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RESEARCH PAPER

Effect of Composition on the Properties of Cementitious Tile Adhesive Complied with EN 12004

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Abstract: *The polymer modified cementitious tile adhesives are very significant in the construction sector. To considerably improve the bond qualities of the tile adhesive in polymer modified mortars, the proportions of constituent ingredients should be carefully selected. Consequently, to design high performance tile adhesives, interactions between all the components, such as the adhesion mechanisms between the polymer film and the substrate and the effect of various additives should be recognized. The effect of vinyl acetate ethylene (EVA), high alumina cement (HAC), and additives such as calcium formate and polycarboxylate on the adhesion qualities of ceramic tile adhesive was explored in this study. The findings indicated that these ingredients had an impact on the mortars' adhesive properties, and it is necessary to find their optimal amounts to achieve maximum adherence. The results showed that the tensile strength of mortar was increased with increasing the polymer amounts. A microstructural analysis revealed that the polymer was distributed homogenously throughout the mortar. The optimum amount of the used high alumina cement was determined at 3 wt.%. Additionally, increasing the amount of accelerator and super plasticizer increased the tensile strength of ceramic tile adhesive by approximately 20-30%.*

Keywords: *Cementitious tile adhesive, Adhesion properties, Re-dispersible polymer powder, High alumina cement, Additive.*

1. INTRODUCTION

Ceramic wall and floor tiles offer strong resistance and durability to water, chemical agents, and abrasion, as well as being hygienic and washable. Cement-based mortars are frequently used in both modern and historic construction to adhere ceramic tiles to a variety of surfaces. The properties of cementitious tile adhesives (CTA) can be significantly influenced by the type and quantity of components, the method of mixing, implementation and curing conditions [1-2]. Commercially available tile adhesive mortars now comprise a hydraulic binder and inorganic fillers and are typically modified with cellulose ether (CE) and re-dispersible polymer powder (RPP). These additives fulfil various functions during the evolution from fresh to hardened mortar [3]. The main objectives of CE are thickening, air entrainment, and water retention to establish proper workability properties [4-8].

The incorporation of re-dispersible polymer powders (RPP) into the adhesive formulation results in noteworthy characteristics in the cementitious ceramic adhesive as a ready-to-use product. The mortar's tensile strength, shear resistance plasticity, wear resistance, and flexural strength are all improved by redistributable polymers, which also produce a suitable degree of flexibility. These polymers also improve the mortar's water retention capacity and prevent evaporation by generating a film. The polymer film seals the pores and cracks in the hardened grout, preventing water evaporation. In addition, the polymer strengthens the mortar by forming an extra bond [2, 9-14].

Until now, the effect of polymers has been studied primarily by comparing the mechanical properties (compressive, flexural, and adhesive strengths) of various mortar formulations. In general, these researches confirmed that increasing strength is related to polymer concentration and type. According to Jenni et al. [15] investigation on the impact of polymers on the microstructure revealed that the polymer is uniformly dispersed throughout the cement-polymer matrix. SEM images showed polymer films with a width of 10-100 nm in the mortars that contained cellulose ether. The formation of this film in the matrix increases the adhesive's adhesion strength. The formation and thickness of cellulose ether-

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polymer composite films are influenced by the type of re-dispersible polymer utilized (e.g., SA (styrene acrylic), EVA (ethylene vinyl acetate), and VC (vinyl acetate vinyl ethylene) copolymers) [15]. In another study, it was found that the polymer could retain water in the adhesive composition, decrease the amount of water required to prepare the adhesive paste, and also distribute the water by the polymer throughout the system and prevent the separating of the water from the adhesive paste [16, 17].

In addition to the hydraulic binder, RPP and CE, various additives and ingredients are also used in the cementitious tile adhesive composition to optimize the product formulation and achieve the desired adhesion properties. Different types of cement, retarders, fibers, accelerators, thickening agents, secondary water retention agents, wetting agents, defoamers, superplasticizers, dispersants, surface activating agents, calcium chelating agents, calcium complexing agents, and water repellants are the additives that are used in the composition of tile adhesives. It has been reported that sometimes even 15 different types of components have been used in the formulation of ceramic tile adhesive [18-19].

Today, high alumina cement is also employed as a hydraulic binder in the production of tile adhesives, in addition to Portland cement. High alumina cement (HAC) is a hydraulic cement with calcium aluminates as its major phase. This cement contains more alumina than Portland cement (PC) and is often 4–5 times more expensive. High alumina cement-based mortars are frequently used as very rapid mortars to fix highways, dams, and other structures. It outperforms PC in terms of early strength (compressive strength may be greater than 50 MPa after 24 h), resistance to high temperatures, excellent chemical resistance to sulfates and acids, and resistance to abrasion and mechanical stress [20-24]. Along with Portland cement, high alumina cement speeds up the setting and hardening of the adhesive and increases its shrinkage. This alteration in properties is owing to the presence of high alumina cement, which completely controls the ettringite formation during the cement hydration process. Faster hardening of the adhesive in CTA is crucial since the tile and adhesive may be put under a lot of stress and pressure right after installation [19].

Plasticizers, superplasticizers, dispersants or water-reducing agents are additives that disperse binder's particles and increase the fluidity of the binder (cement or plaster). The superplasticizer increases the fluidity of the mortar and opening time and also has a positive effect on the mechanical strength of the adhesive [25]. Melamine-based agents, lignin-based agents, and poly-carboxylate-based compounds can be mentioned as plasticizer agents [7].

