Evaluation of effectiveness of methyl methacrylate as retarder additive in polymer concrete

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HIGHLIGHTS

• Methyl methacrylate performs effective retarder additive for polymer concrete in room ambient of 30 ± 2 °C.
• Retarder additive of methyl methacrylate could improve properties of polymer concrete.
• Retarder additive of methyl methacrylate was not affected curing process of polymer concrete.

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ABSTRACT

It is a known fact that most thermoset resins are very sensitive to hot temperature, which hinders its ability to produce polymer-based products in a large scale. This study aims to investigate the potential of manufacturing polymer concrete in ambient room temperature of 30 ± 2 °C. A laboratory test was conducted with the introduction of polyester retarder additive into polyester resin formulation. All tests were carried out strictly in ambient room temperature (30 ± 2 °C). For comparison purpose, polyester resin without retarder additive was prepared as the control formulation under identical condition. Visual inspection was done on the fresh working life of polyester resin with 0%, 0.1%, 0.15%, and 0.2% of retarder additive in two different types of polyester resin-isophthalic and orthophthalic. Characterization on retarder additive was conducted under X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and, 1H and 13C Nuclear Magnetic Resonance (NMR). Investigation on the effects of polymer retarder additive on the physical and mechanical properties of polymer resin, polymer blended, and polymer concrete showed that the retarder additive had prolonged the working life and improved properties of polymer concrete. These proved the potential of adding retarder additive in polymer concrete in ambient room temperature of 30 ± 2 °C.

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1. Introduction

Thermoset polymer resin such as epoxy, vinyl ester, and unsaturated polyester resin are some typically available commercial resins which are solely used as a binder in polymer concrete (PC) and preferred over thermoplastic polymers due to its higher strength and stiffness [1–3]. However, since epoxy and vinyl ester resins are more expensive than polyester resins, most researches tend to opt for unsaturated polyester resin as a binder [4], even when it is very sensitive toward temperature [4,5]. Due to this reason, PCs are less popular in most Southeast Asia and equatorial countries. High temperatures tend to accelerate the polymerization process [4,6] and jeopardizes the early strength development of PC while causing other related problems such as poor workability, high porosity, honeycomb, and weaker material bonding [7]. This can be solved by casting the PC in a cool room, but this does not make the PCs more cost competitive since the polymer itself is already expensive [8]. Therefore, this paper intends to discuss on a modification done on resin formulation to produce competitive PC with desirable strength.

The main objective of this research, which is to modify polymer binder formulation, is achieved by incorporating retarder additive of methyl methacrylate (MMA) in ambient room temperature.

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Evaluation was initially done on the characterized properties of the retarder additive under X-ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR). Then, the effect of polymer retarder additive on physical properties of fresh working life and hardens of hardened polymer resin was investigated. In this study, binder formulations with and without polymer retarder additive were compared to identify the desired working life of polymer resin at ambient room temperature. The hardness of solidified specimen was observed to verify the curing quality. Further investigation was done on the effect of retarder additive on the physical properties of polymer blended and PC. The test covered the flowability of polymer blended and the physical appearance of PC. Lastly, the potential of PC with retarder additive was investigated in terms of its strength and morphology properties. The findings of this work are expected to provide information to scientists, engineers, fabricators, and manufactures on the production and potential usage of PC.

2. Experimental program

2.1. Materials

2.1.1. Polyester resin and polyester additives

Polyester resins used in PC are commonly unsaturated isophthalic and orthophthalic polyester resins [9]. In this study, polyester additive with 0.5% of promoter of cobalt naphthenate (CoNp) and 1% of cross linker of methyl ethyl ketone peroxide (MEKP) by resin weight were added into the polymer binder formulation. Additionally, methyl methacrylates (MMA) was added as polyester retarder additive into the binder formulation before promoter and cross linker were added. In this study, polymer retarder additive was limited to 0.1%, 0.15%, and 0.2% by resin weight in order to get a sufficient time to cast the PC [10]. In this study, the ‘sufficient time’ must cover the time during casting, pouring, compacting, and finishing of the fresh concrete. Nevertheless, it should preferably cover the time for cleaning the tools before transferring the sample into the oven for heat curing. General properties of these polyester resins and polymer retarder additive of MMA are presented in Tables 1 and 2, respectively. Even though both isophthalic and orthophthalic polyester resins belong to the family of unsaturated polyester, they have slightly different properties in terms of viscosity and tensile properties. Therefore, the viscosity of fresh polyester resin and the tensile properties of hardened polyester resin for both isophthalic and orthophthalic resins were tested (see Table 1). Viscosity test was conducted according to ASTM D2983 [11]. In this test, the viscosity was measured using a digital Brookfield viscometer in controlled temperature of 25 °C; the SI unit is in centipoises (cPs). Meanwhile, tensile test was carried out according to ASTM D3039 [12] using the Instron universal testing machine with a capacity of 50 kN (with loading rate 0.6 mm/min) to determine the tensile properties; the SI unit here is in megapascal (MPa).

