+6%Cl 2%P+5%Br

3.3-3- PRESENT STUDY

In present study we did not use any halogen, phosphorus or antimony type of additives. We used industrial fillers(as mentioned in chapter 1) and found out the rate of burning of polymer cement concrete. The testing was made according to ASTM D635-81.

PROCEDURE

For testing the specimens, each specimen of 125mm in length and 12.5mm in width and 0.4mm in thickness was casted. At least 10 specimens are necessary for single test. Each specimen was marked by scribing two lines 25mm, and 100mm from one end of the specimen.

Each specimen was clamped in horizontal position as shown in Fig.3.20. Bunsen burner with blue flame of approximately 25mm high was used to apply flame for 30 sec.

The average time of burning (ATB) was calculated as

$$ATB = \frac{\sum (t-30 \text{ sec})}{\text{No. of specimen}}$$

Figs.3.16 to 3.19 shows ATB of samples at various percentages of fillers. These figs. shows that all fillers are helpfull to reduce the average time of burning.

Trihydrated alumina was found to be the most effective among the all four fillers. Terra alba ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) gives results close to that of Trihydrated alumina .

The other fillers such as calcium carbonate and franklin fiber (CaSO_4) also reduces flame time but this effect is only due to the fact that the larger the surface area the more they are helpfull to protect entrance of oxygen during burning

Trihydrated alumina and Terra alba release water vapors on heating and eventually suppress the flame.