Accelerators increase the rate of cement hydration and reduce setting time, consequently increasing the strength of the adhesive. Calcium formate is an organic accelerator that is widely used in the composition of CTAs [7].

Although CTA is an old technology, only a few research investigated the role of polymers in modified mortars as manifested by their morphology and distribution within the microstructure. Correspondingly, there is a need for more systematic studies on the role of other ingredients in the adhesive properties of tile adhesive.

The goal of this study is to thoroughly explore the effect of polymer content and other additives such as high alumina cement (HAC), calcium formate as an accelerator and Poly carboxylate as a superplasticizer on the mechanical and adhesive properties of CTAs in compliance with the EN12004-1 standard. This standard specifies and determines the criteria for the characteristics of distinct classes of products and classifies cementitious tile adhesives based on their mechanical qualities and technical performance [26].

The microstructure of mortars and phase development in hardened adhesive were explored after measuring the aforementioned parameters. Mortars were synthesized and tested following EN 12004 -2 procedures [27].

2. EXPERIMENTAL PROCEDURES

2.1. Materials and Sample Preparation

To evaluate the impact of various formulation parameters on RPP-modified cementitious adhesive, typical ceramic tile adhesive compositions were proportioned.

Portland cement type I-425 complying with EN-197 standards was used to prepare the mortars which were supplied by Abyek Cement Co. (Iran). Also, high alumina cement is utilized as an additive and supplied by Kerneos Aluminate Technologies

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(China). Table 1 lists the chemical composition and physical characteristics of used cements.

Furthermore, a commercial grade admixture such as vinyl acetate ethylene (EVA) copolymer with a glass transition temperature (Tg) of 15°C, hydroxyl propyl methyl cellulose (HPMC), which is 2% solution viscosity was 15000 mPa.s, polycarboxylate as a superplasticizer, calcium formate to accelerate mortar hardening, polyvinyl alcohol (PVA), used in this study. Additionally, calcium carbonate fine powder with a grain size below 0.1 mm and silica sand with a grain size of 75-300 µm. To achieve comparable findings, the standard test method was followed to prepare the sample because the mixing process can impact the mortar's qualities. According to EN12004-2, the water was first mixed with the powders (binder, sand, and admixtures). After that, the mortar was blended for 30 s at 62 rpm. The mixing was homogenized for a further 60 s at 62 rpm after a 60 s rest period. A five-minute break was followed by the final 15 seconds of mixing. Following EN12004-2, all of the raw materials and machinery were kept at a constant temperature of 23°C.

2.2. Test Methods

2.2.1. *Adhesive strength test*

Standard tensile tests following EN 12004-2 were used to assess the adhesive's strength on a substrate-mortar-tile system. The fresh mortar was applied in two steps on a concrete slab which was produced according to Annex A in EN 12004-2 and repeatedly troweled with a toothed trowel. After five minutes, the fully vitrified ceramic tiles with a water absorption ≤ 0,5 % by mass accordance with ISO 13006 and dimensions 50 x 50 mm were laid down and loaded for 30 seconds with 2 kg. The samples were then aged and stored in various conditions following Table 2. An average of 10 samples was used to determine the tensile strength in each circumstance. The tensile test device (Santam, STM 150) was utilized for the direct pull tensile force test. This device should be capable of applying the load to the pull-head plate at the rate of (250 ± 50) N/s through a suitable fitting that does not exert any bending force.

2.2.2. *SEM evaluation*

The basic sample preparation resulted in a specimen consisting of three layers, as indicated in Figure 1, the concrete substrate, the mortar bed, and the tile. Scanning electron microscopy (SEM, Tescan (MIRA 3 LMU)) was used to examine the morphology of polymer and ether cellulose film in hardened mortar on fracture surfaces over the xy segment in Figure 1. Energy dispersive X-ray spectroscopy (EDX) element mappings along the y-axis were used to assess concentration patterns across the mortar bed.

Table 1. Characteristics of the PC and HAC.

Chemical characteristics (wt.%)		
	Portland cement	**High Alumina cement**
SiO_2	21.52	7.33
Al_2O_3	5.07	48.45
Fe_2O_3	3.87	1.9
CaO	63.66	37.87
MgO	2.12	0.46
SO_3	1.69	0.46
Na_2O	0.36	0.45
L.O.I	2.33	0.3
Physical characteristics		
	Portland cement	**High Alumina cement**
Specific gravity (g/cm^3)	3.1	3.32
Blain specific area (cm^2/g)	4440	3750
Vicat initial setting time(min)	135	30
Vicat final setting time(min)	180	360
Compressive strength (MPa)		
	Portland cement	**High Alumina cement**
3-days	24.4	40
7-days	31.9	50
28-days	43.9	Not detected

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Table 2. The storage condition for adhesion strength of CTA according to EN12004-2.

