

Acid Attack on Cement Mortars Modified with Rubber Aggregates and EVA Polymer Binder

Konstantinos Sotiriadis, Michael Tupý, Nikol Žižková, Vít Petráněk

Abstract—The acid attack on cement mortars modified with rubber aggregates and EVA polymer binder was studied. Mortar specimens were prepared using a type CEM I 42.5 Portland cement and siliceous sand, as well as by substituting 25% of sand with shredded used automobile tires, and by adding EVA polymer in two percentages (5% and 10% of cement mass). Some specimens were only air cured, at laboratory conditions, and their compressive strength and water absorption were determined. The rest specimens were stored in acid solutions (HCl, H₂SO₄, HNO₃) after 28 days of initial curing, and stored at laboratory temperature. Compressive strength tests, mass measurements and visual inspection took place for 28 days. Compressive strength and water absorption of the air-cured specimens were significantly decreased when rubber aggregates are used. The addition of EVA polymer further reduced water absorption, while had no important impact on strength. Compressive strength values were affected in a greater extent by hydrochloric acid solution, followed by sulfate and nitric acid solutions. The addition of EVA polymer decreased compressive strength loss for the specimens with rubber aggregates stored in hydrochloric and nitric acid solutions. The specimens without polymer binder showed similar mass loss, which was higher in sulfate acid solution followed by hydrochloric and nitric acid solutions. The use of EVA polymer delayed mass loss, while its content did not affect it significantly.

Keywords—Acid attack, mortar, EVA polymer, rubber aggregates.

I. INTRODUCTION

THE amount of discarded automobile tires is estimated to about 10 billion tires per year, on a worldwide basis. The scrap tires market utilizes around 80% of the used tires. The rest 20% is disposed in landfills, stockpiles or illegal dumping grounds [1], [2]. These disposal methods are of environmental concern due to the difficult degradation of tire rubber, increased risk of accidental fires and public health hazards, as well as due to aesthetic reasons [3]–[5]. The European Union has introduced directives which include significant restrictions on landfill disposal of used tires. Alternatively, their use in materials and energy industries is favored [2].

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Building industry is widely using cement concrete and mortar, due to their versatility, ease to obtain raw materials, low cost, easy fabrication and significant mechanical strength and durability [6]. In some applications, the need to modify their properties, such as tensile strength, hardness and ductility, could allow the use of scrap tires [7]. The reuse of rubber waste as aggregate is a possible disposal solution, which provides a significant market potential for waste recycling [2], [5].

Another category of materials has been developed for certain applications, known as polymer-modified mortar (PMM) and concrete (PMC). These materials are produced by adding polymeric admixtures in mortar or concrete during preparation process. Polymer admixture modifies or improves workability, strength, durability, adhesion, deformability, waterproofness and drying shrinkage [8], [9]. The polymer addition usually ranges between 10-20% of the Portland cement [10].

Mortars containing tires, as rubber aggregates, and polymer binders can be used in various applications and environments. The present study was focused on investigating the durability of such materials when subjected to acid attack. The polymer used in the present study was *poly-ethylene-co-vinyl acetate* (EVA).

EVA co-polymer is a water redispersible powder added to mortar and concrete to improve some of their properties. EVA can be added to anhydrous cement and aggregates before mixing with water, or it can be added as an aqueous latex dispersion. It is considered that EVA particles prolong the induction period and reduce the cement reaction rate in the acceleration period [11].

II. EXPERIMENTAL

A. Materials

Mortars were produced using a type CEM I 42.5 Portland cement (*Českomoravský Cement - Heidelberg Cement Group*); aggregates to cement ratio of 2, and water to cement ratio (W/C) of 0.50-0.55. Both mineral and rubber aggregates were used; siliceous sand (maximum size of 2mm) and shredded used automobile tires (size range of 1-2mm). Vinnapas 7220 E (*WACKER*), which is an EVA polymer powder redispersible in water, was used as a polymer binder in two percentages (dry polymer addition: 5% and 10% of the cement mass). Each mortar composition and its plasticity are presented in Table I.

TABLE I
MORTAR COMPOSITION AND RELEVANT PLASTICITY

Code	CM (g)	SN (g)	RA (g)	PB (g)	W (g)	W/C	PL (cm)
REF	500	1000	-	-	250	0.50	13.0
PAG	500	750	250	-	275	0.55	13.0
PAG-5V	500	750	250	25	275	0.55	17.0
PAG-10V	500	750	250	50	275	0.55	17.5

CM = cement; SN = sand; RA = rubber aggregates; PB = polymer binder; W = water; W/C = water to cement ratio; PL = plasticity

Mortar specimens (prisms: 40mm × 40mm × 160mm) were prepared. The specimens were left in the moulds for 24 hours and then air-cured at laboratory temperature (25±2°C). A certain number of specimens remained in laboratory conditions, subjected only to air-curing (AC). The rest specimens, after 27 days of air-curing, were fully immersed in three different acid solutions (CA: hydrochloric acid solution; SA: sulfate acid solution; NA: nitric acid solution) of the same concentration (10% w/w), and stored at laboratory temperature. The acid solutions were replaced every two weeks.

