STUDIES ON MACRO DEFECT FREE CEMENT

by

Y.CHANDRI NAIDU
Centre For Polymer Science And Engineering

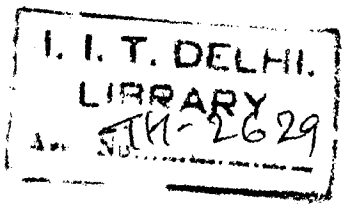
Submitted
in fulfillment of the requirements of the Degree of

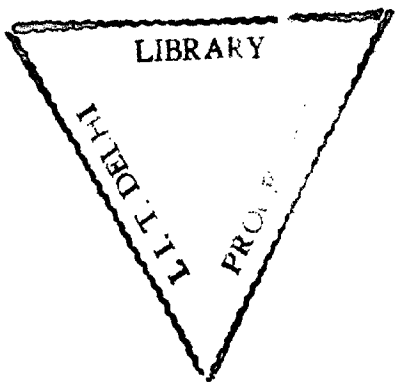
DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

DECEMBER, 1998





Dedicated

To

my son & daughter

CERTIFICATE

This is to certify that the thesis entitled **"Studies on Macro Defect Free Cement"** being submitted by **Mr Y Chandri Naidu** to the Indian Institute of Technology, Delhi for the award of the degree of **Doctor of Philosophy** in polymer Science and Technology is a record bonafide research work carried out by him. Mr. Naidu has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis which to our knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other university or Institute for the award of any degree or diploma.

Prof A K Gupta
Thesis Supervisor
Professor
Centre for Polymer Science & Engineering
Indian Institute of Technology, Delhi
New Delhi – 110 016 (INDIA)

Prof S N Maiti
Thesis Supervisor
Professor
Centre for Polymer Science & Engineering
Indian Institute of Technology, Delhi
New Delhi – 110 016 (INDIA)

Dr S N Ghosh
Thesis Supervisor
6 Sadhan Majumdar Lane
Shibpur (P.O.)
Howrah – 711 102 (INDIA)

ACKNOWLEDGEMENTS

My sincere and honest thanks to my supervisors Prof. A.K. Gupta, Prof. S.N. Maiti and Dr. S.N. Ghosh for their excellent guidance and continuous motivation in carrying out this work. I always indebted to them for their generous help, constant encouragement and valuable suggestions during the course of this work.

I am thankful to Director General, National Council for Cement and Building Materials for permitting me to pursue this study. I am also thankful to Dr A.K. Mullick (Director NCB), Dr K. Mohan and Dr S.K. Handoo for giving me time and encouragement to pursue this study.

I am thankful to Mr A.K. Sikri for his help in carrying out Mercury Intrusion Porosimertry studies, Mr. A.K. Solanki for SEM Studies, Dr L.H. Rao for Optical Micrograph studies, Dr. M.M. Ali, Mr. D.K. Panda, Mr. N.K. Sharma and Dr S.H. Jafari, IITD for their help in formulating the report. I am also thankful to Mr. D.K. Singla and Mr. L. Hans for their help in making diagrams.

I am thankful to my parents, my wife Mrs. Suneetha and my other family members for their continuous encouragement in pursuing this study.

Y. Chand. Nair

ABSTRACT

Cement based cast materials, in addition to their low energy content relative to plastics, ceramics and metals have drawn considerable attention as inorganic polymers because of their potential incombustibility and inertness. Inspite of substantial plasticity of hydraulic cement paste needed for moulding and fabrication, poor mechanical performance of hardened material limits its applications presently dominated by synthetic polymers and metals. However recent studies hace shown that there is a vast scope of improving the performance in cement based products through technological manipulations.

A curious feature of hydraulic cements, such as those based on calcium silicate, calcium aluminate and calcium sulphate is that it exhibits similarly low flexural strengths, typically between 3 and 10 Mpa, despite their differing chemical composition, varying degrees of hydration and contrasting setting mechanism. Because of these low strength values, unreinforced cements are never used in flexure or tension, and studies of cement strength are usually confined to compression. As was done in concrete to obtain polymer concretes, the same is extended to improve cement also with polymer addition. After considerable work at present, polymer concretes have found various potential areas of applications. The engineering of the new class of high strength material was pursued originally by Birchall and co-workers. Birchall et al have demonstrated that the commonly observed flexural weakness of cement is due to presence of large voids which are largely undetected by conventional methods of pore analysis such as gas absorption

and mercury porosimetry. They envisaged that the removal of such macro defects result in flexural strength up to 70 M pa, despite large volume of gel pores remaining in the material. These strength figures, comparable with those of sintered ceramics have been achieved without the use of elevated pressures of temperatures, and fibrous reinforcement. Macro Defect Free (MDF) refers to the absence of relatively large voids or defects which are normally present in conventionally mixed cement pastes because of entrapped air and inadequate dispersion. Such voids and defects limit the strength values that can be achieved by acting as stress concentrators. The term MDF should not be interpreted as implying pore-free systems.

The studies were conducted on both Ordinary portland cement (OPC) and High Alumina cement (HAC) based Macro Defect Free cement (MDF) systems. Apart from cement, the materials required and used were poly vinyl alcohol and superplasticizer, sulphonated napthalene formaldehyde condensate. Silica powder was also used to replace cement in the system. The process for making for MDF cement is adopted from plastic processing technology. The PVA solution is mixed with cement in planetary mixer and then it is further processed in a two roll mill. In determining the properties of the end product, mixing at two roll mill is a crucial step. One has to have a control on shear rate to manipulate microstructure of the product and thus the structural properties.

