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Surface interactions of chemically active ceramic tiles with polymer-modified mortars

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ABSTRACT

Adhesion mechanisms and interfacial strengths of poly(vinyl alcohol) (PVA) modified mortar and chemically active tiles with five different silane coupling agents were studied using the Fourier Transform Infrared (FTIR) technique and mechanical testing. The results revealed that small and hydrophilic silane functionalities and isocyanate groups improved interfacial strength between tiles and modified mortar while the silane bearing hydrophobic functional group decreased adhesion resistance. The adhesion mechanism performed by hydrophilic silanes suggested the contribution of covalent chemical bonds between PVA cement modifier and coupling agents at the interface.

1. Introduction

Adhesion between tiles and mortars are of paramount importance to the overall stability of ceramic tile systems. The interfaces between ceramic tiles and polymer modified Portland cement mortar are derived from several physical and chemical phenomena that take place when they are formed. The interfacial resistance is affected by a number of factors, such as ceramic tile water absorption, cement amount and composition, the amount and type of polymer used as cement modifier, installation procedures, water to cement ratio, among other factors [1]. In addition, it should be noted that the ceramic tile/mortar interface is not a static system but an evolutionary process depending on weathering, mortar drying and hydration shrinkage, cement degree of hydration, tile size and location on the construction site [2].

Polymers have been used as property modifiers of cement systems for several years [3,4]. Poly(vinyl alcohol) (PVA or PVOH) is a water soluble polymer commonly used as a cement modifier. PVA polymer is usually added in small amounts (up to 3 wt.% based on cement mass) as aqueous solutions to cement pastes, mortars, and concretes [3,5–8]. PVA polymer is also present in latex polymeric mortars as stabilizers originating from emulsion polymerization and spray drying processes to obtain polymer powders [9,10]. At present, most latexes used in mortar modification are generally commercially manufactured with the presence of up to 5% surfactants, including PVA, for latex stabilizations [11]. In addition, poly(ethylene-co-vinyl acetate), EVA, the standard choice for a polymer in a dry-set mortar, after the hydrolysis of acetate groups in the alkaline media characteristic of cement systems, presents the same hydroxyl pendents groups of PVA. In this sense, PVA selection represents a model to understand the behavior of commercial products for ceramic tile installation [1].

Based on the chemical features of the PVA and cement, mechanical anchoring, hydrogen bonds, and weak van der Waals forces are expected to develop at the tile/PVA-modified mortar interface [1]. The improvement of bonding at the interface between ceramic tiles and modified mortars is crucial for the use of cement mortars when installating ceramic tiles. In recent years, the lack of confidence in the ceramic tiles and mortar industries has increased worldwide, with an overall result of a reduction in the industry's growth and, indirectly, an adverse impact upon all manufactures, merchants, and installers [12–14].

Current concepts of the methods applied to improve interfacial adhesion include molecular chain entanglements, good mechanical contact, the matching of surface tensions, and the formation of chemical and physical bonds through the use of chemical coupling agents [15]. In the case of coupling agents, the organofunctional alkosilanes possess both organic and inorganic properties. These

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hybrid materials may react simultaneously with the polymer (PVA) and mineral components (ceramic tile), forming durable covalent bonds across the interface. It has been also proposed that these bonds are hydrolyzable, but can re-form, and therefore provide a means of stress relaxation at the organic/inorganic interface. The results are improved adhesion and durability [16].

Research of the effect of organosilanes on polymer modified cement systems has been quite rare in prior literature. To date, few studies have been published using silanes in systems based on Portland cement without polymer modification [17–22]. However, some works have been published concerning silicate-poly(vinyl alcohol) hybrids using alkoxysilanes [23,24]. These studies show the occurrence of reactions involving both hydroxyl functional groups from hydrolyzed silanes as well as from PVA forming crosslinking bonds between polymer and inorganic networks.

