PVME as a Sustainable Alternative to Improve Performance of Dense Mortar at Elevated Temperature

Vikash Kumar Singh and Gaurav Srivastava(✉)

Indian Institute of Technology Gandhinagar, Palaj, Gandhinagar 382355, Gujarat, India
gauravs@iitgn.ac.in

Abstract. The exceptional strength and durability make High strength concrete (HSC) an ideal material for application in shear walls, tall buildings and offshore structures. There have been concerns about using HSC under fire conditions, particularly due to the possibility of explosive spalling. Polypropylene (PP) fibre has shown to mitigate spalling in concrete. Polypropylene is a thermoplastic fiber which is composed of hydrocarbons and is extracted from fossil fuels. The production of PP fibre releases toxic chemicals in the environment and is non-biodegradable, hence sustain in our biosphere for several years and thus contribute towards the ever-increasing air and water pollution. When mixed in concrete, PP fibres negatively impact the workability and can result in non-homogeneous mixes because the fibres agglomerate during compaction. Polyvinyl methyl ether (PVME) is a water-soluble polymer which can be sustainably synthesized from biomass and its addition to HSC can be a creative approach to prevent spalling in fire-related situations. The present work investigates the influence of PVME on its pore creation ability and mechanism in mortars at elevated temperature. PVME demonstrated pore formation capabilities in mortars at high temperature, which was found to be similar to that of PP fibre modified mortars. The volume of interconnected pores increased as a result of PVME addition, which allows gases and moisture to escape and reduce spalling during the event of a fire. The current work proposes a more sustainable alternative to improve the fire performance of HSC.

Keywords: PVME · High strength concrete · Elevated temperature

1 Introduction

Demand from the construction industry has significantly boosted the pursuit for the creation of high strength concrete structures in recent years. High strength concrete (HSC) has become increasingly popular over Normal strength concrete (NSC), owing to the economic, architectural, and structural advantages that HSC may give over conventional NSC. The higher strength in HSC is typically achieved by using low water-cement (w/c) ratio and finer materials, which leads to lower permeability of HSC compared with NSC. With the increased use of HSC, concern has developed regarding the behavior of such

A. Jędrzejewska et al. (Eds.): SynerCrete 2023, RILEM Bookseries 44, pp. 820–828, 2023.
https://doi.org/10.1007/978-3-031-33187-9_75

concretes under fire exposure. The occurrence of fire induced spalling is one of the major reasons for this concern. The high compactness and low permeability of HSC cause pore pressure development leading to spalling, that can be explosive under some conditions. Spalling reduces the cross-sectional area of structural members, resulting in increased heat penetration to the reinforcements [3, 7].

Addition of different type of polymer fibres into the HSC has shown to reduce the problem of spalling at high temperatures. Polyvinyl alcohol (PVA) fibres increased the permeability of engineered cementitious composites (ECC) at elevated temperatures. The enhanced void formation around these PVA fibres result in spalling free composites [8]. Mixing of polypropylene (PP) fibres to HSC enhanced the voids formation, thereby decreasing the risk of spalling. PP fibres have melting point around 170 °C, which creates connected pores network for the vapors to evacuate [5, 11].

However, polypropylene is a thermoplastic fibre which is composed of hydrocarbons and is extracted from fossil fuels. The manufacturing of PP releases approximately 1.58 kg CO_2/kg of PP [2]. CO_2 is a major greenhouse gas, which has a direct contribution of 9–26% in the greenhouse effect [6]. Being a synthetic fibre, PP fibre is typically non-biodegradable, hence sustain in our biosphere for several years and thus contribute towards the ever-increasing air and water pollution. Another drawback with PP fibres is that they reduce the workability of concrete and can render the concrete mix non-homogeneous. The non-homogeneous mixing of PP fibres in concrete creates highly-connected micro-channels, leading to formation of weak zones which may initiate spalling. Use of a more environment-friendly, water-soluble polymer in the mix can be a sustainable solution to eliminate the problems related to workability and non-homogeneity during the mixing.

Polyvinyl methyl ether (PVME) is a water-soluble polymer, which can be used as an alternative to PP fibres to eliminate the problem of spalling in HSC [10]. Vinyl methyl ether (VME) can be sustainably synthesized from biomass derived ethylene glycol dimethyl ether via the methanol elimination reaction [4]. As PVME is a water-soluble polymer, it has the potential to eliminate the issues related to workability and homogeneity during the mixing process.

