The Effect of Partial Replacement of Polymethyl Methacrylate (PMMA) on the Compressive and Flexural Strength of Ordinary Cement Mortar

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Abstract—In this paper studied the impact of the partial replacement of the cement by self-cure polymer (polymethyl methacrylate PMMA) in different ratios on the compressive strength, flexural strength and microstructural analysis, five ratios of cement replacement (1%, 3%, 5%, 7%, and 9%) by PMMA, these tests have been performed after curing at an early age (7days) and standard age (28days). The preparation of the mortar has been performed with the use of 1:2 cement to sand ratio by weight, with (0.5) water to binder ratio and polymer to self-cure monomer (methyl methacrylate MMA) ratio 2:1. Results have shown that the flexural and the compressive strengths of mortars has been increased with increasing the ratio of the replacement (1%, 3%, 5%) and then decreased at replacement ratio (7% and 9%). The best results of the new cement mortar were reached at the partial replacement of cement with 5% of PMMA were recorded enhancement of compressive strength 15.8% at an early age and 24.4% for standard age and enhancement of flexural strength 16.8% at an early age and 19.4% for standard age, from scanning electron microscopy SEM analysis observed the PMMA filling the pores and form more homogeneous microstructure in G32 as compared with the microstructure of G1.

Index Terms—Polymethyl Methacrylate, Compressive Strength, Flexural Strength, Microstructural Analysis, Methyl Methacrylate, Scanning Electron Microscopy.

I. INTRODUCTION

The use of polymers increasing day after day in cement mortars and repair works. Polymers can be used as a single binder or mixed with cement and aggregate. The composites which have been formed with the use of the polymer and the aggregates have been referred to as the polymer concrete (PC) or polymer mortars (PM), whereas the composites which have been formed by (cement and aggregates) are referred to as the polymer modified concrete (PMC) or polymer modified mortar (PMM), polymer-modified mortar or concrete is preferred due to its lower cost than that of polymer concrete. The adding of polymers enhances the mechanical and the physical characteristics of the mortar and concrete [1, 2].

A wide range of thermosetting or thermoplastic polymers can be used to modify mortars and concrete in a variety of the forms: latexes, liquid resins, re-dispersible powders and water-soluble homo-polymers or co-polymers [3]. The polymer selection is dependent on the specified utilization and requirements of the performances such as the durability, strength, and chemical resistance. In addition to that, the systems of the polymer might as well be altered by using additives such as the stabilizers, surfactants, coloring pigments, and anti-foaming agents [1]. To make the PMM, the majority of researchers utilize the latexes of a one or a combination of polymers like the poly-vinyl acetate, copolymers of the vinyl acetate-ethylene, acrylic, and styrene–acrylic, [1, 3]. Many works were performed on the use of polymers to enhance the mechanical and the physical characteristics of the mortars.

M. Pei et al. [4] Studied the influence of monomer ratio on typical characteristics of the PMMs with the latices of the poly (methyl methacrylate butyl acrylate). PMMs with the methyl methacrylate/butyl acrylate copolymer lattices of a variety of ratios of the methyl methacrylate/butyl acrylate, have been produced with various ratios of polymer to cement and have been evaluated in terms of the compressive strength, workability, flexural strength, air content, and water absorption. Results, the influence the ratio of monomer and polymer to the ratio of cement on typical characteristics have been observed. The characteristics of latex-modified mortar types have been greatly influenced by the monomer ratio as well as the ratio of polymer to cement.

Konar et al. [5] studied the results of (FT-IR spectroscopy) that was carried out on the PMMA-cement pastes in order to understanding the interactions of PMMA polymer with Portland cement after hydration reaction of cement pastes and curing the specimens for 28 days, FT-IR curves obtained show typical interaction aspects of Portland cement mortar modified by poly (methyl methacrylate), Dry PMMA film obtained from latex shows O-H stretching and deformation vibration. The result indicates some bound water molecules (hydrogen bonded C=O group) present in the film. The hydration process in composites varies with the variation of bound water, a shift of PMMA peaks in the composites indicate a strong interaction with cement and of the particular groups of PMMA, Carbonyl bond shielding in composite suggests a strong coordination bond between the C=O group of polymer and metal atom/ion of cement.