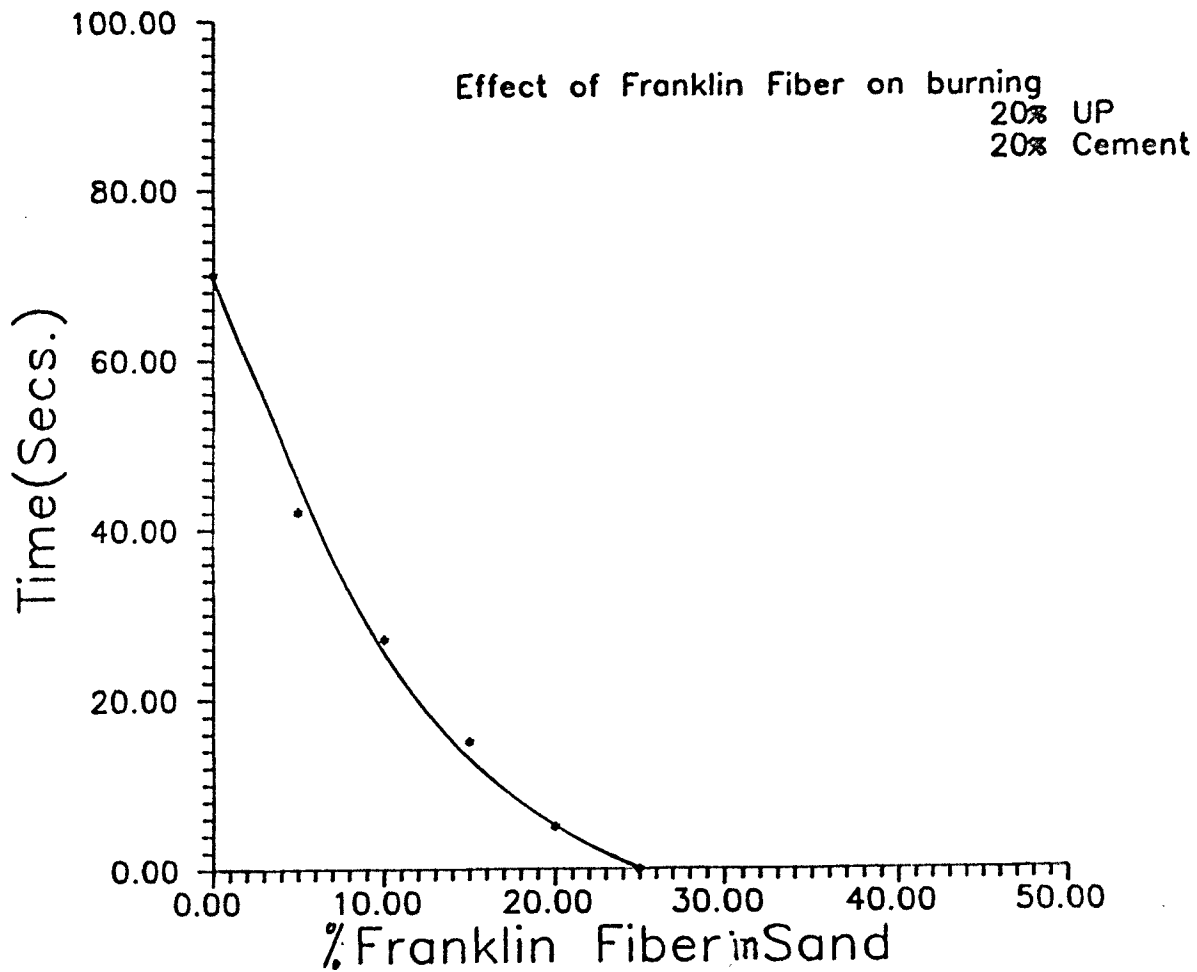


Fig.3.17 Effect on time of burning of PPCC, replacing sand by Franklin fibers.