PVME is a negative thermosensitive polymer and is characterized by lower critical solution temperature (LCST). Lower critical temperature is the temperature below which PVME is still soluble in water. Once the temperature reaches beyond LCST, polymer chains undergo inter-chain contraction and entanglement and form dense aggregates whose volume decreases as the temperature increases [12]. This volume change in PVME above LCST can aid to the formation of additional voids in cement matrix at elevated temperatures, which can help in alleviating the issues of spalling.

The current study proposes the use of water soluble PVME as a sustainable admixture to promote pore creation in cement mortar at high temperature which can lead to alleviation of fire-induced spalling. This is the first instance of PVME being used for the purpose of pore creation in mortar. FTIR (Fourier-transform infrared spectroscopy) analysis was used to characterize the functional groups present in PVME while high temperature behavior of PVME was assessed using TGA (Thermogravimetric Analysis). TGA data also demonstrated the use of PVME as a suitable alternative to PP fibres. Visual confirmations for the mechanism of voids creation were established using SEM

(Scanning electron microscopy) and optical microscopy. Additional pores created at elevated temperatures of 400 °C, 600 °C and 800 °C was quantified using indirect technique of mass loss analysis.

2 Materials and Methods

This section presents the details of different materials such as cement, sand, silica fumes, superplasticizer, PP fibres, and PVME solution. Sample preparation and characterization techniques such as TGA, FTIR, SEM and optical microscopy, are covered, along with protocols for pore volume quantification at high temperatures.

Materials used in this study consisted of Ordinary Portland Cement (OPC) of Grade 53, fine aggregates, silica fume, superplasticizer (Polycarboxylate ether (PCE)), and water. The fine aggregate was local river sand, having a fineness modulus of 3.0 and Zone II grading. PP fibre (Isotactic, cut length = 6.00 mm) was obtained from Sigma Aldrich. PVME was also obtained from Sigma Aldrich (50 wt.% in H_2O). Table 1 shows the physical properties of the materials used.

Table 1. Physical Properties of OPC 53, Silica Fume (SF), Sand, PCE, PP Fibres, PVME

Properties	OPC	Sand	SF	PCE	PP	PVME
Specific gravity	3.15	2.65	2.5	1.108	0.9	1.03
Solids (%)	-	-	-	50	-	50
Standards	ASTM C150	-	ASTM C136	-	-	-

2.1 Sample Preparation

Two types of samples were prepared, a) cylindrical cement paste samples of diameter 15 mm and height 15 mm to obtain the visual confirmation of the role of PVME (5%) in creating voids at elevated temperature, and b) cylindrical cement mortar samples of diameter 25 mm and height 15 mm to quantify the ability of PVME in creating additional pores under high temperature exposure. For this purpose, PVME (1%) and PP fibre (1%) were mixed with mortar samples. Mix design details are given in Table 2. The given mix design is based on target strength of 60 MPa [1].

To quantify the changes in the pore volume, the mortar samples were heated at 400 °C, 600 °C and 800 °C in a muffle furnace of size 250 × 100 × 100 mm. The mortar samples were kept at the target temperature for 30 min followed by natural air cooling for 90 min.

2.2 Quantification of Pore Creation

The pore volume could not be measured directly using methods like Mercury Intrusion Porosimetry (MIP) due to the small size of the mortar samples. The CSH matrix

Table 2. Mix proportion of mortar samples

Designation	Cement	Sand	Water	PVME	PP	SF	PCE
M-C	1	4.85	0.34	-	-	5%	1%
M-PP	1	4.85	0.34	-	1%	5%	1%
M-PVME	1	4.85	0.34	1%	-	5%	1%

may disintegrate under high pressures used for mercury intrusion because of the dense microstructure of high strength mortar mixes, particularly for heated samples. In order to quantify porosity, mass loss analysis was employed. The procedures used to measure the mass loss values of various samples are discussed subsequently.