B. Tests

Compressive strength measurements were performed for all specimens. For those stored at laboratory conditions, the measurements took place at 7, 28 and 60 days after their preparation. For the rest specimens, compressive strength was measured after 14 and 28 days of storing in acid solutions. At the same time, changes of specimens mass were recorded, while visual inspection also took place. Three prisms were used for each measurement of compressive strength and mass. The results presented in this paper are the average of the three values.

Water absorption test was performed using specimens which had remained at laboratory conditions for more than 3 months after their preparation. Before measurement, the specimens were subjected to drying process at 75°C for 6 days. Afterwards, their side surfaces were covered with a waterproof adhesive tape, so as water could be absorbed only from their bottom surface which was immersed in water. The immersion depth was approximately 5mm. In Fig. 1, the schematic diagram of the set-up used to measure water absorption is shown.

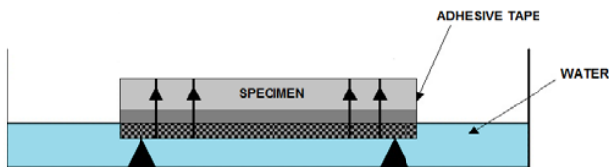


Fig. 1 Schematic diagram of the water absorption test set-up

The water absorption rate (sorptivity (S), mm/min^{0.5}) was determined, which is due to the capillary porosity of the materials tested. For this purpose, (1) was used:

$$i = S \cdot t^{0.5} \quad (1)$$

where i is the total mass increase of each specimen per surface absorption unit (g/mm²); t is the time (min); S is the sorptivity (mm/min^{0.5}).

III. RESULTS AND DISCUSSION

A. Air-Curing

In Fig. 2, the compressive strength of mortar specimens, at 7, 28, and 60 days after their preparation (air-curing), is presented. Between 7 and 28 days an increase of compressive strength values is observed, which is rather slight for the specimens containing rubber aggregates. The measurement at 60 days indicates that hardening process had already been finished. The substitution of sand with tires resulted in significantly lower compressive strength values. The use of EVA polymer binder had not a significant effect on the strength values of the specimens containing tires. The different EVA polymer contents of PAG-5V and PAG-10V specimens had not an impact on their strength values obtained after air-curing.

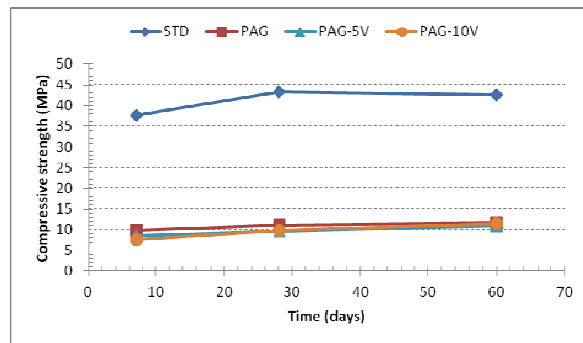


Fig. 2 Compressive strength of mortar specimens at 7, 28 and 60 days after their preparation (air-curing)

Fig. 3 shows the results of the water absorption test. The use of tires, along with sand, as aggregates inhibited water absorption. The sorptivity, determined for PAG, PAG-5V, and PAG-10V specimens, was significantly lower than this of the reference specimens (REF). The use of EVA polymer resulted to lower sorptivity, when tires are used as aggregates. Increasing polymer binder content, a slight decrease of sorptivity was also observed.

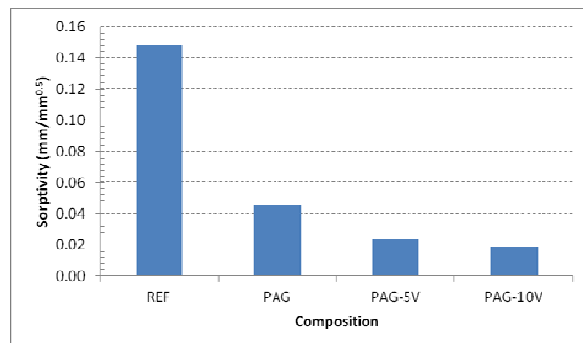


Fig. 3 Sorptivity values of mortar compositions

B. Exposure to Acid Solutions

1. Compressive Strength

The compressive strength values of the mortar specimens, after 14 and 28 days of storing in acid solutions, are presented in Figs. 4 and 5. Table II contains the results of compressive strength loss calculations.