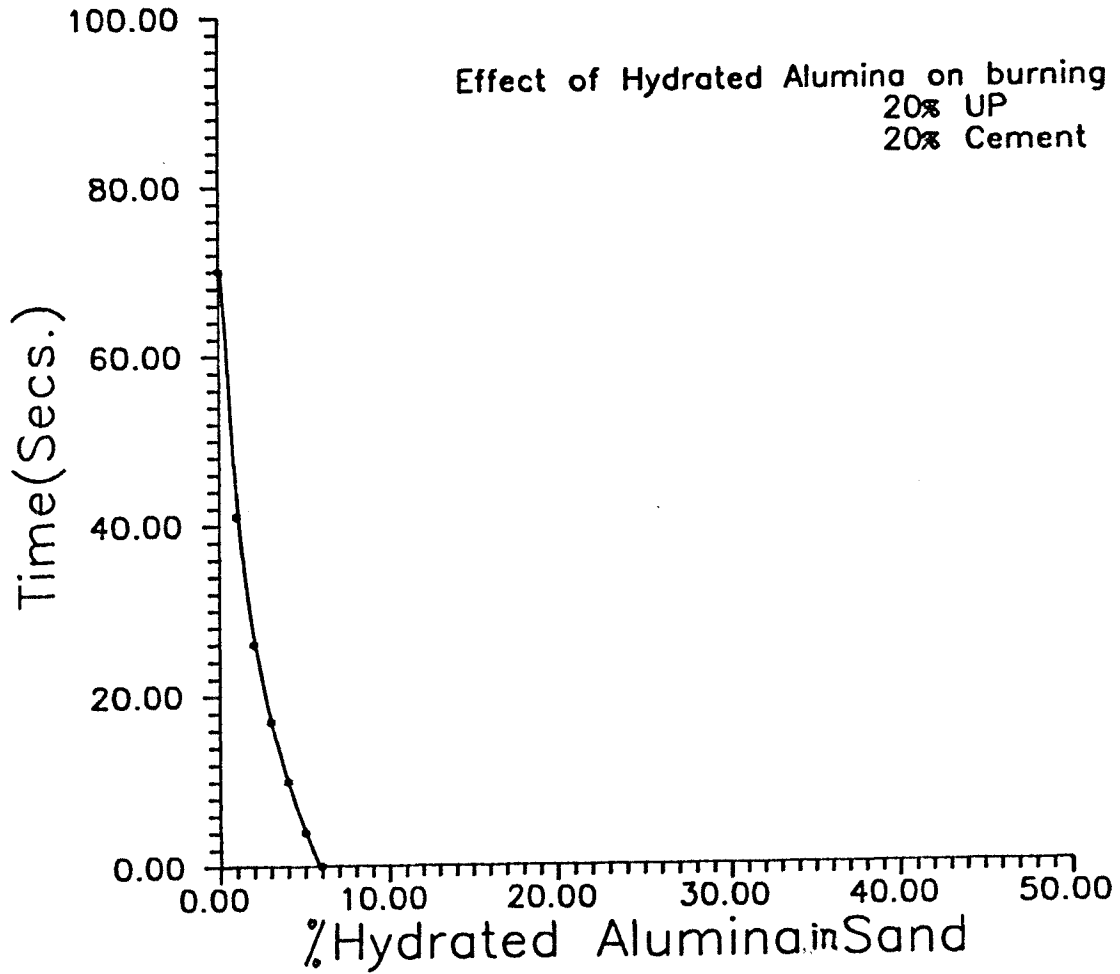


Fig.3.18 Effect on time of burning of PPCC, replacing sand by Trihydrated Alumina.