Adhesion strength	Storage conditions
Initial tensile adhesion strength	28 days in standard conditions (temperature 23±2°C and humidity 50±5%)
Tensile adhesion strength after immersion in water	7 days in standard conditions, then 21 days immersion in water
Tensile adhesion strength after heat aging	14 days in standard conditions, 14 days at 70°C, and then one day in standard conditions
Tensile adhesion strength after freeze/thaw cycles	7 days in standard conditions, 21 days immersion in water then 25 cycles of freezing and thawing cycles: 2 hours at -15°C / 2 hours at 15°C.
Open time	28 days in standard conditions

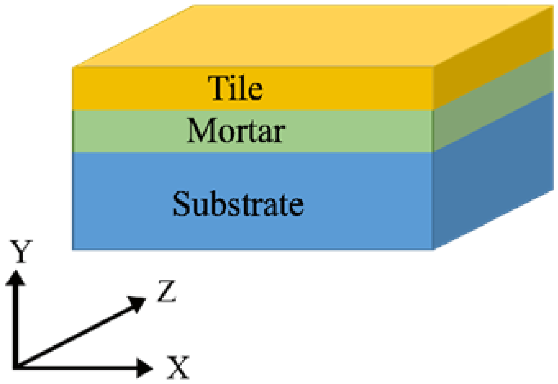

Fig. 1. The schematic of hardened substrate-mortar-tile.

The samples were stored for 28 days at 23°C and 50% relative humidity before the SEM analysis. Table 3 provides a summary of the mortar's composition used for the SEM study.

Moreover, the chemical composition of utilized cements was determined using X-ray fluorescence (XRF, Spectro xepos).

3. RESULTS AND DISCUSSION

3.1. Effect of Polymer Content on the Adhesion Performance

To evaluate the impact of re-dispersible polymer content on the adhesion strength of mortars in various conditions (under EN12004) typical ceramic tile adhesive compositions for the CI and CII classes were proposed. Table 4 lists these compositions. The samples were coded as C1Fx and C2Fx for mix design type CI and CII, respectively, where x is the RPP content of mortar. Several physical and chemical factors contribute to the interface and adhesion properties of ceramic tiles and polymer-modified Portland cement mortars. A variety of parameters influence interfacial strength, including ceramic tile water absorption, composition, softness and amount of cement, type and amount of RPP, installation process, water-to-cement ratio, and the kind and amount of optimizing additives [2].

Table 5 summarizes the results of the initial tensile adhesion strength, tensile adhesion strength after water immersion, tensile adhesion strength after heat ageing, and tensile adhesion strength following freeze-thaw cycles for each type. EN 12004:2007+A1:2012, which is the most recent version of the standard with the requirements for CTAs and listed in the list of European harmonized standards, established two primary classifications, CI and CII.

Table 3. Composition of ceramic tile adhesive used for SEM investigation.

Component	Cement	HPMC	EVA-based RPP	Calcium carbonate	Quartz sand
CTA-5	40	0.5	5	7	47.5

Table 4. The composition of CI and CII ceramic tile adhesives.

Component	Mix design type CI, wt%	Mix design type CII, wt%
Cement type I-425	45	35
Hydroxypropylmethylcellulose (HPMC)	0.2	0.5
EVA-based RPP	1, 2, 3	3, 4, 5, 6
Calcium carbonate	4	7
Polycarboxylate	0.2	0.2
Calcium formate	0	0.5
PVA	0.3	0
Quartz sand	To 100	To 100
water	24	24

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Table 5. Tensile strength of CTA with different RPP content at various standard circumstances.

CTA code	C1F1	C1F2	C1F3	C2F3	C2F4	C2F5	C2F6
Initial tensile adhesion strength (Mpa)	0.69	2.5	3.38	0.85	1.86	2.53	2.56
Tensile adhesion strength after immersion in water (Mpa)	0.64	0.87	1.1	0.26	0.65	1.2	1.22
Tensile adhesion strength after heat aging (Mpa)	0.13	0.5	0.67	0.51	0.79	1.15	1.27
Tensile adhesion strength after freeze/thaw cycles (Mpa)	0.58	0.72	1.13	0.2	0.6	1.08	1.02
Open time (Mpa)	0.39	0.85	1.54	0.83	0.92	1.65	1.41
Complying with standard	-	C1	C1	-	C1	C2	C2

The tensile adhesion strength of the CI class adhesive in different conditions must be at least 0.5 MPa. On the other hand, the standard requirement for characteristics of the CII adhesive is enhanced to 1 MPa [28].

According to the obtained results, the C1F2 and C1F3 comply with CI type whereas C2F5 and C2F6 are in line with CII class, under the EN12004 requirements. Unexpectedly, the tensile strength of sample C2F4 is under CI-type ceramic tile adhesive. The samples C1F1 and C2F3 don't meet the requirements as specified.

Figure 2 (a-d) depicts the obtained data for better comparison. As can be seen in Figure 1, the adhesion properties generally increase with polymer content in mix design type CI and CII.

Sample C1F3 exhibits the highest initial tensile adhesion strength, as well as tensile strength after immersion in water and after the freeze/thaw cycle. However, the C2F6 sample displays the highest tensile strength after heat aging and open time.

The lowest adhesion tensile strength after immersion in water and freeze/thaw cycles is related to sample C2F3. In the other adhesion conditions, sample C1F1 demonstrates the lowest value. The adhesion strength in different conditions is higher in C1F3 in comparison to C2F3. The proportion of re-dispersible polymer and cellulose ether has a crucial impact on the tile adhesive characteristics. The adhesive strength of the mortar improves under various conditions in mix design 1 as a result of increasing the polymer from 1% in the C1F1 composition to 3% in the C1F3 composition. The polymer boosts the mortar's water retention capacity by forming a film. This film closes the pores and cracks of the hardened mortar, preventing water evaporation. In addition, the polymer increases the mechanical strength of the mortar by creating an extra bond.

The water concentration gradient, which is caused by the capillary transfer of water to the concrete substrate, water evaporation in the mortar, and chemical drying because of cement hydration, is one of the crucial factors during adhesive hardening. Early drying can significantly reduce cement hydration.