Both Figs. 4 and 5 indicate that the exposure of mortar specimens to acid solutions was highly detrimental. A significant reduction of compressive strength was recorded, which was increased with time. CA solution was the most detrimental for REF specimens, followed by SA and NA solution. In the case of the specimens containing rubber aggregates, acid solutions had similar impact on their strength at 14 days (Fig. 4). However, at 28 days (Fig. 5) CA solution led to lower compressive strength values, compared to those recorded for the specimens stored in SA and NA solutions. REF specimens retained higher strength after both 14 and 28 days exposure to acid solutions, in comparison to the rest specimens. In some cases, the use of EVA polymer resulted in slightly higher strength values than those of PAG specimens, when stored in acid solutions.

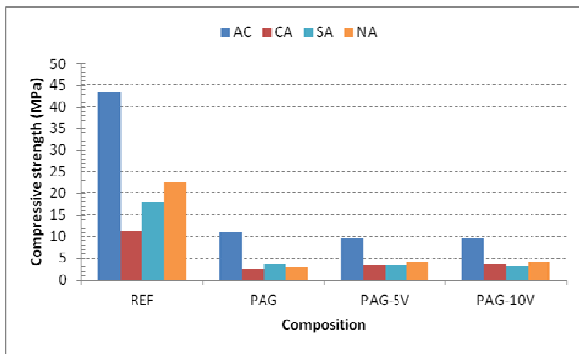


Fig. 4 Compressive strength of mortar specimens after 28 days of air curing (AC) and after 14 days of exposure in CA, SA and NA solutions

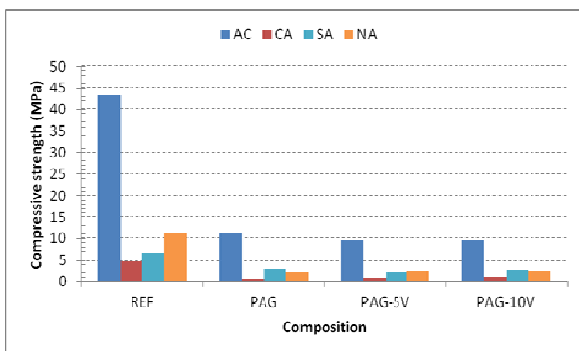


Fig. 5 Compressive strength of mortar specimens after 28 days of air curing (AC) and after 28 days of exposure in CA, SA and NA solutions

Table II shows, that storing in CA solution resulted in higher compressive strength loss of PAG specimens, at both 14 and 28 days, in comparison to the rest specimens. At 14

days, the specimens containing EVA polymer suffered the less strength loss. At 28 days, although REF specimens present the lowest compressive strength loss, the value is not that different of those calculated for PAG-5V and PAG-10V specimens. The use of polymer binder seems to inhibit strength loss of mortars with rubber aggregates after 14 days of immersion in CA solution.

TABLE II
COMPRESSIVE STRENGTH LOSS OF THE SPECIMENS STORED IN ACID SOLUTIONS

Code	Compressive strength loss (%)					
	14 days of exposure			28 days of exposure		
	CA	SA	NA	CA	SA	NA
REF	73.9	58.8	48.0	88.6	84.4	74.1
PAG	77.8	67.5	74.4	95.1	72.1	78.5
PAG-5V	63.9	66.5	58.3	91.4	76.2	74.3
PAG-10V	62.6	68.4	57.0	89.4	72.5	74.9

In SA solution, compressive strength loss calculated at 14 days was the lowest for REF specimens. On the contrary, at 28 days these specimens showed the highest strength loss. Strength loss for the specimens containing rubber aggregates was similar at both 14 and 28 days. Polymer binder had not a significant impact on strength loss of mortars containing tires.

PAG specimens stored in NA solution showed the highest compressive strength loss at both 14 and 28 days, as in the case of CA solution. The use of EVA polymer mitigated strength loss of mortar specimens containing rubber aggregates. Their effect was clearer at 14 days. REF specimens showed the lowest strength loss at 14 days. However, at 28 days the loss calculated for REF specimens was similar to that of PAG-5V and PAG-10V specimens.

The use of EVA polymer delayed compressive strength loss of the specimens stored in CA and NA solutions, which contain tires as partial substitution of sand.

2. Mass

In Figs. 6 and 7, mass change of the mortar specimens of each composition is expressed as an m/m_o ratio; m is the mass after 14 or 28 days (Figs. 6 and 7, respectively) of exposure to each acid solution, and m_o is the mass after 28 days of initial curing, before the immersion in acid solutions.