In the present article, the chemical functionalization of ceramic tile surfaces was performed in an attempt to enhance the interfacial adhesion with a PVA-modified mortar, considering the presence of chemically active areas on substrates covered with five trialkoxysilanes coupling agents. To investigate chemical interactions between organosilanes and PVA that may contribute to interfacial resistance, films derived from PVA and organotrialkoxysilanes were synthesized and characterized through Fourier Transformed Infrared Spectroscopy (FTIR). In addition, tensile strength tests were also conducted to evaluate the effect on interface adhesion properties. To our knowledge, this is the first report involving such system in which five chemical moieties modifying the ceramic tile surface has been extensively investigated.

2. Materials and methods

Glass tile surfaces were prepared with five silane derivatives, each with specific functionalities (R). 3-Amino-propyl-triethoxysilane (R: $-NH_2$), 3-mercapto-propyl-trimethoxysilane (R: $-SH$), vinyl-trimethoxysilane (R: $-CH{=}CH_2$), 3-methacryloxy-propyl-trimethoxysilane (R: $CH_2{=}C(CH_3)COO-$), and 3-isocyanate-propyl-triethoxysilane (R: $-N{=}C{=}O$) were used in this study. The coupling agents were supplied by Sigma–Aldrich. Glass tiles with no chemical modification (as supplied) were used as a reference.

The experimental procedure for the surface treatment of tiles by silane coupling agents was reported in detail in a previous work carried out by our research group [25]. The influence of the chemical structure of the silanes on the interfacial strength between tiles and PVA-modified mortar was evaluated through pull-off assays. Tiles were mounted on a standard concrete substrate using a Portland cement mortar modified with 2% PVA (Polyscience Inc., degree of hydrolysis = 99%) in relation to cement weight [25]. Pull-off tests (replicates, $n = 6$) were performed according to the procedures described in the Brazilian Standard NBR 14084/04 method, allowing the determination of adhesion in tension (also known as bond strength) of the surface modified tiles to the substrate after 24 days of storage. After the adhesion tests, the failed cross-sections of the specimens were observed for failure modes, which may be classified in five types: cohesive failure in ceramic tile, adhesive failure at the interface tile/polymer-modified mortar, cohesive failure in polymer-modified mortar (PMM), adhesive failure at the interface polymer-modified mortar/concrete substrate, and cohesive failure in concrete substrate. Two or more modes can occur simultaneously, resulting in a combined effect.