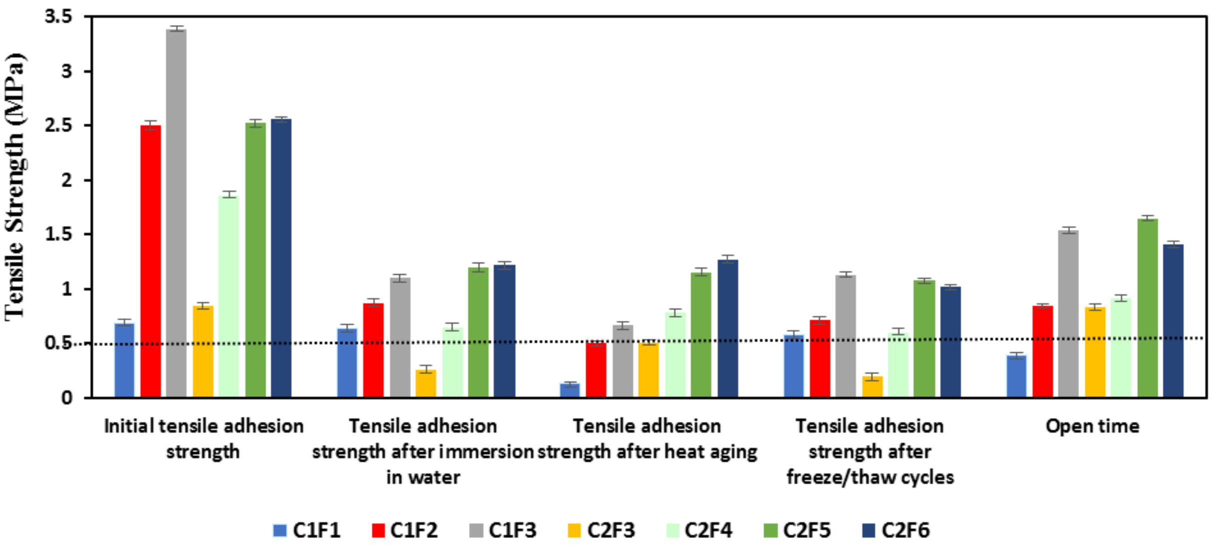

Fig. 2. Tensile adhesion strength in different condition for CTA with various content of RPP. The dashed line shows the requirements of CI type.

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The CE and RPP retain the water and delay the drying of the cementitious system and enhance hydration. The strength of the adhesive is also influenced by the concentration of polymer and cellulose ether at the interface between the tile and the substrate.

Water quickly evaporates from the adhesive's surface in fresh mortar. A thin layer of CE and RPP formed after about 5 minutes, preventing further evaporation. The initial layer is partially dissolved by the water that moves from the center to the surface and then evaporates. This flow of water carries the cellulose ether and polymer to the CTA's surface and gradually increases the concentration of them on the surface until the film is no longer dissolved. On the other hand, the mixing of trapped air in the mortar during tiling is prevented by the formation of the aforementioned film. Remaining the trapped air in the tile-mortar interface decreases the tile-mortar contact surface and consequently CTA's wettability.

Although the development of this layer is necessary to avoid drying the applied mortar surface, controlling its thickness is equally vital. A thin film dissolves quickly, causing surface evaporation, insufficient cement hydration, and hence local separation of the adhesive from the tile. The overly thick film, on the other hand, and the high concentration of RPP and CE in the pore solution limit wetting between the tile and the adhesive as well as the adhesive properties of CTA [5-6, 16].

The thickness of the stated film increases in the C2F3 composition with an increase in the ratio of CE to RPP (raising the amount of cellulose ether in mix design 2 compared to 1). As a result, the wetting of the tile by the adhesive decreases and consequently, the CTA's adhesion properties decline.

The incomplete cement hydration at the tile-adhesive interface, due to the drying has a significant impact on the reduction of tensile strength after heat aging. However, formation of the CE-RPP film and retaining the water, the hydration of the cement paste increases and the mechanical strength of the cement hydrates in the pores is improved. In other words, increasing the proportion of cellulose ether and polymer improves the adhesion strength following heat aging [29].

Although the C1F3 sample exhibits acceptable initial adhesion strength and tensile adhesion after immersion in water and freeze/thaw cycle, a higher polymer amount in the composition is required to achieve the tensile strength of adhesion after heat aging more than 1 MPa under the requirements of class CII ceramic adhesives. The samples C2F5 and C2F6, which contain 5% and 6% of the polymer, respectively, comply with the standard. The sample C2F6 bears the highest amount of re-dispersible polymer and displays the highest tensile adhesion strength after heat aging. Similar results have been obtained by other researchers.

As previously noted, the RPP-CE film is soluble in water. The dissolving of this film decreases the adhesion tensile strength after immersion in water compared to the initial adhesion strength. The migration of the pore solution into the tile's pores during the hydration of cementitious adhesive results in the precipitation of cement hydrates inside the pores and an increase in mechanical strength. This process is stopped when the sample is kept in water, which has an impact on the mechanical locking of cement hydrates in the tile's porous network. As a result, immersion in water decreases the CTA's tensile strength. According to Fig. 1, the tensile adhesion strength after water immersion is lower in all samples than the initial tensile strength.

Furthermore, the freezing of water caused by water diffusion to the tile's pores increased in volume. As the freezing and thawing cycles continue, mechanical tensions rise and become more destructive. Stress can deteriorate the body of the tile and the adhesive, resulting in the loss of tensile adhesion.

