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The influence of silane coupling agents on the polymer mortar

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Abstract

The aim of this work is to investigate the influence of silane coupling agents on the properties of vinylester resin and vinylester mortar. Research work is focused on two methods of modification: direct silane addition to the resin binder and the use of silane pre-treated silica flour as a filler. The results of such modification are described, taking into consideration mixture viscosity, curing conditions, mechanical strength and fracture process. The test results indicated that silane coupling agent can decrease the viscosity of the mortar mixture, extend its pot life, enhance its mechanical strength and resistance for fracture. However, changes in the curing process, which may be disadvantageous and the increase of composite brittleness were noticed and stressed.

Keywords: Resin mortar; Coupling agent; Silane; Viscosity; Curing characteristic; Mechanical properties

1. Introduction

Concrete resin composites have been used in construction for nearly forty years [1,2]. The use of such materials is still growing in many specialised applications. The favourable technical properties such as high mechanical strength, good chemical resistance as well as short time to obtain serviceability are their main advantages. Further development of such materials can be achieved mainly by their modification. Search for the effective modification methods and analysis of the results give an opportunity to adjust the material's characteristic to the requirements of a particular application. The main ways to change the properties of the resin composite are the addition of admixtures to resin and the use of different types of fillers. Final characteristics of such modified composites depend both on properties of the components as well as on the synergy effects between them [3].

Silanes are well known coupling agents which can react with both mineral and organic compounds [4]. They are used as a multi-purpose adhesion promotor. Such applications are also used in polymer mortars [5,6]. Silane addition to the resin binder improved strength of the material and adhesion of the composite to the concrete [7,8].

2. Scope of the experiment

The aim of this work is to investigate the influence of silane coupling agents on the properties of vinylester mortar by comparing the unmodified and modified composites. The modification was done in two ways: by direct addition of silane to the resin binder and by the use the silane pre-treated silica flour as a filler.

Three types of silane coupling agents, which differ in their molecular structure, were used as an admixture to the resin. All these compounds have a trimethoxysilane group ($-Si(OCH_3)_3$), which after hydrolysis react with an aggregate surface forming a siloxan bond (Si–O–Si). Vinyltrimethoxysilane (VTS) presented by formula $CH_2{=}CH{-}Si(OCH_3)_3$ and γ-methylacryloxypropyltrimethoxsysilane (MTS) presented by the formula $CH_2{=}C(CH_3)COO{-}(CH_2)Si(OCH_3)_3$ have additionally double bonds (C=C), which react with the vinylester resin. On the other hand

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3-chloropropylotrimethoxysilan (ClS) $CH_3CH_2CHClSi(OCH_3)_3$ does not react with this type of resin. However, after deposition of ClS on aggregate surface it can improve its wettability. The silica flour pre-treated only with MTS was used in this research program.

In the first part of the experiment the influence of silanes both on the viscosity of the resin and on the viscosity of resin–silica flour mixtures was tested. The time and temperature of curing of the mixtures were measured as well. We dedicated the second part of the experiment to the analysis of mechanical properties and fracture parameters of mortars such as: flexural strength, compressive strength and tensile strength as well as fracture toughness K_{IC}, fracture energy G_f, and characteristic length l_{ch}. For resin and selected micro-mortars a dynamical mechanical thermal analysis (DMTA) was performed and their glass transition temperatures were determined.

3. Test methods

The viscosity of the vinylester resin or resin–silica flour mixtures (1:1 by mass) and the shear rate were measured using Brookfield viscometer (hardness-HA, cone-CP41). To compare the viscosities of the non-modified compositions and compositions modified by silanes (MTS, VTS, ClS) one value of the shear rate was selected from the region where the viscosity almost does not depend on the share rate. It was

37.5 s^{-1} for the resin–silane mixtures,
20 s^{-1} for the resin–silica flour mixtures.

Then the DMTA analysis for the hardened resin and hardened resin–silica flour mixtures was done. 32 × 12 × 2.5 mm prism samples were tested under bending, with frequency 1 Hz in the range of temperature 0–160 °C. In DMTA, sinusoidally oscillating stress is applied to the sample with a given frequency. The generated strain is measured as a function of time. A sine wave amplitude of the strain is proportional to that of the stress, but lags behind it. There is a measurable phase difference δ between the applied stress and measured strain. The delay is related to occurring internal molecular motion and mobility of the molecules in the samples to adjust to the stress. In a pure elastic material the phase angle δ is 0. Values higher than 0 indicate that the material responds in visco-elastic manner. Finally, the storage (elastic) component E' of dynamic Young's modulus and the loss (related to the energy dissipated in the viscous flow) component E'' of the modulus are calculated, where the loss tangent is defined as $E''/E' = \tan\delta$ [9]. Tan δ is also known as a dissipation factor. By observing the changes in $\tan\delta$ over a temperature range, a glass transition temperature (T_g) was determined as a temperature at which tangent has the maximum value.