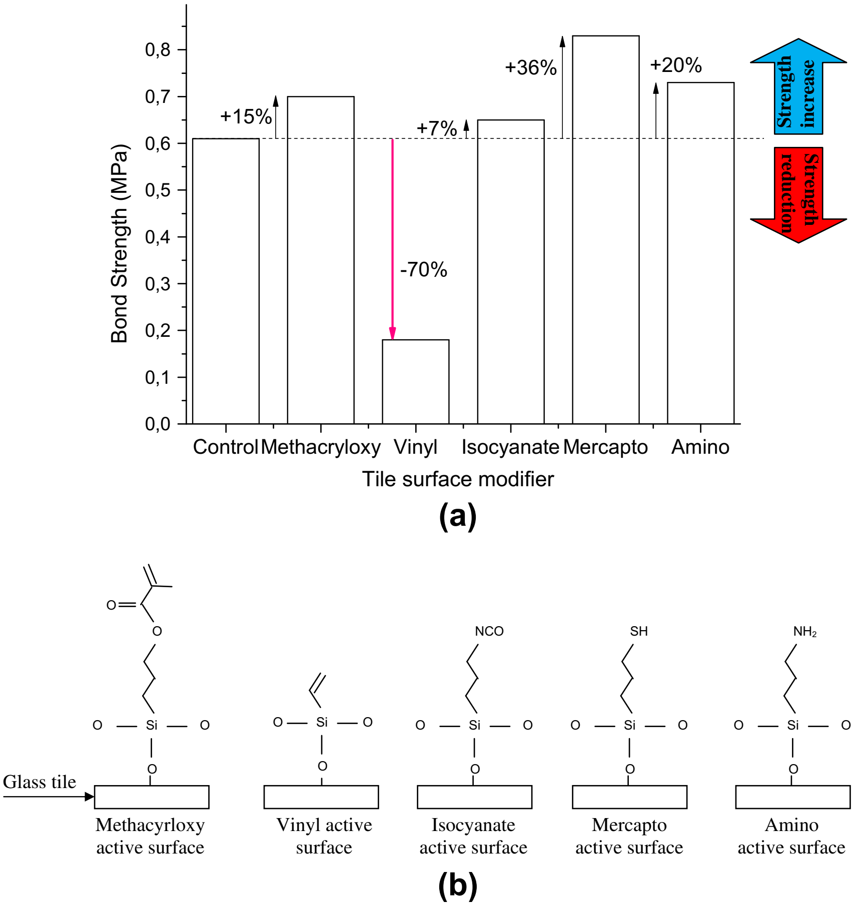


Fig. 1. (a) Effect of surface modification on the bond strength of PVA modified Portland cement mortars in its adhesion to glass tiles, and the variation of bond strength due to surface modification (indicated in the arrows). (b) Schematic representation of active groups on the ceramic glass tile surface.

Films were prepared via aqueous routes. PVA products were supplied as a powder and the solution was prepared by dissolving 5.0 g of polymer powder in 100 ml of deionized water. First, the PVA was dispersed in room temperature water, using sufficient magnetic stirring to wet all particles with water. After 5 min, the temperature was increased to (87 ± 2)°C and magnetic stirring was reduced (avoiding foam) allowing the full dissolution of the PVA. The polymer solution was left to cool down to room temperature. After, under steady stirring, 1.86 ml of the specific organosilane modifier reagent was gently added to 100 ml of previously prepared PVA solution at a temperature of (25 ± 1)°C for a hybrid network formation, resulting in a [SiO_2/PVA] concentration of 10 wt.%. As the pH level is a crucial parameter on coupling silanes to polymers, the films were synthesized from PVA solutions of pH equal to (5.3 ± 0.2) and (12.5 ± 0.2). The first pH was measured after the PVA had been dissolved and the alkaline media was obtained using a $Ca(OH)_2$ suspension to simulate the cement pore solution environment.

FTIR Attenuated Total Reflectance (ATR) mode was used to characterize the presence of specific chemical groups in the PVA/organosilanes films. The spectra were collected with wavenumber ranging from 4000 cm^{-1} to 650 cm^{-1} during 32 scans, with 1 cm^{-1} resolution.