The maximum initial adhesion tensile strength is related to sample C1F3 which can be attributed to the presence of PVA in the adhesive's formulation. PVA has reportedly been found to increase the initial strength of cement-based ceramic adhesives [30-31].

3.2. Microstructure Evaluation

To distinguish between the RPP-CE film and cementitious gels, these criteria are applied: 1) comparison of the BSE and SE images based on the difference between polymer atomic number compared to mineral component and 2) the sensitivity of polymers to the electron beam (polymer phases are prone to be damaged under electron beam). Additionally, the sample's map of the C element helped determine the distribution

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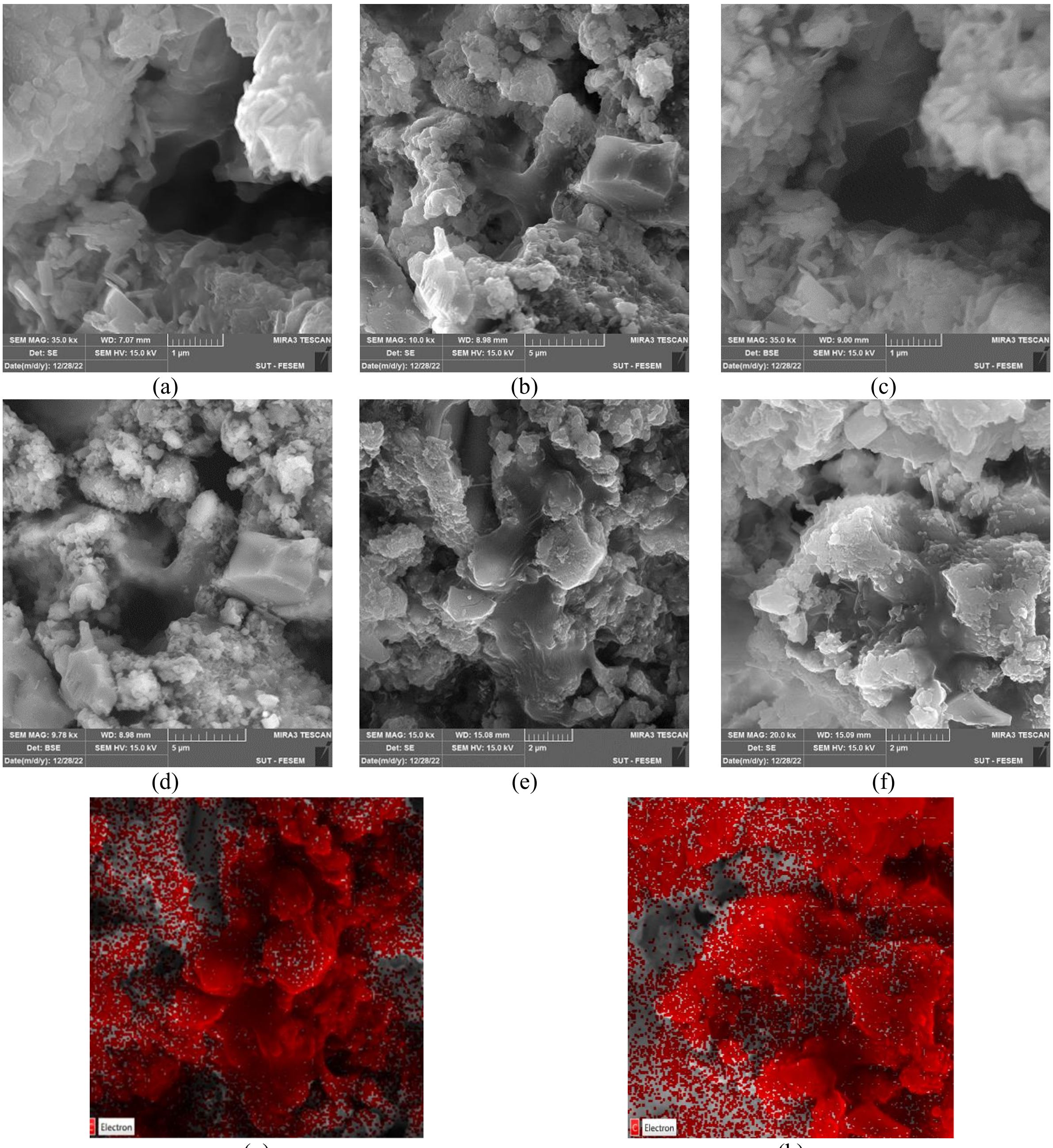
pattern.

Figure 3 depicts the structure of EVA and CE film in the mortar. The composite polymer films were discovered within the cementitious matrix and between two adjacent air voids (Fig. 3a, 3b) and (Fig. 3e, 3f) respectively. On BSE images, polymer microstructures appear dark, in contrast to mineral phases, which have a substantially higher Z value. The distinction between polymer films and cementitious gels can therefore be made with accuracy by comparing BSE and secondary electron (SE) images. (fig. 3c and 3d). The distribution of carbon in the sample is shown in Figures 2g and 2h, where it is more concentrated on films than elsewhere. The film edges are rounded with a smooth surface, as seen in the figures. The composite EVA-CE films are frequently intergrown with the cement phase. It is hypothesized that such films likewise account for the majority of RPP in the matrix.