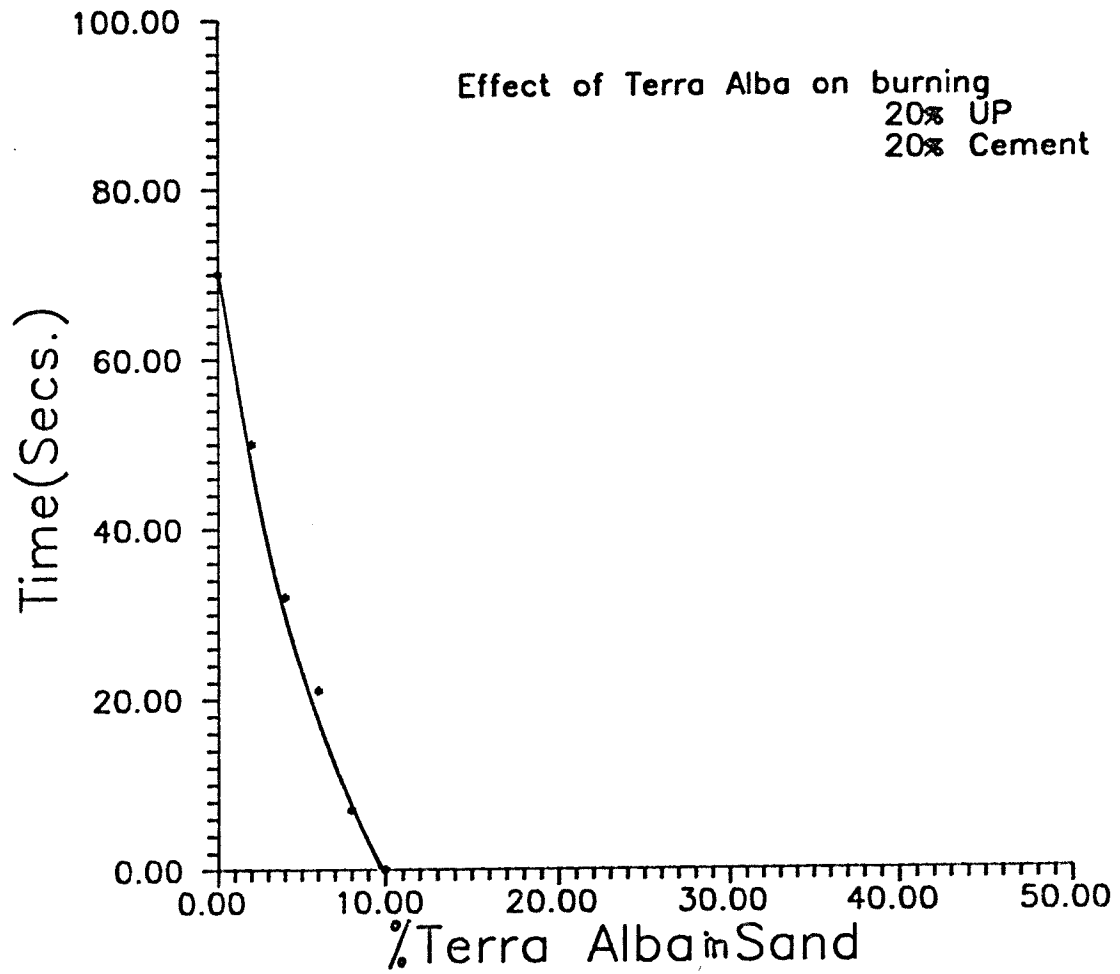


Fig.3.19 Effect on time of burning of PPCC, replacing sand by Terra Alba

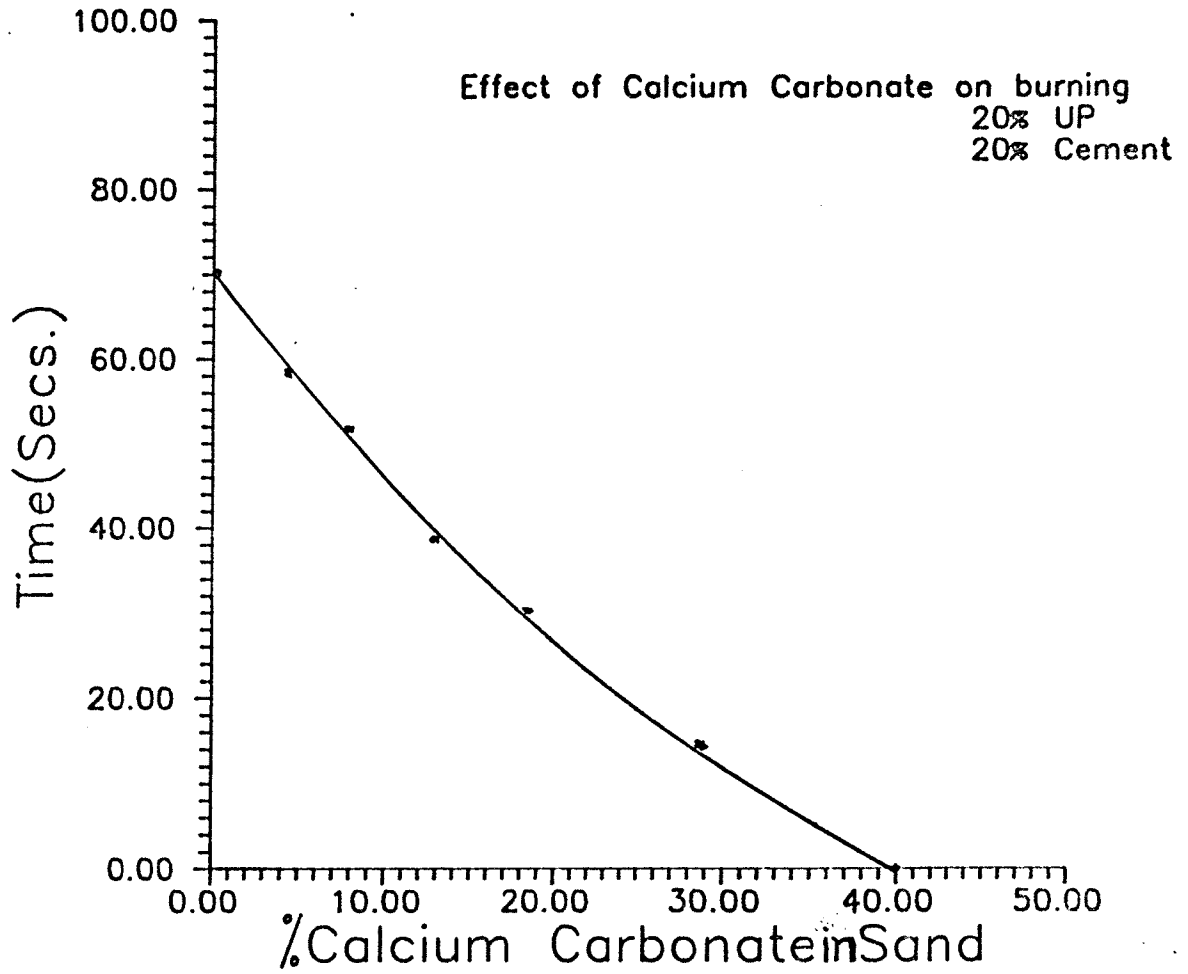


Fig.3.20 Effect on time of burning of PCC, replacing sand by Calcium carbonate.