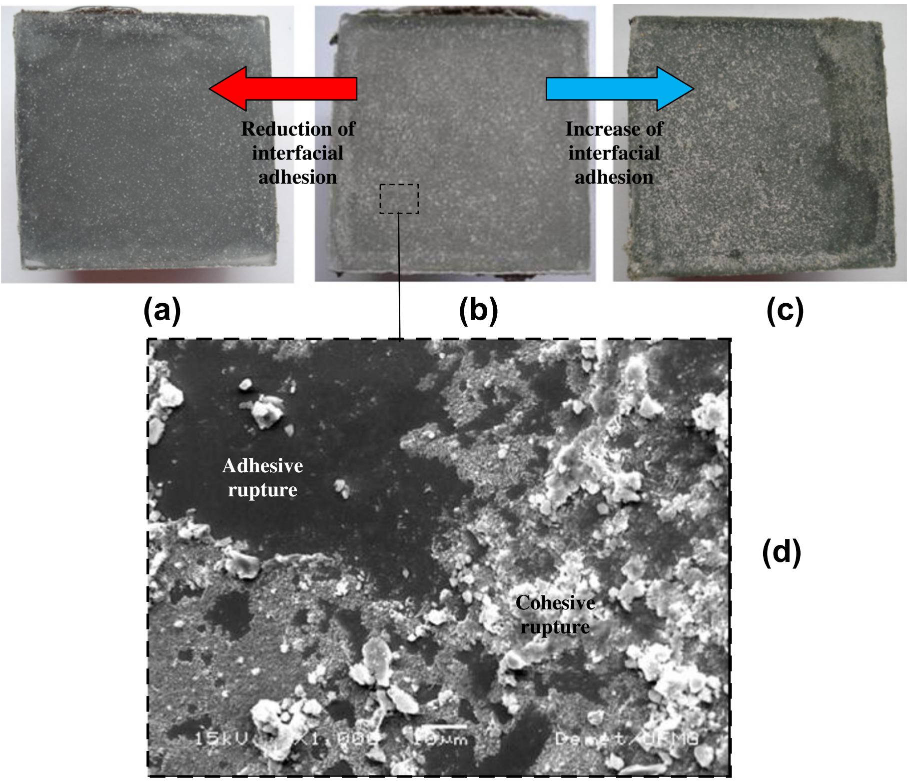
3. Results and discussion

Fig. 1a shows the influence of the surface modification on the bond strength of PVA mortar and the variation of bond strength due to the chemically active tile surface (Fig. 1b). For all tested surface chemical modifiers, except for vinylsilane, an increase in bond strength could be observed. Fig. 2 reveals an increase in the cohesive failure of mortar, simultaneously with the enhancing of bond strength, as a consequence of improvement in interfacial adhesion. A scanning electron microscopy (SEM) image (Fig. 2d), through a microstructural approach, shows the adhesive–cohesive combined mode of rupture. Fig. 3 illustrates the modes of rupture and their relationship with the improvement of adhesion at the tile/mortar interface. It is worthy noting that the increase in adhesion at this interface is decisive in assuring stability and durability of cladding systems. The mathematic modeling of the behavior of a ceramic tile assembly reveals the highest shear stresses at the tile/mortar interface, when considering stresses caused by moisture expansion or thermal movements [26].

From the Portland cement point of view, previous studies [27–29] have reported on the incorporation of organic groups from alkoxysilanes in calcium silicate hydrates in alkaline media at room temperature without disrupting the C—S—H inorganic framework. These results were obtained for very small and hydrophilic organic groups, like amine. For larger-sized or for highly hydrophobic organic functionalities, like vinyl, phase separation has occurred. Based on this fact, for mercaptosilanes and aminosilanes covalent bonds between alkoxy-derived (Si—OH) and calcium silicate hydrates (C—S—H) are, to some extent, likely to occur, in turn increasing the bond strength, while the opposite was found to be true for vinyl groups. Bond strength values presented in Fig. 1 are in agreement with these prior studies.

Figs. 4 and 5 show the FTIR spectrum obtained from PVA-organosilane films in such a way as to understand the interaction between PVA and organosilane ceramic tile modifiers. The FTIR results revealed the major vibration bands (Si—O—Si, ν = 1000–1100 cm^{-1}; Si—OH, ν = 900–950 cm^{-1}) associated with polysiloxane (R—Si—O—) reactions of hydrolysis and condensation [23,24] overlapped with PVA polymer vibrations bands (Table 1) despite the pH of PVA solution.

Moreover, absorption peaks attributed to silicon-alkyl bonds (—Si—CH_x —, ν = 1260–1200 cm^{-1}) and —Si—O—CH (1192 cm^{-1}



Combined mode adhesive-cohesive of mortar failure

Fig. 2. Failed cross-sections after adhesion tests: (a) vinyl modified tile, (b) control tile and (c) amine modified tile, (d) combined mode adhesive–cohesive of mortar failure.

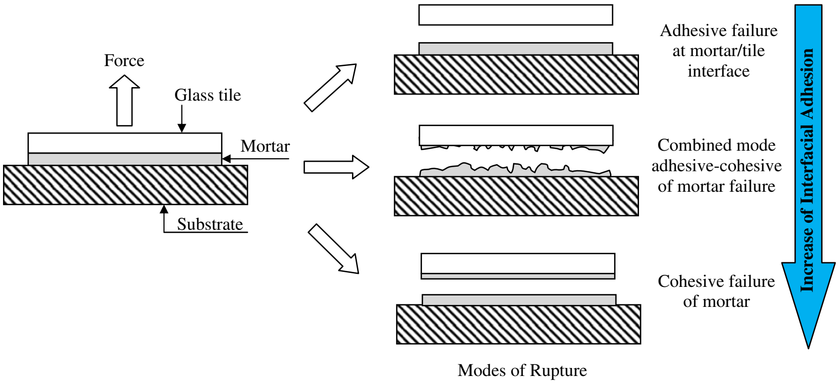


Fig. 3. Modes of rupture.