2.1.2. Aggregates and filler

Oven-dried crushed coarse aggregates and river fine aggregates were used and the moisture content was kept consistently below 0.1% for both aggregates. The size of aggregate was limited to 10–12 mm only; smaller sizes of coarse aggregates were preferred to give higher compressive strength, as suggested by Rashid and Mansur [13]. The incorporation of filler from mineral origin such as calcium carbonate and silica sand in PC production remains a debated issue due to the regular availability of resources. However, the combination of wastes as green material in concrete production remains a debated issue due to the regular availability of resources. Moreover, POFA has attested efficiency in most concrete production when functioning as fillers. In this study, ground POFA that has passed through 45 μm sieve size was used as filler in PC. Fig. 1 and Table 3 gave the information of particle size and chemical composition of ground POFA, respectively. Particle size distribution of ground POFA was obtained by using particle size analyzer with wetting method where the particles were dispersed using distilled water to avoid agglomerated condition. While, the chemical composition of ground POFA was obtained under X-ray fluorescence (XRF).

2.2. Mix proportion

PC mixes incorporating ground POFA based isophthalic and orthophthalic polyester resin were used. Two mix proportions of PC were properly designed and manufactured as shown in Table 4. The mix proportions were limited to low binder content of about 12% of resin and 12% of fillers. The selection of low binder content is in accordance with previous researchers [14–17]. In this study, the low amount of polymer binder enabled to produce PC with adequate strength at low cost. The coarse aggregates was limited to 30% for all mix proportions and the rest of the combined mix was stirred at low speed to avoid air bubbles from being trapped.

2.3. Specimen preparation

To produce the PC, two mixes – dry and wet, were prepared. The dry mix consisted of dry filler and aggregates, which was initially prepared with the required quantities in slow speed mechanical mixer. The wet mix was separately prepared by continuously stirring the resin which was then added with polymer retarder additive, promoter of CoNp, and cross linker of MEKP. After the wet mix was homogenized, it was poured slowly into the dry mix in the concrete mixer. Then, the combined mix was stirred at low speed to avoid air bubbles from being trapped.

Table 1: Properties of isophthalic and orthophthalic unsaturated polyester resin.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Isophthalic polyester resin</th>
<th>Orthophthalic polyester resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Styrere monomer content (%)</td>
<td>39–44</td>
<td>39–44</td>
</tr>
<tr>
<td>Viscosity (Brookfield, 25 °C, 60 rpm (cPs))</td>
<td>538</td>
<td>426</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>300</td>
<td>270</td>
</tr>
</tbody>
</table>

a Manufacturer data.

b Viscosity and tensile properties were tested in this study.

Fig. 1. Ground POFA size distribution.

Table 2: Properties of methyl methacrylate (MMA).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.94</td>
</tr>
<tr>
<td>Molecular mass (g/mol)</td>
<td>100.12</td>
</tr>
<tr>
<td>Molecular</td>
<td>C₅H₈O₂</td>
</tr>
<tr>
<td>Viscosity, 25 °C, 60 rpm (cPs)</td>
<td>0.60</td>
</tr>
<tr>
<td>Appearance</td>
<td>Transparent liquid</td>
</tr>
</tbody>
</table>
in the fresh concrete. Residue of wet mixes was traced based on the working life during casting. After the mixing process, the fresh PC was then poured into a steel mould which had a thin layer of wax. Then, the casted specimen was vibrated on a high frequency electrical vibrating table for 10 s in three layers. After that, all specimens were post-cured at 70 °C for 4 h. A control specimen was produced with no filler. All PC preparations strictly followed JIS A 1181 [18].