(a) (b) (c)

(d) (e) (f)

(g) (h)

Fig. 3. SEM images of hardened mortar. (a, b) SE and (c, d) BSE images of the films in air voids, (e, f) SE image of films in cement matrix and (g, h) map of C in the sample.

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As a result, they are thought to be responsible for the observed increase in adhesive strength. The affinity for forming composite RPP-CE films, as well as their shape, is determined by the kind of RPP. To assess the effects of polymer type on the mortar qualities, more research is required.

Fig. 4 depicts the C element-based line scan analysis of the mortar along the y-axis (Fig. 1). Carbon concentration, which shows the distribution of polymer and CE, is uniform between substrate and tile, according to the line scan profile.

3.3. Effect of High Alumina Cement

C1F1 compound with zero, 3, and 5 wt.% of high alumina cement as a substitute for Portland cement was employed to evaluate the influence of high alumina cement on the tensile properties of tile adhesive, as shown in Table 6.

Table 7 and Figure 5 provide an overview of the measured tensile adhesion strength.

In line with Fig. 5 By substituting 3% of Portland cement with high alumina cement, the tensile adhesion strength of adhesive in various conditions is increased. The tensile characteristics of the adhesive, however, again decline as the amount of high alumina cement is increased. With 3% high alumina cement, there is a noticeable rise in tensile strength during heating and aging.

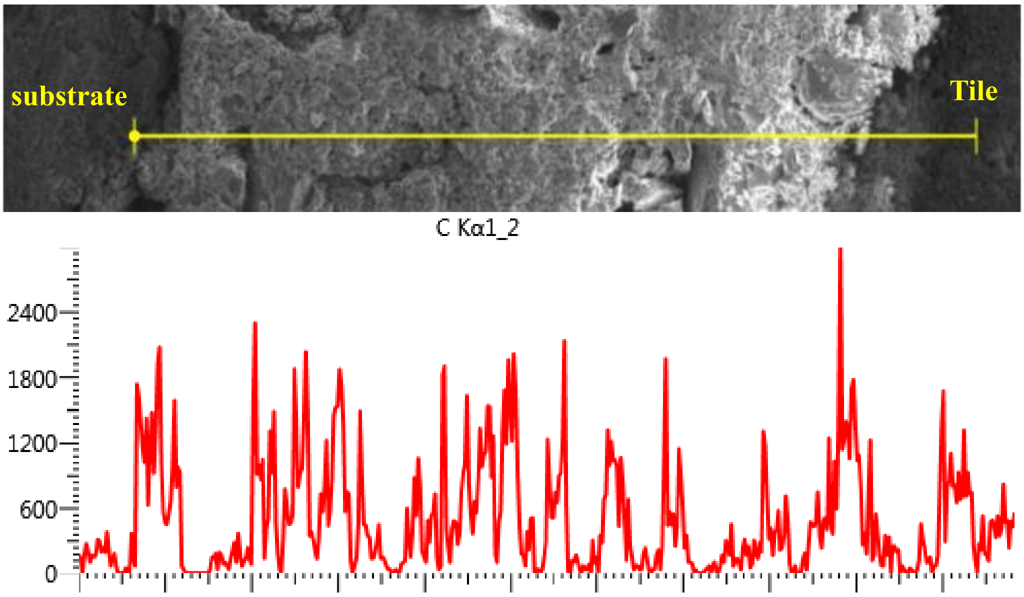

Fig. 4. SEM image and line scan analysis of C element along the mortar.

Table 6. Composition with various high alumina cement content.

Raw materials	**Wt.%**
Cement type I-425	To 100
High alumina cement	0, 3, 5
Hydroxypropylmethylcellulose (HPMC)	0.2
EVA-based RPP	1
Calcium carbonate	4
Polycarboxylate	0.2
PVA	0.3
Quartz sand	49.3
water	24

Table 7. Tensile strength of CTA with different HAC content at various standard circumstances.

HAC content (wt.%)	**0**	**5**
Initial tensile adhesion strength (Mpa)	0.69	0.78
Tensile adhesion strength after immersion in water (Mpa)	0.64	0.61
Tensile adhesion strength after heat aging (Mpa)	0.13	0.15
Tensile adhesion strength after freeze/thaw cycles (Mpa)	0.58	0.58

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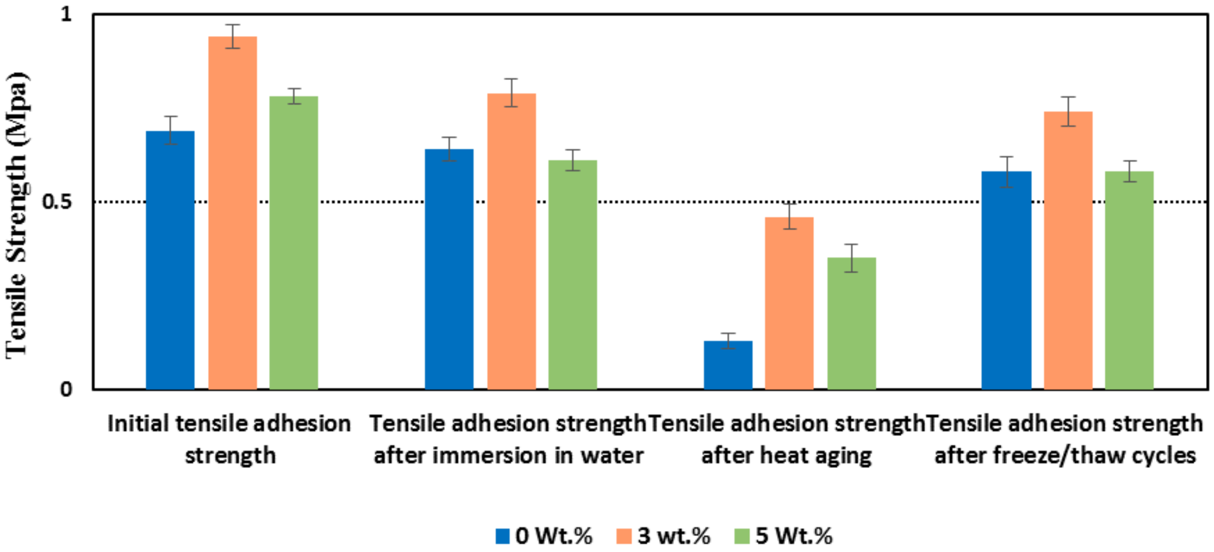