Further investigations were done for mortars composed of vinylester resin, sand (0.5–2 mm) and silica flour (grains below 50 μm). MTS was added as a direct admixture to the resin or with silica flour pre-treated with silane. The composition of the mortars was designed in previous work on statistical significance of synergistic effects between components of the modified mortars (silane admixture, silica flour, sand) [11]. Three unmodified (reference) mortars (Z1, Z2, Z3) and three modified mortars which showed the highest influence of silane on flexural strength (ZD1, ZD2, ZP3) were tested in details (Table 1). The flexural strength of each mortar was measured on the 6 beams 40 × 40 × 160 mm, and compressive strength was measured on the samples after bending. The tensile strength was measured on the 8-shaped samples. Fracture mechanics parameters were determined by wedge splitting test (WST), on three cubic samples 100 × 100 × 100 mm for each test [10] with notch to height ratio equal 0.8.

Table 1
Composition of vinylester mortars

Symbol	Silane modification	Filler to binder ratio		Silane concentration in binder % mass	Silane content in grams on flour's surface in m^2
		Sand/binder S/B	Silica flour/binder F/B		
Z1, Z3[a]	–	5	2	0	0
Z2	–	5	2.4	0	0
ZD1	Binder	5	2	1.1	0.0055
ZD2	Binder	5	2.4	1.32	0.0055
ZP3	Flour's surface	5	2	0	–

[a] Z3 the repetition of Z1 after two months for verification reasons (no significant differences in test results were observed).

4. Test results

4.1. Viscosity

The addition of silanes to the resin does not change the viscosity of the resin (Table 2, Fig. 1), however their influ-

Table 2
Influence of silanes on the viscosity of the vinylester resin and the resin–flour mixture (ratio 1:1 by mass)

Type of modification		Viscosity (cP)	
		Resin Shear rate 37.5 s^{-1}	Flour–resin mixture Shear rate 20 s^{-1}
Without		469.6	2321
Silica flour pre-treated with MTS		–	2306
Admixtures to the resin			
VTS	1%	446.0	638.6
	2%		657.4
ClS	1%	455.2	697.5
MTS	1%	440.8	781.0
	2%	443.7	–

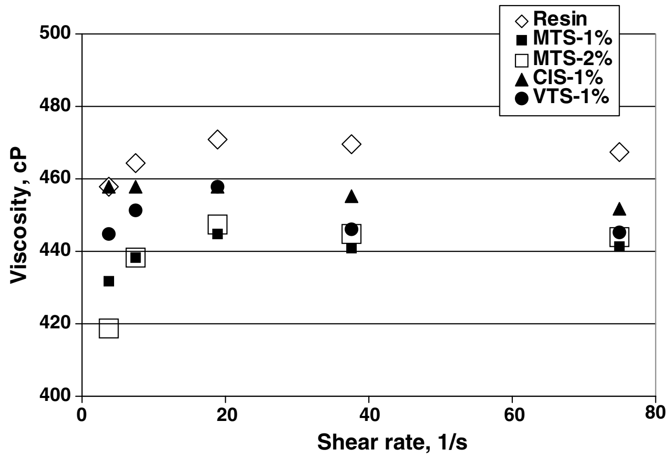

Fig. 1. Relationship between viscosity and shear rate for vinylester resin and the resin with silanes; MTS-1%, ClS-1%, VTS-1%, where 1% is concentration (in mass) of silane in the resin; MTA-2% – 2% (in mass) of silane in the resin.