D. F. M. Machado et.al. [6] Confirmed that the additives have significantly decreased the tested sample’s setting time. Which is why, it has suggested that the reason of the ultimate reactive material’s mass in experimental cement has been lower compared to that for control samples occurred as a result of adding the insoluble solid particles into experimental cement, which is why, the time of the reaction which needs to be completed is expected to be...
decreased. Particularly for the group of the PMMA, in addition to that it has suggested that a potential mixing water sequestering with PMMA polymer beads reduced the ratio of water/powder, thereby reducing the time of hydration.

N. Ghattas et al. [7] investigated Improving cement-composite concrete systems (used for disposal of radioactive wastes) using poly methyl methacrylate (PMMA) and unsaturated styrenated polyester (SPE) to seal or fill the pores to lower the porosity of the cement matrix, consequently to reduce or to retard the release of the radio contaminants to the surrounding environment. Two different techniques were adopted for the addition of organic polymers based on their viscosity. By using impregnation technique where the low density PMMA was added on the other hand high density SPE was mixed with cement paste as a premix process. The impact of the organic polymers on the cement matrix hydration and the properties of the obtained CPC container has been studied by using IR-analysis, X-ray diffraction, thermal effects and weight loss. Porosity, pore parameters and rate of release are also determined.

H. Wu et al. [8] proposed a polymer-based crack repairing material named EMP by synthesizing Epoxy acrylate (EA), methyl methacrylate (MMA), and polyurethane (PU) pre-polymer utilizing interpenetrating polymer network (IPN) technology. The physical and mechanical properties of EMP were evaluated through a series of experiments, and the bonding behaviour of the material for the crack repairing of concrete structure was also evaluated with composite specimens. The Results demonstrate the EMP have a considerable possibility for repairing concrete cracks with desirable operability adhesive strength and cracking resistance and its properties could be adjusted within a certain range through various mix proportions to accommodate different requirements for applications.

II. MATERIALS

A. Ordinary Portland cement:

In the present work the cement which has been utilized is the Ordinary Portland Cement (OPC) type I which is known commercially as the (MASS), produced in Iraq. The physical and the chemical analyses have been carried out and the test results have indicated that the sample complies with the Iraqi specifications (IQS No5 /1984) [9]. The physical characteristics and the chemical composition of the MASS have been listed in Table I and II.

| Property                      | Test result | Spec. Limit according to IQS No5:1984 |
|-------------------------------|-------------|---------------------------------------|
| Setting time                  | 115         | >45min                                 |
| Initial setting (minutes)     | 4.33        | <10 hrs.                               |
| Final setting (h)             |             |                                       |
| Compressive strengths for the cement | 16.59 | >15                                    |
| Mortar cube                  | 24.44       | >23                                    |
| 70.7mm at (MPa)               |             |                                       |
| 3days                        |             |                                       |
| 7 days                       |             |                                       |
| Soundness with the use of Autoclave (%) | 0.31 | <0.80                                  |
| Fineness (cm²/g-1) with the Blaine approach | 2765 | >2300                                  |

III. MIXTURES

The mixtures were prepared as two groups of mixtures, first group G1 mixtures were Prepared as control specimens made of cement, sand and water only. Second group G2 mixtures were prepared with different ratios of replacement of cement by PMMA. Where G21, G22, G23, G24, G25 represent 1%, 3%, 5%, 7%, 9% respectively (PMMA to cement ratio). For every mixture the sand to cement ratio has been fixed to (2:1), PMMA to MMA (2:1), and the ratio of water to binder has been fixed to (0.47). Table IV presented the proportions of the mixtures.

B. sand:

AL-Ukhaidher, Kairbalaa, Iraq, natural sand is [which has been utilized in the present work which has a 2.74 fineness modulus (FM), 2.60 bulk specific gravity (Sp. gr.) and sulfate content, (SO3%) of (0.39%) by the weight of the sand, conforming with the Iraqi standard specification limit No: 45 / 1984[10]. In this work, only the sand less than (4.75mm) was used to achieve the mixing requirements and properties.

C. Self-curing polymer:

Self-curing polymer (polymethyl methacrylate PMMA) with self-curing monomer (methyl methacrylate MMA) are used in this work. Physical and chemical properties of Self-curing polymer (PMMA) given in Table III.