Fig. 5. Tensile adhesion strength in different conditions for CTA with 0, 3 and 5 wt.% high alumina cement. The dashed line shows the requirements of CI type.

Monocalcium aluminate (CA), the primary phase of HAC, exhibits delayed setting but very quick hardening. CA2, C12A7, C4AF, C2S, and C2AS of HAC are further phases. High alumina cement has no C3S. C4AF has no effect on setting time or strength increment, C12A7 sets quickly but has no effect on strengthening the HAC, and C2S and C2AS both contribute to late-age strength.

Following the hydration process, the subsequent hydrates are formed: C2AH8, CAH10, C3AH6, and AH3 [5, 6]. CAH10 is the primary hydration product at temperatures below 23°C, while C2AH8 and AH3 become dominant at temperatures between 23 and 25°C. When the temperature rises over 35°C, the major hydrates C3AH6 and AH3 are formed, accompanied by an increase in porosity and a significant retraction in compressive strengths [20-22, 24, 32-34].

The faster hardening of hydraulic binders with the addition of high alumina cement is attributed to the improvement in the tensile strength of the adhesive under varied conditions. The strength of the adhesive system rises as the binder hardens faster. This increase in strength is substantial in the tensile strength of the sample following heat ageing, which loses the required water for hydration due to 14 days of storage at 70°C.

The phase conversion of this cement and the destruction of ettringite, which results in the porosity in the adhesive structure and a decrease in the tensile strength of the adhesive, are the explanations for the decrease in tensile strength of the adhesive with 5% substitution of HAC. The described favorable effect is eliminated by the phase conversion effect. Under heat aging, phase conversion, the loss of ettringite, and the development of porosity in the system occur more intensely, which accounts for the continued decline in the tensile strength of the adhesive. In addition, drying during heat aging appears to increase the porosity quantity. It is reported, that the porosity distribution changes as a result of the heat of hydration. After heat aging, macropores with a size range of 0.05–10 m predominate over mesopores with a size of 0.05–10 m. This is in line with the findings of our investigation [35].

3.4. Effect of Additives (Accelerator and Superplasticizer)

Portland cement interacts with water; the compounds are first ionized, and subsequently hydration products are created in the solution. Due to the low solubility of hydration products, these substances precipitate out of the solution as crystals. The phenomena of Portland cement paste's hardening, setting, and strengthening are caused by the gradual crystallization of hydration products. As a result, it may be predicted that adding some soluble chemicals to the mixture of Portland cement and water will modify the rate of ionization of cement compounds and the crystallization progression of hydration products which will affect the setting or hardening of the cement paste. According to Table 8, a C1F1 composition containing 0, 0.4, and 0.8 wt.% of calcium formate and 0, 0.1, and 0.2 (wt.%) of

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polycarboxylate was used to study the effects of calcium formate and polycarboxylate as an accelerator and superplasticizer, respectively, on the tensile properties of tile adhesive.

Table 9 and Figure 6 summarize the measured tensile adhesion strength. As can be seen in Fig. 6, in different conditions, the addition of a superplasticizer and accelerator improves the tensile adhesion strength of the adhesive.

As the hydration process initiates, the rate of decomposition of calcium silicates, particularly tri-calcium silicate (C3S), is faster than the rate of diffusion and dispersion of the created ions. As a result, the liquid part becomes supersaturated with hydrated silicates (C-S-H) and a layer of hydrated products, with low permeability, precipitates on the surface of cement silicates which decreases the hydration rate of C3S.

The accelerators raise the amount of calcium in hydrates by incrementing the Ca^{2+} ions in the pore solution, reducing C-S-H formation time, and increasing their precipitation rate.

Table 8. Composition with various calcium formate and polycarboxylate content.