Mass loss was observed for the reference specimens (REF) and the specimens in which a part of sand had been replaced by rubber aggregates (PAG), after both 14 and 28 days of exposure to acid solutions. REF and PAG specimens show quite similar mass loss, especially at 28 days. SA solution resulted in more intensive mass loss for these specimens, compared to that observed for the specimens stored in CA and NA solutions. PAG-5V and PAG-10V presented both mass gain and mass loss. At 14 days, PAG-5V specimens suffered mass loss in SA and CA solutions, being more intensive for the specimens stored in the first one. On the contrary, mass gain was observed for PAG-5V specimens stored in NA solution. In the case of PAG-10V specimens, mass gain was recorded in SA and NA solutions, while mass loss was observed in CA solution. At 28 days, the PAG-5V specimens

stored in all acid solutions showed similar mass loss. The same result was observed in the case of PAG-10V specimens after 28 days of storing in CA and NA solutions. It was observed that PAG-10V specimens exposed to SA solution had a mass increase at 28 days. The mass loss values of PAG-5V and PAG-10V specimens are rather similar when stored in CA and NA solutions at both 14 and 28 days. It seems that polymer binder content does not affect mass loss at a high extent, when these specimens are stored in these solutions. The specimens containing polymer binder (PAG-5V and PAG-10V) show less mass loss compared to REF and PAG specimens, after 14 days of storing in all acid solutions. At 28 days, mass loss, except of the specimens in SA solution, is rather similar with those calculated for REF and PAG specimens. It seems that polymer binder delays mass loss.

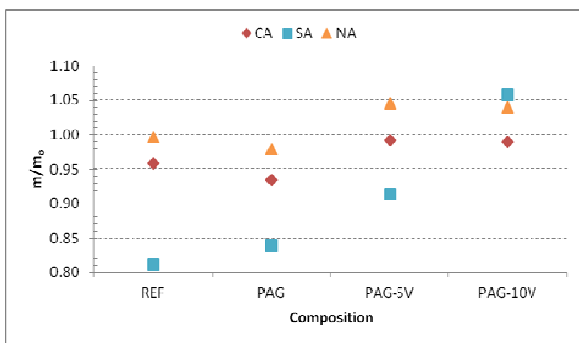


Fig. 6 m/m_0 ratio of mortar specimens after 14 days of exposure in acid solutions (m : mass after 14 days of exposure; m_0 : mass after 28 days of initial curing)

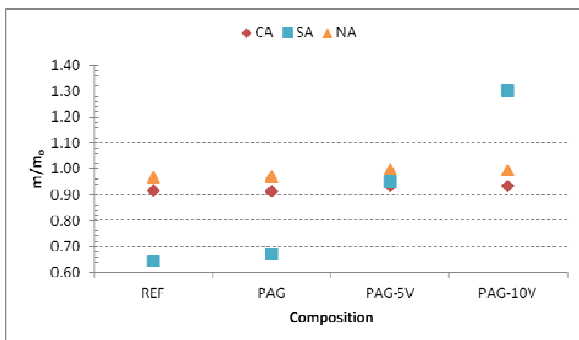


Fig. 7 m/m_0 ratio of mortar specimens after 28 days of exposure in acid solutions (m : mass after 28 days of exposure; m_0 : mass after 28 days of initial curing)

3. Visual Inspection

The specimens exposed to each acid solution had similar deterioration characteristics, independently of their mortar composition. In all cases, a soft layer was formed around a core, which consists essentially of hydrated silicates. This is due to the transportation of calcium and aluminum toward the mortar surface as acid attack keeps on [12]. The deterioration characteristics observed were dependent on the type of the acid used. In the case of the specimens stored in CA and NA solutions, the layer formed was relatively stable. Its color was

slightly different in comparison to the color of the mortar that suffered no acid attack. The layer of the specimens exposed to SA solution had a white color and an expanded form. Furthermore, it was unstable and collapsing with time. In Figs. 8-11, photos of PAG-10V specimens are presented.



Fig. 8 PAG-10V specimen before the immersion in acid solution



Fig. 9 PAG-10V specimen after 28 days of storing in CA solution



Fig. 10 PAG-10V specimen after 28 days of storing in SA solution



Fig. 11 PAG-10V specimen after 28 days of storing in NA solution

IV. CONCLUSIONS

The present study led to the following conclusions:

In the case of the air-cured specimens, compressive strength and water absorption were significantly decreased when rubber aggregates substitute part of sand in the mortar mixture. The addition of EVA polymer binder further reduced water absorption, while had no important impact on strength when rubber aggregates are used.

In general, the specimen exposure to CA solution led to lower strength values, followed by the values obtained for those stored in SA and NA solutions. The addition of EVA polymer delayed compressive strength loss for the specimens with rubber aggregates stored in CA and NA solutions.

The specimens without polymer binder (REF and PAG) presented similar mass loss, which is higher in SA solution followed by CA and NA solutions. The use of EVA polymer delayed mass loss, while its content did not affect it significantly.

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