TABLE I: THE PHYSICAL CHARACTERISTICS OF THE MASS SAMPLE

| Property                      | Test result | Spec. Limit according to IQS No5:1984 |
|-------------------------------|-------------|---------------------------------------|
| Lime saturation factor (LSF) (%) | 0.36 | 0.66 - 1.02 |
| Loss on ignition (wt.%)        | 2.54 | <4.00 |
| Insoluble residue (wt.%)       | 0.44 | <1.50 |
| SiO2 (wt.%) Blaine approach    | 19.34 | ---- |
| Al2O3 (wt.%)                   | 4.32 | ---- |
| Fe2O3 (wt.%)                   | 4.42 | ---- |
| CaO (wt.%)                     | 61.08 | ---- |
| MgO (wt.%)                     | 2.18 | <5.00 |
| SO3 (wt.%)                     | 1.82 | <2.5 |
| C3S                            | 91.11 | ---- |
| C3A                            | 3.97 | ---- |
| C4AF                           | 13.43 | ---- |

TABLE II: THE CHEMICAL COMPOSITION OF THE MASS SAMPLE

| Property                        | Test result | Spec. Limit according to IQS No5:1984 |
|---------------------------------|-------------|---------------------------------------|
| Chemical formula                | (C5H8O)n   |                                       |
| Appearance                      | Fine powder |                                       |
| Density                         | 1.25 g/cm3  |                                       |
| Molecular weight                | 800.000     |                                       |
| Particle size                   | 75µm        |                                       |
| Absorption                     | 19.50µg/mm3 |                                       |
| Solubility                      | 3µg/mm3     |                                       |
| water Solubility                | Insoluble in water, soluble in acetone | |
| Chemical Stability              | This product is very stable. When it is overheated or in presence of a catalyst, a new polymerization process may start again | |
| Flexural strength               | 62 MPa      |                                       |
| Flexural modulus                | 1780 MPa    |                                       |
| Residual monomer content        | 3.16%       |                                       |

TABLE III: PHYSICAL PROPERTIES OF SELF-CURE POLYMERS

| Chemical formula                | (C5H8O)n   |                                       |
| Appearance                      | Fine powder |                                       |
| Density                         | 1.25 g/cm3  |                                       |
| Molecular weight                | 800.000     |                                       |
| Particle size                   | 75µm        |                                       |
| Absorption                     | 19.50µg/mm3 |                                       |
| Solubility                      | 3µg/mm3     |                                       |
| water Solubility                | Insoluble in water, soluble in acetone | |
| Chemical Stability              | This product is very stable. When it is overheated or in presence of a catalyst, a new polymerization process may start again | |
| Flexural strength               | 62 MPa      |                                       |
| Flexural modulus                | 1780 MPa    |                                       |
| Residual monomer content        | 3.16%       |                                       |

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TABLE IV: THE PROPORTIONS OF THE MIXTURES

| Sample | Cement% | PMMA%  | (water /cement) ratio | (sand / cement) ratio | (PMMA /MMA) ratio |
|--------|---------|--------|-----------------------|-----------------------|--------------------|
| G1     | 100     | 0      | 0.5                   | 2:1                   | 2:1                |
| G21    | 99      | 1      | 0.5                   | 2:1                   | 2:1                |
| G22    | 97      | 3      | 0.5                   | 2:1                   | 2:1                |
| G23    | 95      | 5      | 0.5                   | 2:1                   | 2:1                |
| G24    | 93      | 7      | 0.5                   | 2:1                   | 2:1                |
| G25    | 91      | 9      | 0.5                   | 2:1                   | 2:1                |

IV. PREPARATION OF TEST SPECIMENS

To obtain a homogenous mixing of materials of mortar:

Weighing the elements with a 0.01 gm digits sensitive digital balance. Dry mixing of PMMA with cement for G2 to obtain the homogenous binder. Sand and binder mixed by hand for about two minutes, the water and MMA has been added into the mix and mixed for 4 min. based on the ASTM C-305 [11]. The mortar has been removed from mixer and then poured in oiled clean molds, the samples’ densification has been performed on a vibrating table in 2 layers where every one of the layers has been vibrated for (1.0 to 1.50) min. to the point where there have been no bubbles emerging to the casting surface. The samples’ surface finish has been carried out using of a spatula. Following the molding, the molds have been covered by plastic sheets for preserving their moisture and the samples have been left in laboratory for 24h, at room temperature. Then the samples were de molded and cured in the water where they have been left to the time of testing.

V. MECHANICAL TESTS

A. Compressive strength Test:

The test of the compressive strength of the mortars has been carried out based on the (ASTM: C-109-02) [12]. The compressive strength for every one of the mixtures has been specified from an average of 3 cubic samples (50mm × 50mm × 50mm) tested at 7days of age (i.e. at early age) and 28 days (standard age) after the curing.