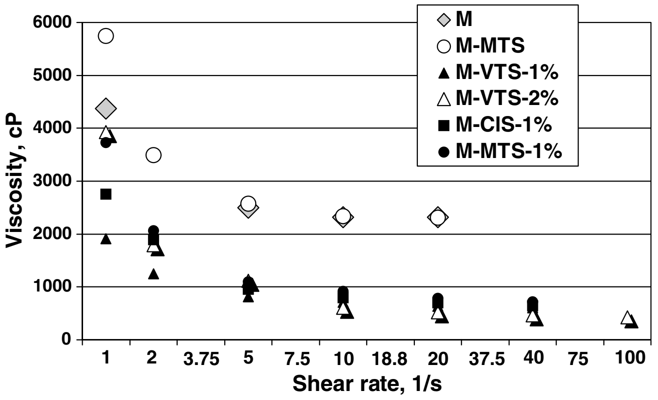

Fig. 2. Influence of the silane admixture on the viscosity of the silica flour–resin mixture (M) for filler to resin ratio equal one, where: M – mixture without modification, M-MTS mixture with silica flour pre-treated with MTS; M-VTS-1%, M-VTS-2%, M-ClS-1%, M-MTS-1% mixtures with 1% or 2%, (in mass) of silane in the resin.

ence is evident in the case of silica flour–resin mixtures (Table 2, Fig. 2). We can observe 70% decrease in silica flour–resin mixture viscosity when 1% of admixture is added directly to the resin. The presence of silane pre-treated silica flour does not change significantly the viscosity of the mixture.

4.2. Curing

For each type of silane (1% by mass added to the resin) slight delay (from 41 to 53 min) to reach peak curing temperature of the resin was observed (Table 3). Similar effect is observed for resin–silica flour mixtures modified by MTS. The time of detecting the $T_{\max}$ is shifted from 39 to 62 min. It indicates that silanes can extend the pot life of the reacting mixture.

Table 3
Influence of silanes on gelation temperature ($T_{\max}$) and time after which $T_{\max}$ arises for vinylester resin and resin–silica flour mixture

Composition	Maximum temperature $T_{\max}$ (°C)	Time of $T_{\max}$, detection t (min)
Resin	119	41
Resin + 1%VTS	106	45
Resin + 1%ClS	109.5	47
Resin + 1%MTS	126	53
Resin + silica flour	85	39
Resin + silica flour pre-treated MTS	90	47
Resin + 1%MTS + silica flour	102	62

Silanes can also change the value of $T_{\max}$. VTS and ClS admixtures decrease (106–109 °C) this temperature to values lower than the temperature characteristic for pure resin (119 °C), whereas MTS silane causes its increase to 126 °C. The resin used in the experiment has relatively high exothermic effect of curing. Addition of the MTS silane through the surface of silane pre-treated silica flour results in smaller changes in the $T_{\max}$ in comparison with the case when the MTS is added directly to the resin. The increase of the curing temperature is a disadvantage due to the thermal shrinkage of the resin. It can have an impact for example on the adhesion between the resin mortar and the concrete substrate in construction application.

4.3. Loss tangent and glass transition temperature

The changes of loss tangent ($\tan\delta$) with temperature were measured for the vinylester and the silane modified resin cured at 20 or 60 °C. For the resin sample cured at 20 °C two peaks of $\tan\delta$ are observed at 69.2 and at 121.5 °C (Fig. 3). The first peak indicates the glass transition temperature for material cured at room temperature and the second, shifted peak, is related to the material additionally cured during the DMTA test. In case of the resin sample cured at 60 °C, only one peak is observed at 123.1 °C. The results obtained for the vinylester resin as a reference material are consistent with the published data [12,13]. On this basis the influence of increased amount (1 and 2.5%) of MTS silane admixture to the resin was investigated. The first peek positioned at 69 °C shows the tendency to shift to 76 °C after adding the MTS silane, which means slight increase in T_g (Fig. 4). It is due to the strong exothermic effect of resin curing in the presence of MTS. The opposite tendency is observed for the second peak of loss tangent. The increase in the silane admixture concentration results in decrease of resin glass transition temperature from 123 to 118 °C. A similar tendency (decrease of about $6 \div 8$ °C) was observed for the VST and ClS admixtures. It indicates that presence of silane in the resin can slightly decrease the crosslinking of the binder. At room temperature that effect can be even stronger.