28 days cured samples were taken out from the curing tank, and saturated surface dry weight (W_1) was measured. The samples were then kept inside hot oven at 110 °C for 48 h, and the oven-dried weight of samples was taken (W_2) Thereafter, the samples were heated for 30 min in a muffle furnace at the target temperature (400 °C, 600 °C, and 800 °C). The heated weight of the samples (W_3) was measured after allowing them to cool for 90 min in an open atmosphere. The conditioning protocol for the control and polymer mixed samples is given in Fig. 1.

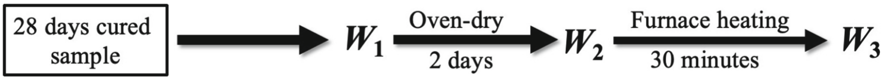

Fig. 1. Conditioning protocol for control and polymer mixed mortar samples

Mass loss (ML) for various samples, due to high temperature exposure can be calculated from Eq. (1),

$$ML(\%) = \frac{W_2 - W_3}{W_2} \times 100 \tag{1}$$

3 Results and Discussion

Qualitative information of PVME, derived from different characterization techniques like FTIR, SEM, Optical microscopy is discussed in this section. Also, the quantification of pore creation using mass loss analysis of mortar mix treated to various elevated temperatures is discussed.

3.1 FTIR

Figure 2 shows the FTIR spectra of pure PVME polymer. Peaks at 2971 and 2927 cm^{-1} indicate the antisymmetric –C-H stretching of –CH_3 and –CH_2, respectively. Peak at 1378 cm^{-1} shows the presence of methoxy (O-CH_3) groups. It represents the symmetric bending of the methoxy compound. All the different FTIR peaks are summarized in Table 3.

Table 3. FTIR spectra of PVME polymer

Wavenumber (cm^{-1})	Descriptions
2971	Antisymmetric C-H stretching of –CH_3
2927	Antisymmetric C-H stretching of –CH_2
2819	Symmetric C-H stretching of –CH_3
1457	Bending vibration of C-CH_2
1378	C-O-C and Symmetric bending of methoxy(O-CH_3)
1187	C-C skeletal vibration
1087	C-O stretching vibration
787	C-H rocking vibration of –CH_3
552	C-O vibration

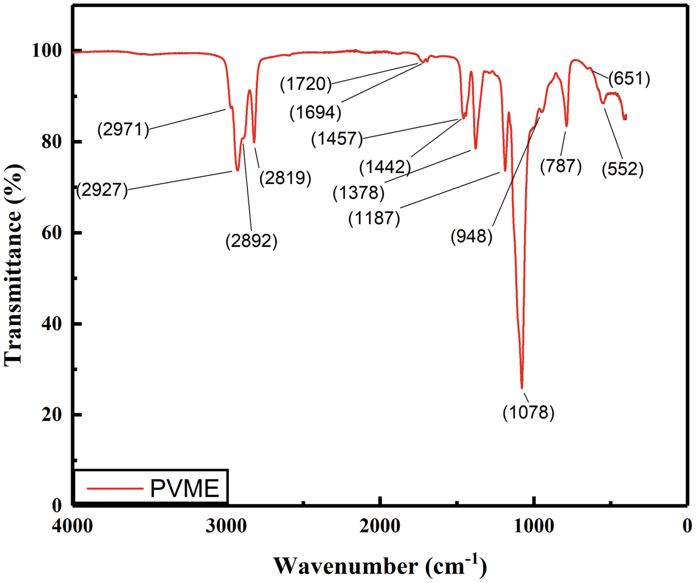

Fig. 2. FTIR spectra of pure PVME polymer

3.2 TGA

Figure 3 shows the TGA plots of PP fibres and PVME polymer. Comparison of TGA plots of the polymers was an essential criterion to select the suitable alternative of PP fibre. PP fibre shows stability till 300 °C. However, PP fibres showed decomposition in the temperature range of 300–475 °C. PVME polymer also showed decomposition in the temperature range of 300–475 °C. Since PVME is a water-soluble polymer, it shows mass loss near 100 °C too. Similar behavior of PVME as compared to PP fibre, corroborates the use of PVME as a suitable replacement of PP fibre.