### 2.4. Polymer retarder additive characterization

The retarder additive was characterized using XRD, FTIR techniques, and 1H and 13C NMR (1D). XRD was conducted to confirm the presence of polymer retarder additive-based materials where small amount of powder sample was placed on the diffractometer's holder and automatically scanned in the diffraction angle range of 10°–90° of theta scale. In this study, polymer resin without retarder additive was taken as the control sample.

This was followed by the FTIR characterization to analyze the functional groups in the retarder additive. The FTIR spectrophotometer was used to record the infrared (IR) spectrum in the range of 400–4000 cm⁻¹. Small amount of retarder additive liquid was applied on FTIR glass plate and an average result was obtained after 128 scans.

Lastly, NMR was done to visually check the structure of retarder additive at each stage of a multi-stage synthesis. The Nuclear Magnetic Resonance, 1H NMR and 13C NMR (1D) spectra were carried out in deuterated chloroform (CDCl₃), which acted as the solvent, on a Bruker Avance Spectrometer at 400 MHz and 100 MHz, respectively using tetramethylsilane (TMS) as an internal standard [19].

### 2.5. Physical test on fresh and hardened polymer resin

#### 2.5.1. Working life of fresh polymer binder

Working life is the time for polymer binder to reach a viscosity where it becomes unworkable. A simple test of working life was conducted in accordance to JIS A 1181 [18]. The test methods are designed specifically for PC from the fresh binder preparation stage until mechanical testing on solidified PC. In order to have sufficient time to produce PC at ambient room temperature of 30 ± 2 °C, the polymer retarder additive was added as designated into the binder formulation followed by 0.5% of CoNiP. The resin and the additive were stirred using stopper until the color became homogenously apparent. Then, immediately after the addition of 1% of MEKP, the resin was observed for apparent changes. The stirring process continued until the resin threads appeared to stick at the mixer container. The stopper was stopped at this point.

#### 2.5.2. Hardness of hardened polymer resin

Similar wet mixes were prepared separately and fresh polymer binder with and without polymer retarder additive were prepared. The wet mix was poured into a smooth and flat mould with a dimension of 200 × 25 × 6 mm. The specimens were left in the fresh stage at ambient room temperature of 30 ± 2 °C until it had completely cured. The solidified specimens were tested for hardness using barcol hardness tools as shown in Fig. 2. In this test, the needle of an impressor was attached vertically and pressed onto the specimen. The peak gauge reading was due to sudden impact on the specimen. Immediately following this, the reading was recorded in barcol value. The test was conducted strictly according to ASTM D2583 [20] and this step was termed the “curing verification”.

#### 2.6. Physical test on fresh polymer blended and hardened polymer concrete

##### 2.6.1. Flowability of fresh polymer blended

The blended polymer (combination of resin and filler only) underwent a flowability test that strictly followed JIS R 5201 [21] to the filing ability of blended polymer into inert materials (between fine and coarse aggregates). The flowability test was conducted because the PC had zero slumps. The blended polymer was poured into V-funnel slump cone (with diameter of 70 mm and 100 mm and height of 50 mm) and the cone was immediately uplifted once the blended polymer had fully filled it. The flow spread diameter was measured after the flow spread had ceased. Similar findings on workability was reported by Saffuddin et al. [22].

##### 2.6.2. Physical appearance of hardened polymer concrete

PC with and without polymer retarder additive was casted strictly followed the aforementioned testing procedure. The surface of concrete was cleaned with acetone to remove the substances. Then, the physical appearance of hardened PC was captured using camera.

### 3. Results and discussions

#### 3.1. Characterization of polymer retarder additive

##### 3.1.1. X-ray diffraction (XRD)

Fig. 3 shows XRD result to investigate the presence of retarder additive in polymer resin. From the result, polyester resin with retarder additive has identical amorphous pattern with and without polymer retarder additive. The results demonstrated that the retarder additive used in this study was a non-crystalline material and strongly found based on monomeric and polymeric compound. Further characterization was conducted using FTIR and NMR spectroscopy test.

##### 3.1.2. Fourier transforms infrared spectroscopy (FTIR)

For IR analysis, small amount of retarder additive liquid was placed uniformly between two solid sodium chloride discs. A broad band was observed at 3100–3600 cm⁻¹ region, which suggested that the sample analyzed contained water residues. The IR spectrum of the retarder additive in Fig. 4 showed the characteristic of ester carbonyl stretching at 1724.69 cm⁻¹. The band for C–O stretching appeared at 1164.52 cm⁻¹, which for C–C in alkene aliphatic. The presence of alkene structure in the retarder additive could be traced to the absorption band at 3100–3600 cm⁻¹.