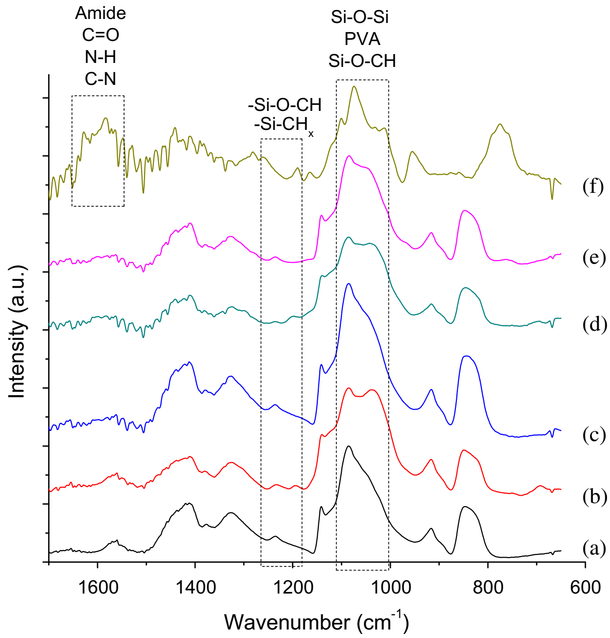


Fig. 4. FTIR spectra of PVA and PVA-derived hybrids modified by organosilanes functionalization at pH = 5.3. (a) PVA; (b) PVA + aminosilane; (c) PVA + mercaptosilane; (d) PVA + methacryloxysilane; (e) PVA + vinylsilane; (f) PVA + isocyanatesilane.

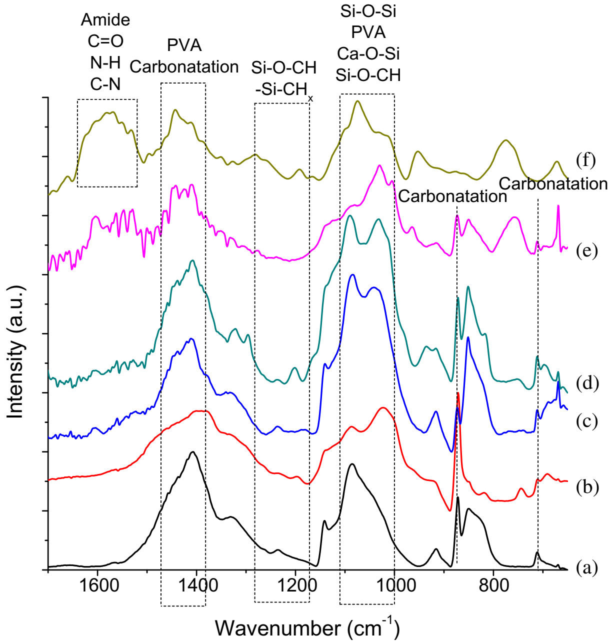


Fig. 5. FTIR spectra of PVA and PVA-derived hybrids modified by organosilanes functionalization at pH = 12.5. (a) PVA; (b) PVA + amine; (c) PVA + mercapto; (d) PVA + methacryloxy; (e) PVA + vinyl; (f) PVA + isocyanate.

and 1092 cm^{-1}) could be observed, indicating hybrid organic–inorganic structure formations [23,30] for silanes with hydrophilic functional groups. For vinylsilane modified samples, these species were not detected by FTIR.

FTIR spectra of the isocyanate coupling agent/PVA (Figs. 4f and 5f) have also shown the presence of the polar urethane groups (—NH—CO—O—) in a carbamate structure (R$_1$—NH—CO—O—R$_2$) supported by the detection of its three major bands: 1800–1600 cm^{-1} from stretching oscillations for C═O group (so-called amide range I); 1600–1500 cm^{-1} from distortion oscillations of N—H and stretching oscillations of C—N (so-called amide range II); and 3500–3200 cm^{-1} from valence oscillations for N—H bonds (not shown) [31]. Some studies have reported covalent and hydrogen bonds between isocyanate groups and polar species, including hydroxyl groups from PVA [32–34]. Based on these results, it is reasonable to state that the urethane links were developed between the isocyanate functional group and the hydroxyl group of PVA sequences, favoring the increase in adherence measured through bond strength tests.