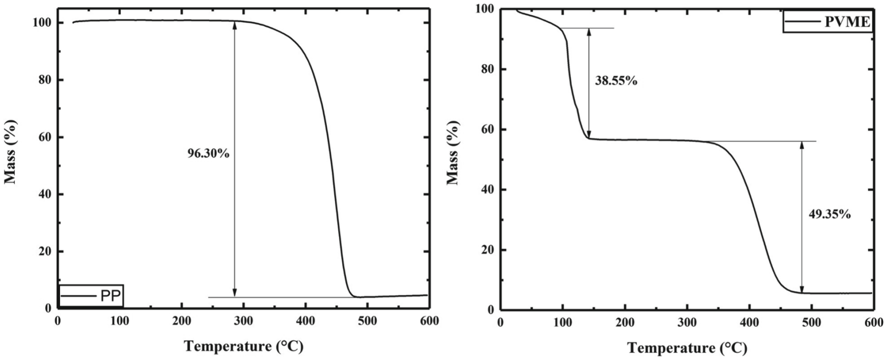

Fig. 3. TGA graphs of a) PP Fibres, b) PVME

3.3 SEM and Optical Microscopy

Figure 4 shows the SEM images of the cement samples mixed with PVME in non-heated and heated conditions. Figure 4(a) shows the interconnected chain type structure of PVME in the non-heated condition of the PVME mixed cement samples. These interconnected structures start to disintegrate when the temperature rises beyond 300 °C(Fig. 4(b)).

TGA plot of PVME also shows mass loss beyond this temperature range (Fig. 3). The decomposition of the interconnected chains create voids, which can result in the easing of the internal pressure created by vapors at high temperature.

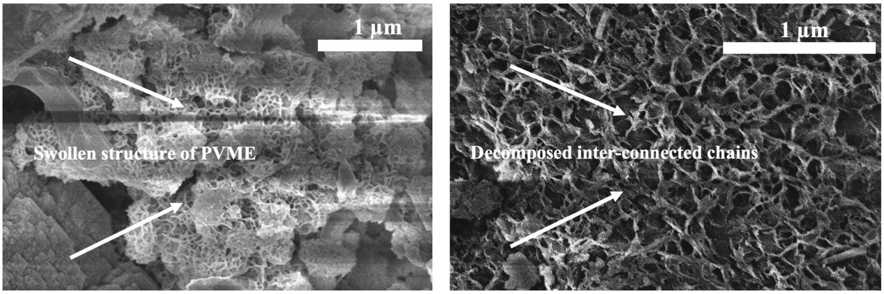

Fig. 4. SEM images of cement mixed with PVME polymer a) Structure of PVME above LCST b) Breaking of inter-connected chains of PVME beyond 300 °C

Figure 5 shows the optical microscopy images of cement samples with PVME in non-heated and heated conditions. It was difficult to recognize PVME in cement samples at temperature below LCST, as the polymer was present in dissolved form. When the temperature was increased beyond LCST, PVME chains agglomerated and became visible (Fig. 5(a)). PVME do not form clusters and is homogeneously spread over the total surface. When the temperature increases beyond 300 °C, the interconnected chains in

PVME polymer starts to disintegrate, which can be observed by Fig. 5(b). This decomposition results in the formation of micro-channels through which water vapor can escape during heating, which can reduce the possibility of spalling.

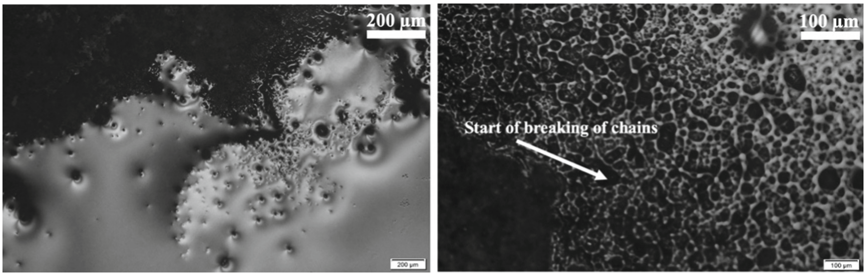

Fig. 5. OM Images of modified samples a) PVME below LCST, b) Disintegration of chains at 300 °C

3.4 Quantification of Pores

Figure 6 shows the mass loss in the control and polymer mixed samples at different elevated temperatures. Mass loss in all the samples was observed to increase with temperature. Up to 400 °C, mass loss corresponds to the decomposition of CSH, calcium sulfate, ettringite, other minor hydrates, and dehydration of various types of water in gel pore, chemically bound water and capillary water [9].