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<table>
<thead>
<tr>
<th>Polymers</th>
<th>Chemical composition of ground POFA (%)</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>53.5</td>
<td>1.9</td>
<td>1.9</td>
<td>6.5</td>
<td>0.8</td>
<td>8.3</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Table 3: Chemical composition of ground POFA (%)
3106.41 cm$^{-1}$ for $\text{C}=$H alkene. These observations have been summarized in Table 5.

3.1.3. Nuclear Magnetic Resonance (NMR)

Analysis of the $^1$H NMR spectrum of polymer retarder additive (see Fig. 5) showed eight protons with four different peaks. The most shielded peaks with singlet signals resonated at $\delta$ 6.09 and $\delta$ 5.55 represented to terminal methylene of H-3a and H-3b. A singlet signal which integrated three protons and resonated at $\delta$ 3.74 belonged to the methoxyl protons (OCH$_3$) for ester functionality. Another singlet signal resonated at $\delta$ 1.93 represented the three protons of methyl group attached to C-2.

A total of five carbon signals were observed in the $^{13}$C NMR spectrum of retarder additive (see Fig. 6). The spectrum detected carbonyl carbon at $\delta$ 167.88 (C=O); a quaternary carbon at $\delta$ 136.20 (C-2); and a methoxyl carbon at $\delta$ 51.73 (OCH$_3$). The carbon signal at $\delta$ 18.27 corresponded to methyl carbon while methylene carbon (C-3) appeared at $\delta$ 125.36. The presence of a carbonyl, quaternary, methylene, methyl, and methoxyl carbons in $^{13}$C NMR spectrum is in agreement with the structure of polymer retarder additive of methyl methacrylate (MMA). Fig. 7 shows the structure of retarder additive while Table 6 tabulates the chemical shifts.

3.2. Effect of retarder additive on physical properties of fresh and hardened polymer resin

3.2.1. Fresh working life of fresh polymer resin

The fresh working life of fresh polyester resin was visually observed to record the duration taken to become viscous before the curing process was complete. Fig. 8 shows the duration of fresh working life of polyester resins with different retarder additive contents. Results demonstrated that the overall fresh working life of polyester resins had gradually increased when the retarder...
additive content increased. The duration was approximately 40 min for both isophthalic and orthophthalic polymer resins and the increment was approximately 2.6 times more than the polymer resin without retarder additive. The overall working life of isophthalic polyester resin was slightly better than orthophthalic polyester resin when the retarder additive was added because of its better properties (see Table 1). All-in-all, these indicated that the addition of polymer retarder additive is workable to prolong the duration of fresh working life of polyester resin. Similar outcomes have been achieved by Li and Lee [10]. From a chemical perspective, it is a known fact the aliphatic has long molecular interaction. Therefore, the crosslink can be interfered by the aforementioned chemical characteristic and this prolongs the working life of polymer binder when retarder additive is added.

At this point of investigation, the addition of polymer retarder additive especially in ambient temperature has become significant. The pattern indicates that both polyester resins can be employed in ambient room temperature after adding retarder additive into the

<table>
<thead>
<tr>
<th>Wave numbers (cm⁻¹)</th>
<th>Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>3106.41</td>
<td>≡C–H</td>
</tr>
<tr>
<td>1724.69</td>
<td>C=O</td>
</tr>
<tr>
<td>1636.78</td>
<td>C=O</td>
</tr>
<tr>
<td>2955.35</td>
<td>C≡H</td>
</tr>
<tr>
<td>1164.52</td>
<td>C=O</td>
</tr>
</tbody>
</table>

Table 5

Functional groups of polymer retarder additive.

Fig. 5. ¹H NMR spectrum of polymer retarder additive.

Fig. 6. ¹³C NMR spectrum of polymer retarder additive.

Fig. 7. Structure of monomer methyl methacrylate (MMA).
important to prolong the working life of polymer resin in ambient temperature for PC.