Table 1
Vibration modes and band frequencies in PVA (copolymer poly(vinyl alcohol-co-vinyl acetate) – PVA–PVAc).

Wavenumber (cm^{-1})	Chemical group	Polymer
1461–1417	δ (CH)-CH$_2$	PVA
1376	δ (CH)–R—CH$_3$	PVAc
1330	δ (OH)-C—OH	PVA
1270	ν_{as} (═C—O—C)	PVAc
1145	ν (C—O)	PVA
1096	ν (C—O)-C—OH	PVA
1026	ν_s (═C—O—C)	PVAc
945	(C—C)	PVAc
916	δ (CH)-CH$_2$	PVA e PVAc
849	ν (C—C)	PVA
602	(C═O)	PVAc

For hybrids obtained in an alkaline medium (pH = 12.5), some of the Si—O—Si tetrahedral bonds were replaced by linear Ca—O—Si bonds [11], resulting in the shift of the peak associated with the polymerization of Si—O—Si to a lower wavenumber. Furthermore, carbonates bands (1497–1420 cm^{-1}; 875 cm^{-1}; 713 cm^{-1}) were identified as a consequence of the carbonatation of $Ca(OH)_2$ used to mimic a Portland cement environment [23]. The hybrid organic–inorganic structure characteristic vibration bands were also verified. These results are highlighted in Fig. 6.

Based on the results, it could be seen that the vinyl active tile surface does not contribute to adhesion between tile and PVA mortar. On the contrary, due to its hydrophobic nature it does not interact with C—S—H and PVA, thus promoting phase separation and reducing the bond strength at the interface. Fig. 7 summarizes this behavior.

Fig. 8 presents a schematic representation of the interactions between hydrophilic silane active surfaces and PVA mortar, which can enhance adhesion. In addition, to hydrophilic interactions ($NH_2 \cdots OH$ and $SH \cdots OH$), the development of covalent bonds between alkoxy-derived (Si—OH) from surface modifier and hydroxyl groups from PVA (alcohol units) should be emphasized. Moreover, the same strong bonds are expected to bind Si—OH to calcium silicate hydrates (C—S—H). The observed increase of adhesion for the system is due to the formation of this complex nanostructured layer at the interface.

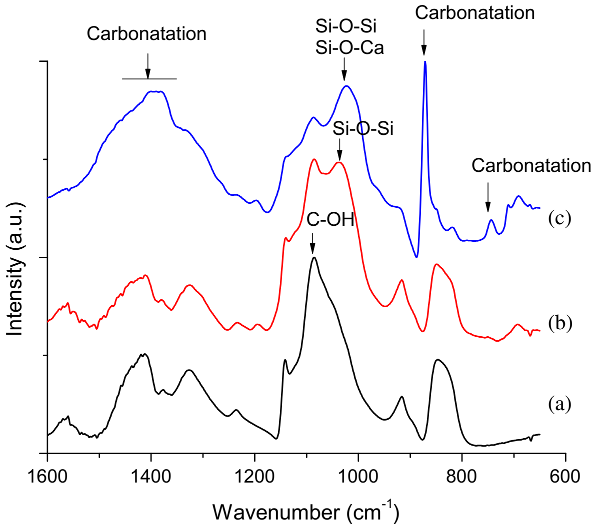


Fig. 6. Spectra from (a) PVA (pH = 5.3) and PVA + amine at pH = 5.3 (b) and 12.5 (c).

In the case of the isocyanate active surface, the enhancement of bond strength at the modified tile/PVA mortar interface is due to the development of urethane linkages (Fig. 9), according to following Eq. (1) [31].

$$\text{Tile—NCO} + \text{PVA—OH} \rightarrow \text{Tile—NH—CO—O—PVA} \qquad (1)$$

For the methacryloxy silane modifier, the causes of bond strength improvement are not directly identified, but it is believed that this results from the overall balance of functional organic groups, unsaturated bonds, spacer, cement system pH levels, among other key factors.