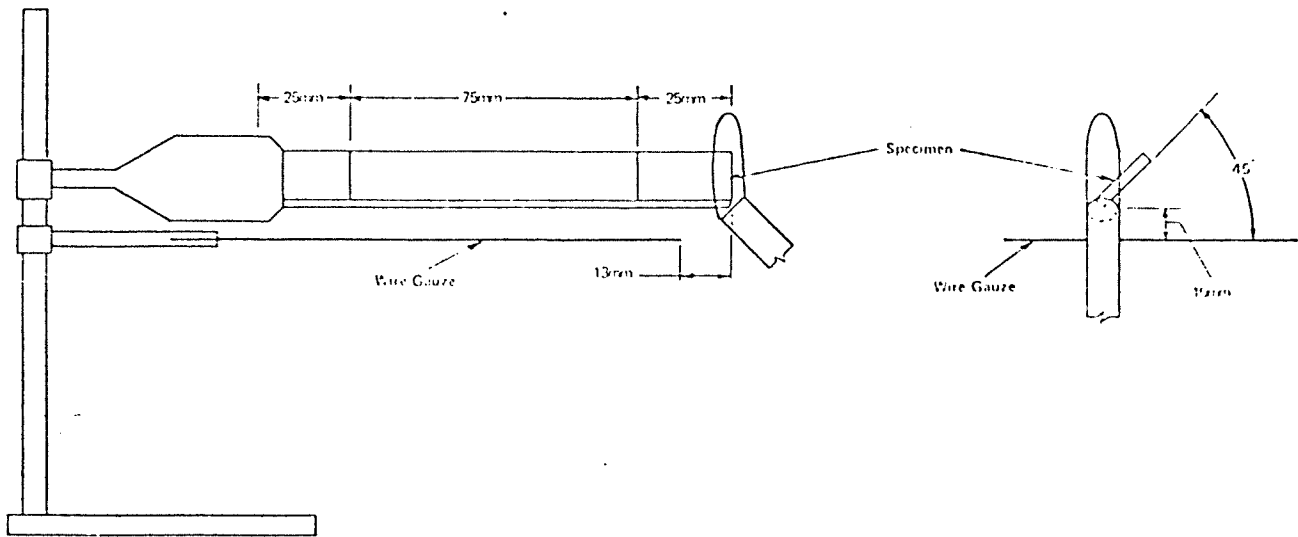


Fig.3.21 Indicates testing method of ATB.

CHAPTER 4

CONCLUSION

1) PPCC shows better tensile strength over normal concrete but not over PC.

2) With 20% U.P, 25% Portland cement, 6% Fiber Glass and 6% water, the maximum strength can be achieved with,

a) Fibrous Calcium sulfate (Franklin fiber) 15%.

b) Trihydrated alumina 30%

c) Terra alba 25%.

d) Calcium carbonate 25%.

3) The Tensile strength with 30% Trihydrated alumina for given composition shows slightly better results over Terra alba (25%) and 15% Franklin fiber shows maximum tensile strength, which is a clear indication that gypsum based fillers are more favourable for PPCC.

4) The modulus of elasticity for PPCC is higher than that of the normal concrete due to the crosslinking of U.P.

5) In underwater construction Franklin fiber requires high percentage of U.P but Terra alba requires least U.P. therefore, at lower amount of U.P. Terra alba is better.

6) As a fire retardent Trihydrated alumina was found to be the best one among four fillers. Terra alba gives close results to the Trihydrated alumina.

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