Construction and Building Materials 144 (2017) 598–607

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Properties of hardener-free epoxy-modified mortars utilizing pyrolysis tar replacement

Wan-Ki Kim [a], Deuck-MO Kim [b,*], Hwa-Sung Ryu [b], Won-Jun Park [c], Sung-Min Ham [a]

[a] Department of Architectural Engineering, Hyupsung University, Hwaseong 445-745, South Korea
[b] Hanyang Experiment and Consulting Co., 1271 Sa 3-dong, Ansan 426-791, South Korea
[c] Department of Building System Engineering, Kangwon National University, Samcheok 25913, South Korea

HIGHLIGHTS

- The properties of hardener-free epoxy-modified mortar (HFEMM) with pyrolysis tar (PT) replacement are studied.
- This study evaluated the properties according to the PT substitution in the range 5–20% for 1% epoxy resin.
- The amount of calcium hydroxide in the HFEMM decreased as the PT replacement rate increased in the cement matrix.
- The semi-adiabatic temperature of the HFEMM decreased as the PT replacement rate increased.
- The compressive, flexural, and adhesive strengths of the HFEMM are influenced by the PT replacement rate.

ARTICLE INFO

Article history:
Received 20 October 2016
Received in revised form 3 March 2017
Accepted 15 March 2017

Keywords:
Cement mortar
Epoxy-modified mortar
Polymer
Pyrolysis tar

ABSTRACT

This study focused on the performance of hardener-free epoxy-modified mortar (HFEMM) with pyrolysis tar (PT), a by-product of the green wood industry. HFEMMs were prepared with amounts of 1, 3, and 5% epoxy resin. For the HFEMM with a 1% epoxy resin mixing rate, 5, 10, 15, and 20% of the epoxy resin were replaced with PT. The highest hardening rate was observed for the HFEMM with 1% epoxy resin, whereas the amounts of hardened and unhardened epoxy resin were the largest at 5%. When 1% epoxy resin was replaced with PT, the hardening rate increased to 10%. When 10% PT was substituted with 1% epoxy resin, the compressive, flexural, and adhesive strengths increased because of the higher hardening rate. X-ray diffraction result showed that an increase in the epoxy resin content and the PT replacement rates resulted in lower amounts of calcium hydroxide and lower semi-adiabatic and maximum exothermic temperatures. These results showed that the use of PT in the HFEMM could improve its performance while providing an avenue to recycle PT.

1. Introduction

Reinforced concrete structures are the most commonly used in the construction industry for the purpose of semi-permanent constructions. However, their endurance life decreases with the degradation of reinforced concrete due to various deteriorating factors such as chloride ions, carbon dioxide, and freezing and thawing. In particular, when these deteriorating factors affect the inner reinforcing bar, the steel reinforcement corrodes and expands causing cracks in the structure, thereby dramatically decreasing the endurance life. Therefore, to extend the endurance life of reinforced concrete structures and to use them semi-permanently, a protective layer is necessary, which can prevent the external deteriorating factors from affecting the steel.

Paint, finishing materials, and cement mortar can be used as a protective layer for concrete structures. Among these, lining the structure with cement mortar is the most affordable option, in addition to being very durable and capable of forming a protective layer of uniform thickness. A 2–10 mm thick layer of cement mortar is applied to the faces of the exterior walls or the floor, which prevents harmful salt or acidic solutions from permeating the structural concrete.

Mixing the cement mortar with a polymer can effectively improve the performance of the cement mortar as a protective layer on the concrete structures. The polymer forms thin films inside the cement mortar and is used to constrain cracking caused by the contraction of the cement mortar, to improve waterproofing, and to enhance the tensile and flexural strengths. The

* Corresponding author.
E-mail address: golanhae@naver.com (D.-MO Kim).

http://dx.doi.org/10.1016/j.conbuildmat.2017.03.135
0950-0618/© 2017 Published by Elsevier Ltd.

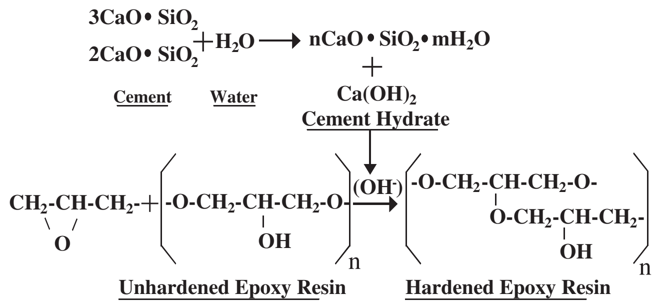

Fig. 1. Hardening mechanism of epoxy resin in cement mortar [4].

polymers used in the polymer cement mortar are typically categorized into water-based polymer dispersions, redispersible polymer powder, water-soluble polymers, and liquid polymers [1]. In 1965, J.H. Donnelly was the first to mix cement mortar with an epoxy resin. The method used a hardener to harden the epoxy resin inside the cement mortar [2].