In the present study, to address the complexity of the real systems (ceramic tiles and dry-set mortars), a model system based on glass tile and PVA polymer was used [35]. Nevertheless, these results can be used as supporting evidence to better understanding practical settings, such as porcelain tiles installed with EVA-modified mortar [36].

4. Conclusions

The results have clearly suggested that the use of organosilane coupling agents with hydrophilic functional groups, such as mercaptan (—SH) and amine (—NH_2), as surface modifiers of ceramic tiles have significantly improved the interfacial strength (+36% and +20%, respectively) between tiles and PVA-modified mortar. Such behavior of enhancing the adhesion was attributed to the development of covalent bonds among the PVA chains and chemically modified ceramic tile surface. On the other hand, the unsaturated functional group (vinyl) drastically reduced interfacial adhesion (−70%). In summary, the present work successfully developed and explained a novel procedure of ceramic tile activation in an attempt to increase the bond strength between ceramic tiles and polymer-modified mortar.

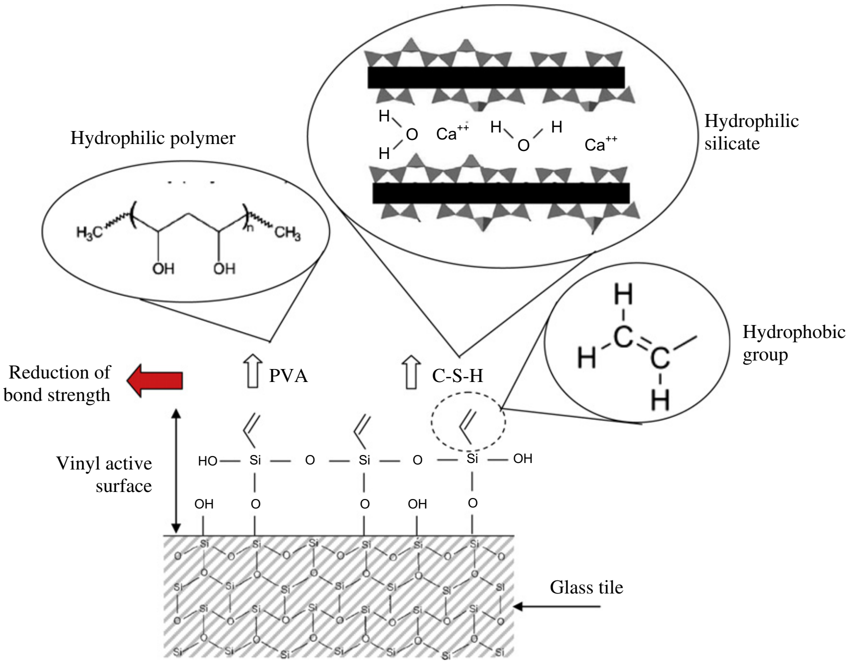


Fig. 7. PVA mortar/vinyl active surface interaction model.