From the studies carried out, it appears that the compressive strength and flexural strength of the material are dependent on the total porosity and particularly

the pore size distribution. The porosity and pore size distribution are mainly dependent on water/cement (W/C) ratio. The optimum W/C ratio at which the maximum compressive and flexural strength were obtained were different for different polymer percentage. It is also observed that the optimum W/C ratio is lower for HAC based MDF compared to OPC based MDF cement systems. For example in OPC based MDF cement system, at 3% polymer content, the maximum strength is obtained at 0.14 W/C ratio, whereas at 5% polymer content, it is at 0.15. However in HAC based MDF cement systems, the optimum strength were obtained for 3% and 5% polymer at 0.12 and 0.13 W/C ratio respectively. For both the systems the optimum W/C ratio increases with increase in polymer content.

The compressive strength and flexural strength decreases non-linearly with increase in total porosity. Apart from this, the maximum pore size plays a significant role in controlling the strength. For the same total porosity, the larger the pore, the lower the strength. The increase in water/cement ratio increases total porosity in a systematic pattern. At higher W/C ratio, a larger pore volume is predominant in comparison with smaller pores. As the W/C ratio increases, both the volume fraction of pores greater than 10 μm and maximum pore diameter increases. As an example, the OPC based MDF cement system (22% W/C ratio and 6% polymer) contains only 20% more pores greater than 10 μm. Whereas 12% W/C ratio and 6% polymer contains only 8% of the pore volume occupied by pores greater than 10 μm. At higher W/C ratio, an increase in polymer content did not reduce porosity significantly. Whereas at lower W/C ratio, an increase in polymer content reduces

porosity and thus increases strength and improves mechanical properties, except water resistance which is highly sensitive to polymer increase. The increase in polymer content requires additional water for good mixing and thus the best improvement in strength. Beyond a certain limit of polymer content in the system , no further improvement in strength was observed.

An increase of polymer content and reduction of W/C ratio have considerable effect on the microstructure of OPC-PVA composite. The microstructure of the composite becomes more uniform with a reduction of W/C. A compacted structure is noticeable at low W/C ratio where there is a large quantity of unhydrated cement grains. This is deleterious to long term properties. The microstructure of the samples exposed to atmosphere for more than five years have shown some irregularity attributed to slow hydration of the initial unhydrated cement particles. The extent of irregularity is considerably reduced in the sample with silica powder. Microstructural studies of the fracture surfaces of MDF cement suggested the existence of a continuous matrix of polymer with cement grains firmly embedded in it. XRD analysis indicated the formation of a calcium acetate compound.

The DTA curves for hydrated OPC-PVA composites showed significant differences from the DTA curves of hydrated OPC especially in the temperature range of 250-500°C. The new exothermic peaks were observed in the 250-500°C region, i.e. at 290°C, 365°C. The intensity of the $Ca(OH)_2$ peak was also reduced. The curve of PVA showed these peaks were not attributed to PVA. Further it was

seen that none of the peaks observed in the DTA curve of PVA appear in the DTA curve of the OPC-PVA composite. The DTA curves for the HAC-PVA systems showed some significant differences from the DTA curve for hydrated HAC. The most important differences were observed in the 230°C-450°C region : (a) the C_3AH_6 peak, observed at 310°C in the case of hydrated HAC, was either absent or greatly diminished in the intensity; (b) the relatively narrow peak corresponding to AH_6 at 280°C was replaced by a much broader peak. Instead of single broad peak, a broad doublet was observed with individual peaks of the doublet centered at 250°C and 270°C; (c) The 300°-450°C region of the DTA curves for HAC-PVA systems showed the presence of exothermic peaks.

The IR spectra of hydrated HAC-PVA systems showed that the band at 1720 cm^{-1}, corresponding to the acetate group of partially hydrolysed polyvinyl alcohol was not observed. Further as compared to HAC only, the spectra of HAC-PVA systems showed a new band at 1560-1470 cm^{-1}, which was one of the bands attributed to a metal carboxylate. It was also seen that the bandnot only 1720 cm^{-1}, but other bands of PVA as well, such as at 1096 cm^{-1} (C-O str., OH bend), at 1245 cm^{-1} (C-O str.), and at 3360 cm^{-1} (OH str.) did not appear in the HAC-PVA spectra.

The samples which were immersed in water absorbed a higher percentage of water compared to the samples exposed to even 100% Relative Humidity (RH). These experiments revealed that there was a sharp increase of water absorption at the initial period and later on the percentage increase in absorption reduced. As

water was absorbed, the driving power for further water absorption reduced. When cement was replaced by silica filler the compressive strength and flexural strength were reduced. The rate of strength reduction was low up to 20 percent of filler and then the rate was found to be high. It was found that 10% of filler reduced water absorption by 5%. It was found that two percentage decrease in polymer causes between 3 to 5 percentage reduction in water absorption. The strength was reduced with increase in percentage of weight change. The rate of strength reduction was sharp up to 7 percentage weight change and then the rate in reduction of strength was slow. Even at low percentage of weight change, the reduction in strength was quite high.

CONTENTS