However, the mass loss between 400 °C and 600 °C is mainly due to CH decomposition. Beyond 600 °C, mass loss is primarily due to the decomposition of $CaCO_3$. At 400 °C, PP fibre mixed samples and PVME mixed samples showed additional mass loss of 0.72% and 0.23% compared to the control samples, respectively. Higher mass loss in the polymer modified samples can be correlated with the mass loss shown by the polymers as observed in earlier TGA discussions. At 800 °C, PP fibre mixed and PVME mixed samples showed 1.85% and 1.35% higher mass loss compared to the control samples, respectively.

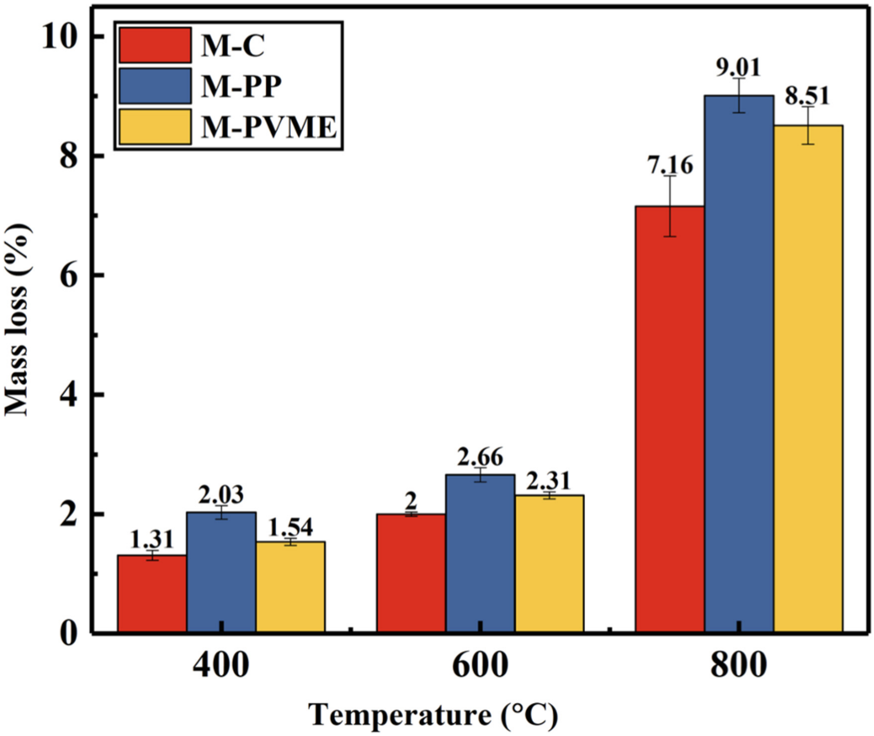

Fig. 6. Effect of temperature on mass loss in Control, PP Fibre mixed and PVME mixed mortar samples

4 Conclusions

This study established the usability of PVME as a sustainable polymer admixture to alleviate the issues related to explosive spalling observed in HSC at elevated temperatures. Detailed material characterization of PVME polymer was carried out to understand the behavior in cement. Subsequently, polymer modified mortar samples were considered to confirm the creation of micro-channels upon heating of samples – a mechanism that alleviates explosive spalling in concrete. Comparisons were also made with PP modified mortar samples as PP is a known polymer used for this purpose.

PVME polymer and PP fibre showed similar decomposition temperature range. Hence, PVME was found to be a suitable alternative of PP fiber for high temperature applications. In order to quantify the pore creation at elevated temperatures, control, PP modified and PVME modified mortar samples were considered. Both PP and PVME caused the creation of approximately equal amount of pore volume in the mortar samples upon heating. These results established PVME to be a sustainable alternative to PP fires for high temperature applications. SEM and optical microscopic images provided a visual confirmation for the creation of interconnected micro-channels in the samples.

The effectiveness of PVME in creating additional voids at elevated temperature establishes PVME as a potential admixture to eliminate the issues of spalling. The advantage of using PVME over PP lies in the fact that PVME is a water-soluble polymer and can also be synthesized through an eco-friendly method.

Acknowledgements. The support of the work by Centre for Safety Engineering is acknowledged. The authors are grateful to Mr. Nikhil O and Mr. Harsh Shah for their contribution to the work.

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