B. Flexural strength Test:

according to (ASTM C293) [13] The test method was carried out. A block of rectangular cross section (100 ×25×25) mm rests on 2 supports and has been loaded using a loading nose mid-way between support (1-point load). The flexural strength for every one of the mixtures has been specified from an average of 3 specimens of the prism, which have been tested at 7 days of age (early age) and 28 days (standard age) after the curing.

C. SEM analyses samples:

The specimens were broken into pieces of suitable size that are used for examination carried out at 28 days for SEM analysis.

VI. RESULTS AND DISCUSSION OF MECHANICAL PROPERTIES

The results for mechanical tests are the average of the three samples for each replacement ratio.

The Compressive strength test results and the ratio of enhancement for all samples are shown in Fig. 1.

From Fig. 1 can be observed for early and standard ages all mixtures of G2 (containing PMMA) ( G21, G22, G23, G24, and G25 ) have compressive strength higher than that of control mixture (G1), the value of the compressive strength gradually increases with increasing the PMMA ratio until reaching G23 and after that, the compressive strength decreases with the increase in the PMMA ratio, the maximum value of compressive strength recorded at G23 where increased 15.8%at(7days) and 24% at (28 days) as compared with the value of G1.

Increasing the compressive strength value as a result of the presence of Pendant groups snap of PMMA on the neighboring groups almost eliminating the slip between the chains of the polymer which results in the PMMA-cement mortar to have higher strength than G1 [14], Carbonyl bond shielding in the composite indicates a strong bond of coordination between the C=O group of the polymer and metal atom/ion in the cement [5]. The decrease in the value of the compressive strength after G23 for early and standard ages may be due to the increase in PMMA concentration in the mortar that leads to dispersion cement particles and hinder the cement hydration process. The Flexural strength test results and the ratio of enhancement for all samples shown in Fig. 2.

From Fig. 2 can be observed the same effect of PMMA, the flexural strength value gradually increased with the increased of PMMA ratio until reaches G23 and then the decreased with increase of PMMA ratio, the maximum value recorded at G23 where increased 16.8%at(7days) and
19.4% at (28 days) as compared with the value of G1.

And also, increasing in flexural strength value as a result of the presence of the Pendent groups snag of PMMA on the neighboring groups almost prevent slip between the chains of the polymer that cause PMMA-cement mortar to have higher strength than G1, may be as a result of strong bond of coordination between C=O group of the polymer and the metal atom/ion of the cement [5], while The decrease in the value of the flexural strength after G23 may be due to the increase in PMMA concentration in the mortar that leads to dispersion cement particles and hinder the cement hydration process. From the results of mechanical tests, the sample G23 have the higher enhancement ratio for the tests of the compressive as well as the flexural strength, so that the scanning electron microscope analysis was carried out to compare the microstructure of standard sample G1 as Shawn in Fig. 3(a,b) with the microstructure of G23 as Shawn in Fig. 2 (a,b). As can be seen in Fig. 1 (a,b) for the standard sample (G1) the microstructure contains the large crystals and can be observed the pores and empty spaces.

As shown in the figure (4-a and b) for the sample G23, the microstructure contains fine crystals and the pores disappeared, due to the PMMA was filled the pores and free spaces in the microstructure of the mortar, the fine crystals maybe were formed due to the addition of PMMA particles to the cement decreased the ratio of water/powder, thereby reducing the time of the setting [6], besides of that, the PMMA maybe reduce the contact area between the cement particles with water by forming a thin film have been an overlap with the microstructure of cement, that lead to preventing the formation of massive crystals.

VII. CONCLUSION

According to experimental results of the compressive and the flexural strength, it is predictable The replacing of part of cement by different ratios of PMMA was enhanced the compressive and flexural strengths in various levels depending upon the ratio of replacement may be due to the formation of strong coordinate bonds between the (C=O) group contained in polymer with the ions of the cement, the

Fig. 3. (a,b) the microstructure of standard sample G1

Fig. 4. (a,b) the microstructure of sample G23
presence of pendant group in PMMA was contributed in the increase the strength of samples containing PMMA, the sample G23(contain 5%PMMA ) was recorded the best results as compared with other samples of group G2 and also have been higher results as compared with standard sample G1, from SEM analysis observed the PMMA filling the pores and form more homogeneous microstructure in G32 as compared with the microstructure of G1.

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