In 1992, Ohama [3] and others succeeded in developing a hardener-free epoxy-modified mortar (HFEMM) based on the discovery that epoxy resin hardens by the catalytic action of OH^- generated in cement. HFEMM has improved durability without the use of a hardener and enables the production of quality polymer cement mortar at a low cost. The hardenability of epoxy resin inside the HFEMM is shown in Fig. 1. In 1995, Demura and others proposed a formula to calculate the hardening rate of epoxy resin in a polymer-modified mortar (PMM) mixed with epoxy resin [4–8]. The hardening rate of HFEMM can be improved through cement hydration; however, a 28-days epoxy resin specimen exhibited a low hardening rate. Therefore, the initial hardening rate must be increased in order to improve the performance of HFEMM.

Pyrolysis tar (PT), a by-product generated during the production of pyrolysis acid, was previously used as a basic material in the chemical industry. However, with the progress of the petrochemical industry, it is now discharged as waste. The precursor to pyrolysis acid can be obtained by liquefying the smoke emitted during the process of charcoal production. The liquid is then refined by deposition, and the refined material is separated into PT deposited at the bottom and pyrolysis acid. PT constitutes 4–11% of the yield, while pyrolysis acid constitutes 31–37%. The main component of PT is phenol [9]. PT has been used as a germicide and an antiseptic in the past, but now it is mostly burnt or neglected, i.e., not used as a resource. It has been reported that well-performing phenol-based adhesives can be developed from PT by addition of NaOH [10,11]. Phenol, the main component of PT, is also used as a hardener, and it has been proposed that the performance of HFEMM can be improved by using PT.

Therefore, this research aims to use PT to improve both the initial hardening rate and the physical performance of HFEMM. In this study, we determined the compressive, flexural, and adhesive strengths of HFEMMs that were produced by changing the polymer-cement ratio and replacing the epoxy resin with PT. We have also investigated the hardening rate of the resin in the cement matrix. We validated the performance of the HFEMM by analyzing the semi-adiabatic temperature and the XRD characteristics.

2. Experiment

2.1. Materials

Ordinary Portland cement as specified in KS (Korea Standard) L 5201 was used. The physical properties and chemical compositions of the cement are given in Tables 1 and 2. Silica sand was used as fine aggregates. The properties of silica sand are listed in Table 3. Diglycidyl ether of bisphenol A was used as the epoxy resin, and its properties are shown in Table 4. Pyrolysis tar obtained in the wood vinegar production process was used as an auxiliary hardening agent for the epoxy resin.

2.2. Preparation of specimens

According to ASTM C 348 (Standard Test Method for Flexural Strength of Hydraulic-Cement Mortars), epoxy-modified mortars were mixed with a cement-to-fine-aggregates weight ratio of 1:0.5, polymer-cement ratios (P/C) of 0, 1, 3, and 5%, and pyrolysis tar replacements of 0, 5, 10, 15, and 20% relative to the amount of epoxy resin. The mix proportions are given in Table 5. The cubic test specimen for compressive strength measurement was fabricated with dimensions of 50 mm × 50 mm × 50 mm. The beam test specimen for flexural strength measurement was fabricated with dimensions of 40 mm × 40 mm × 160 mm. Their flows were adjusted to be constant at 170 ± 5 mm with a water-cement ratio of 60% [4–8]. Beam specimens were cast in a mold with dimensions of 40 × 40 × 160 mm. A two-step curing process was performed on the samples. First, they were moist cured in 90 ± 5% humidity at a temperature of 20 ± 2 °C for 2 days. Then, they were dry cured at 20 ± 2 °C and 60 ± 5% humidity for 26 days.

2.3. Flexural and compressive strength tests

Flexural and compressive strength tests were conducted by the ASTM C 109(Standard Test Method for Compressive Strength of Hydraulic Cement Mortars) and ASTM C 348(Standard Test Method for Flexural Strength of Hydraulic Cement Mortars). As shown in Fig. 2, the cured specimens were tested for adhesion in tension in accordance with ASTM C 321(Standard Test Method for Bond Strength of Chemical-Resistant Mortars).

2.4. Determination of hardening rate of epoxy resin

Determination of hardening rate of epoxy resin was conducted as follows.

The weight of the target sample was measured, and the cured specimen was crushed and passed through a 1.2-mm sieve to obtain a powder sample. After approximately 5 g of the powder sample was collected, 200 g of propylene glycol monomethyl ether [$CH_3OCH_2CH(OH)CH_3$] (PGME) was added to the flask, and the solution was rotated for approximately 10 min to dissolve the uncured epoxy in the cement. Then, the sample was poured to a vacuum distillation apparatus, and the uncured epoxy was extracted. To remove the remaining uncured epoxy in the cement, the residual uncured epoxy was extracted by spraying methanol. The mixture of extracted uncured epoxy and methanol was dried at 80 °C for 48 h, and the weight was measured. Subsequently, the degree of curing was calculated using the following formula [12].

$$\text{Weight of EP} \quad A = T_1E/M \tag{1}$$

$$\text{Weight of Unhardened EP} \quad B = T_2C/S \tag{2}$$

$$\text{Hardening rate of EP} \quad (\%) = (A - B)/A \times 100 \tag{3}$$

A: Weight of EP + PT in HFEMM (g)
B: Weight of Unhardened EP + PT in HFEMM (g)
T1: Weight of HFEMM after moisture curing (g)
T2: Weight of HFEMM according to dry curing (g)
M: Total weight of cement + silica sand+(EP + PT) (g)
E: Weight of EP + PT in sampling of HFEMM (g)