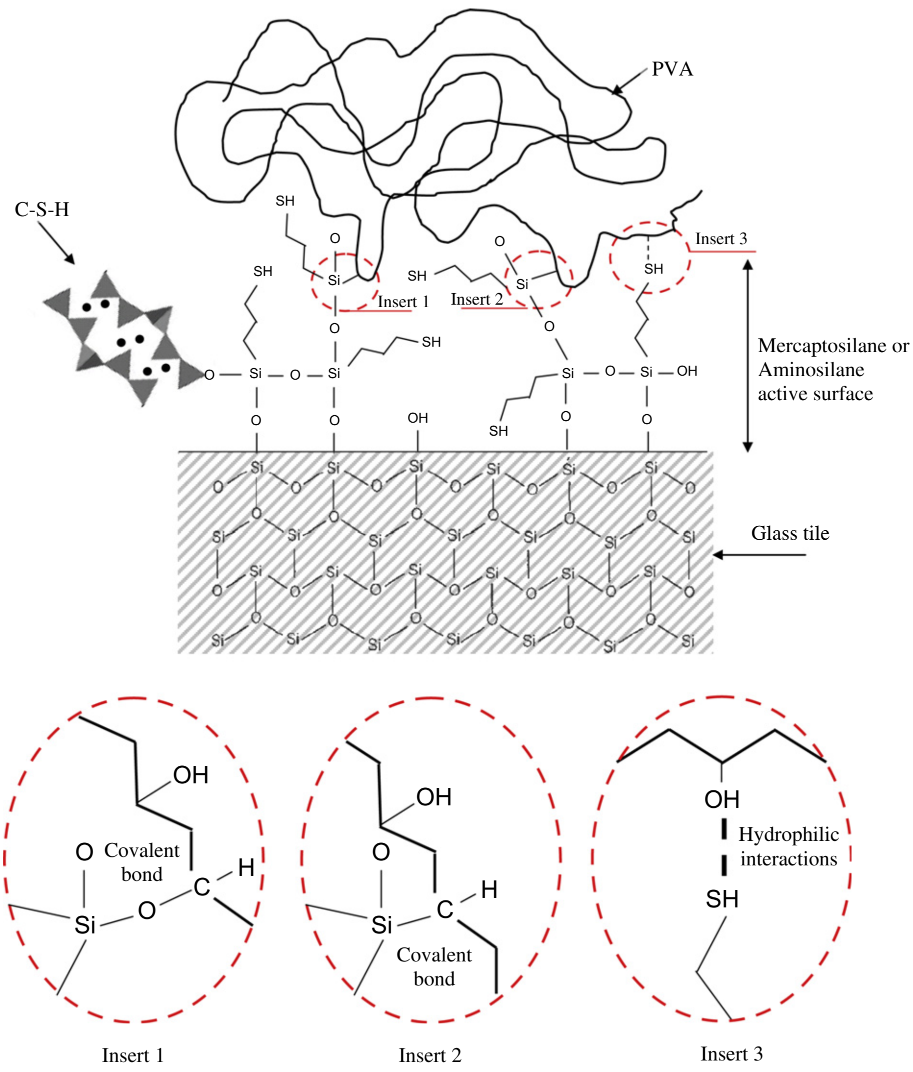


Fig. 8. PVA mortar/hydrophilic active surface interaction model.

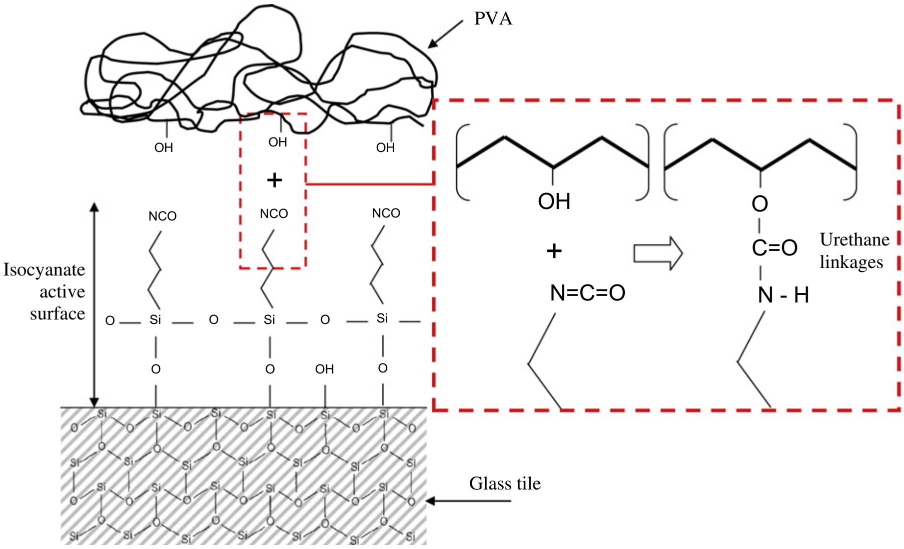


Fig. 9. PVA mortar/isocyanate interaction models.

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