Raw materials	**Wt.%**	**Wt.%**
Cement type I-425	45	45
Hydroxypropylmethylcellulose (HPMC)	0.2	0.2
EVA-based RPP	1	1
Calcium carbonate	4	4
Polycarboxylate	0, 0.1, 0.2	0.2
Calcium formate	0	0, 0.4, 0.8
PVA	0.3	0.3
Quartz sand	To 100	To 100

Table 9. Tensile strength of CTA with different calcium formate and polycarboxylate content at various standard circumstances.

additive	**Calcium formate content (wt.%)**			**Polycarboxylate content (wt.%)**		
	0	0.4	0.8	0	0.1	0.2
Initial tensile adhesion strength (Mpa)	0.69	0.8	0.92	0.52	0.60	0.69
Tensile adhesion strength after immersion in water (Mpa)	0.64	0.74	0.85	0.49	0.53	0.64
Tensile adhesion strength after heat aging (Mpa)	0.13	0.24	0.33	-	-	0.13
Tensile adhesion strength after freeze/thaw cycles (Mpa)	0.58	0.68	0.79	0	0.1	0.2

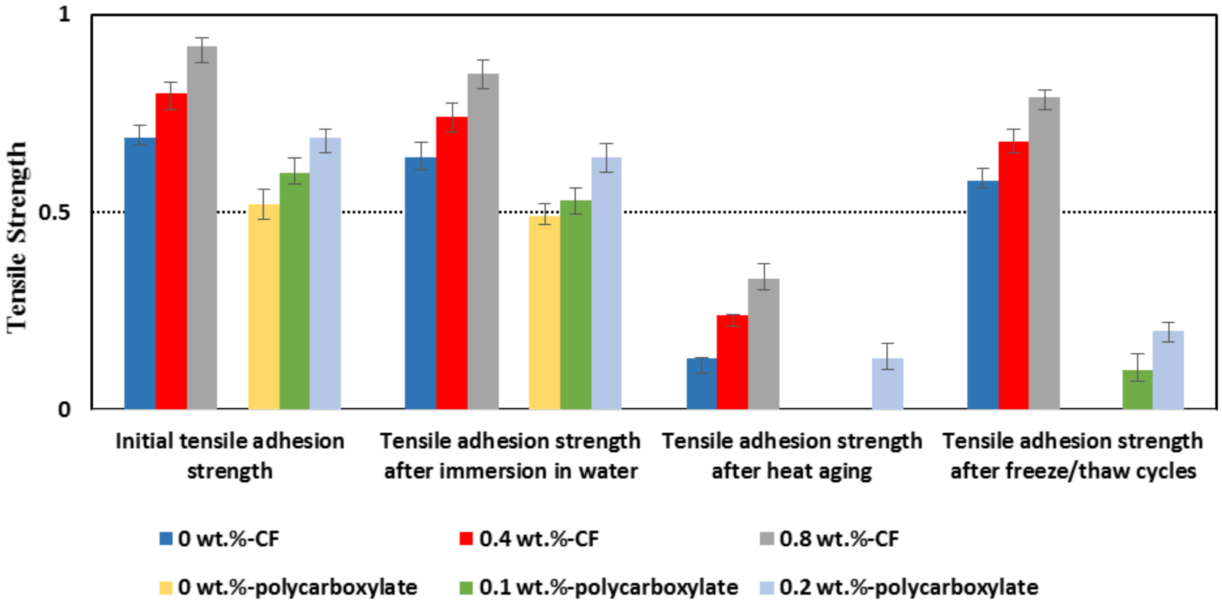

Fig. 6. Tensile adhesion strength in different conditions for CTA with various content of CF and polycarboxylate. The dashed line shows the requirements of CI type.

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On the other hand, raising the proportion of calcium to silica (C/S) in hydrated calcium silicate (C-S-H) increases the permeability of the hydrated layer that has been deposited on the surface of silicates and consequently enhances the hydration of silicates.

Calcium formate (CF) is an accelerator for the hydration of C3S. According to Heikal research, CF improves early and late strength and speeds up C-S-H formation. The $HCOO^-$ ions diffuse significantly faster than Ca^{2+}. Formate ions ($HCOO^-$) can diffuse to the hydrated layers around the C3S and C2S grains. As a result, the precipitation of $Ca(OH)_2$ and the decomposition of calcium silicates is accelerated. Consequently, more C-S-H gel is produced which increases the strength [35]. Raising the cement strength in cement-based tile adhesive will improve the adhesive's adhesion properties. It is more critical to achieving higher strength and complete hydration of the mortar before exposure to high temperature, especially for adhesion following heat aging.

Figure 6 also demonstrates that the adhesive strength rises by 20–30% under various settings as the superplasticizer concentration increases from 0 to 0.3 (wt%).

The plasticizers, superplasticizers, dispersants, or water reduction agents are additives that improve the fluidity and opening time of the mortar as well as the mechanical strength of the adhesive by altering the surface energy.

In other words, superplasticizers such as polycarboxylate, disperse cement grains from one another, expose more surface of grains to water absorption reaction. As a result, for a certain amount of water, the interaction of cement particles is sped up, increasing the amount of C-S-H gel and the mortar’s strength and enhancing the mechanical properties of CTA [26, 37].

4. CONCLUSIONS

According to the EN 12004 standard, the impact of composition on polymer-modified ceramic tile adhesive was examined. The following conclusions seem justified in light of the findings reported here:

- The addition of a re-dispersible polymer in the CTA composition improves the adhesive strength of a tile adhesive mortar. Microstructural studies demonstrate that EVA is dispersed homogeneously in the cement-polymer matrix, which improves the adhesion. At the air-void interface, polymer films are observed. These films are frequently intergrown with cement phases. As a result, they are thought to be responsible for the observed increase in adhesive strength.
- The substitution of high alumina cement for Portland cement resulted in a considerable increase in adhesive strength of up to 3 wt.%. The further addition of HAC causes a loss in adhesive characteristics due to the phase conversion of HAC, as well as an increase in porosity and a significant retraction in the adhesive’s tensile strength.
- In the studied dose range, the addition of a complex modifier additive containing calcium formate as an accelerator and polycarboxylate as a superplasticizer resulted in a considerable improvement in adhesive strength.

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