3.2.2. Hardness of hardened polymer resin

Curing verification was done to ensure that the retarder additive did not delay the curing process, but only prolonged the time for polymer binder. Fig. 9 shows the hardness value of solidified sample (after curing completed) at different retarder content. The hardness was measured to verify that sufficient curing or crosslinking had occurred [6,21]. The hardness of solidified sample for isophthalic and orthophthalic polyester resins with retarder additive was similar to the polyester resin without retarder additive content. This proved that the retarder additive did not delay the curing process even though the fresh working life of polymer binder had been prolonged, as discussed in Section 3.2.1. However, isophthalic polyester resin seems to increase the hardness value more than orthophthalic polyester resin. This is attributed to its denser molecular structure which has resulted in superior engineering properties to those of orthophthalic resin [23]. But, all-in-all, once the polymers had been crosslinked, sufficient hardness would be achieved.

3.3. Effect of retarder additive on physical properties of polymer blended and polymer concrete

3.3.1. Flowability of polymer blended

In flowability test, the flow spread diameter of blended polymer was determined before the fresh PC was produced to judge the filing ability of polymer blended between inert materials [24]. Fig. 10 shows the flow spread diameter at different retarder additive content. Higher retarder additive content gives larger flow spread diameter, an indication of better filing ability, when compared to blended polymer without retarder additive. From the results, the flow spread diameter improved about 90% and 80% for Iso-GPOFA and Ortho-GPOFA blended polymer respectively when compared to polymer blended without retarder additive. However, Ortho-GPOFA polymer blended had superior filing ability to Iso-GPOFA polymer blended. This outcome may be attributed to the fact that the viscosity of orthophthalic resin was lower than isophthalic resin, as previously presented in Table 1. The outcome proved that the polymer retarder additive can decelerate the curing process even when the PC is not produced at ambient room temperature of 30 ± 2°C.

3.3.2. Physical appearance of polymer concrete

The overall physical appearance of PC at ambient room temperature of 30 ± 2°C was observed visually before the specimen was crushed and the bonding investigation was done; the results are as shown in Fig. 11. The specimen without retarder additive content in Fig. 11a shows the worst appearance, i.e., poor workability, high porosity, and honeycomb. However, the quality of PC improved when polymer retarder additive was added (see Figs. 11b till 11d). The physical characteristics of PC improved very well where visible pores reduced significantly after retarder additive was incorporated. Generally, the polymer retarder additive has shown high potential as an alternative additive in polymer binder to produce PC in ambient room temperature of 30 ± 2°C.

3.4. Effect of retarder additive on strength and morphology properties of polymer concrete

3.4.1. Compressive and flexural strength

The strength of PC was measured under compression and flexural tests to ensure that the retarder additive had not disturbed the strength performance. Figs. 12 and 13 show that increasing retarder additive content has enhanced the compressive and flexural...
strength of both PC types. Perfect formation and quality of PC had been achieved up to 0.2% of retarder additive content. The compressive and flexural strength of both PC enhanced more than 1.3 and 1.5 times, respectively as compared to PC without retarder additive. Even though Ortho-GPOFA of polymer blended had satisfactory filing ability, the PC of Iso-GPOFA was better in terms of compressive strength. This is because isophthalic resin has a denser molecular structure which gives superior engineering properties to those of orthophthalic resin [23]. Thus, the retarder additive content is potentially viable to be used in both PCs at ambient room temperature of 30 ± 2°C.

3.4.2. Morphology

The results are also supported by morphology images which showed that the specimen with retarder additive had superior material bonding in polymer (Fig. 14a) to specimen without retarder additive (see Fig. 14b). Again, this further solidified the claim that polymer retarder additive can be used in PC since the curing process has been decelerated at ambient room temperature to produce good PC.

4. Conclusions

From the results of the experiments on the effect of polymer retarder additive in polymer concrete, the following conclusions can be drawn:
(1) The retarder additive had been characterized as monomer of methyl methacrylate (MMA); MMA has long chemical molecular interaction of alkene aliphatic that prolongs the curing process.

(2) Polymer retarder additive of MMA has prolonged the fresh working life of polymer binder.

(3) Polymer retarder additive up to 0.2% content did not significantly affect the hardness of solidified resin.

(4) Higher retarder additive content increases the flowability of polymer blended.

(5) Higher retarder additive content improves the physical appearance, enhances the bonding materials, and has superior compressive strength of PC.

(6) The retarder additive not only prolongs the working life of polymer concrete, but also improves the overall performance of polymer concrete.

(7) In this study, the effect of incorporating retarder additive into polymer concrete was done only at room temperature of 30 ± 2 °C. Therefore, further intensive research is needed to solve the challenge in producing PC at higher temperature, particularly in tropical climate. This study may also serve as pilot exploratory study for similar future studies.

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