In the case of resin–silica flour mixture with 1% of the silane admixture, this decreasing tendency of T_g is even

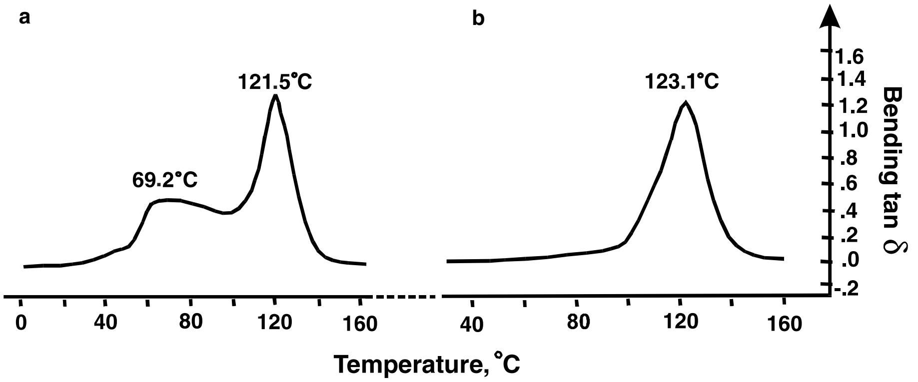

Fig. 3. Loss tangent (tan δ) measured in bending as a function of temperature, for vinylester resin binder cured at temperature: (a) 20 °C and (b) 60 °C.

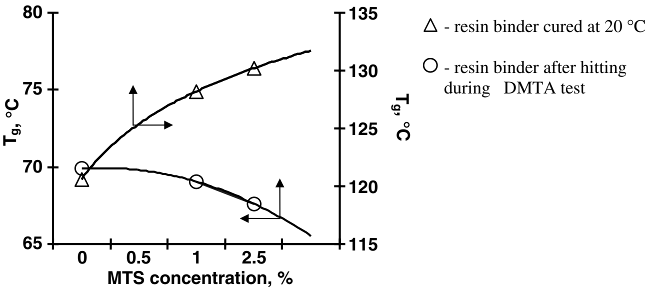

Fig. 4. Influence of MTS admixture on the glass-transition temperature (T_g) of vinylester resin cured at 20 °C and after heating during DMTA test.

smaller (from 111–117 to 109 °C). No changes are observed, when the MTS pre-treated silica flour was used; $T_g = 110$ °C for reference and modified samples.

As expected the loss tangent decreases with the increase of the filler-to-resin ratio (Table 4). At the same time, the presence of silane on the silica flour surface results in higher value of loss tangent of the micro-mortar in comparison to the mortar where silane was added directly to the resin. A similar effect was found by another author [14]. Such a phenomenon, if appears together with increased tensile strength of the composite material is attributed to a strong adhesion between the polymer binder and the filler. It is due to an interaction, which creates a kind of stiff "envelope" around the mineral grains [14].

Table 4
Influence of the silica flour to resin ratio and the type of silane modification on the loss tangent of the cured resin micro-mortars

Silica flour to resin binder ratio	tan δ		
	Type of MTS silane modification		
	Without	Admixture to the resin	Silica flour surface
0	1.24		
2	0.67	0.66	0.81
2.4	0.58	0.53	

4.4. Mechanical strength of the mortars

Flexural, compressive and tensile strength of the mortars were measured and the data obtained for modified (MTS) and non-modified mortars were compared using analyses of variances (Table 5, Fig. 5). It was established that:

- there are no statistically significant differences between average values of the mechanical properties of non-modified mortars (Z1, Z2, Z3),
- properties of silane modified mortars (Z1D, Z2D, Z3P) differ significantly from the non-modified mortars.

Silane addition to the resin caused a 15% increase in compressive strength and 10% increase in flexural strength (ZD1, ZD2). When silica-flour modified with silane was used (ZP3), a similar increase in flexural strength of mortar (12%) and much higher increase in compressive strength (28%) were observed. In case of tensile strength the biggest increase in strength (30%) was found when the silane admixture was added directly to the resin (ZD1). Much lower increase was observed for the mortar (ZP3) containing silica flour with surface modified by silane (13%). From the statistical point of view samples ZD1 and ZP3 differ significantly, while the sample ZD2 (higher than in ZD1

Table 5
Mechanical properties of silane modified and unmodified vinylester mortars

Mortar	Flexural strength		Compressive strength		Tensile strength	
	(MPa)	s_x (MPa)	(MPa)	s_x (MPa)	(MPa)	s_x (MPa)
Z1	36.7	1.89	97.6	5.7	13.3	1.00
Z2	38.2	1.05	99.8	7.6	13.6	1.00
Z3	38.1	1.23	100.0	6.6	13.9	1.10
ZD1	40.8	1.72	112.2	7.4	17.4	0.56
ZD2	40.9	1.25	113.6	6.1	16.7	0.89
ZP3	42.7	0.75	128.2	6.8	15.7	0.72

s_x – standard deviation.

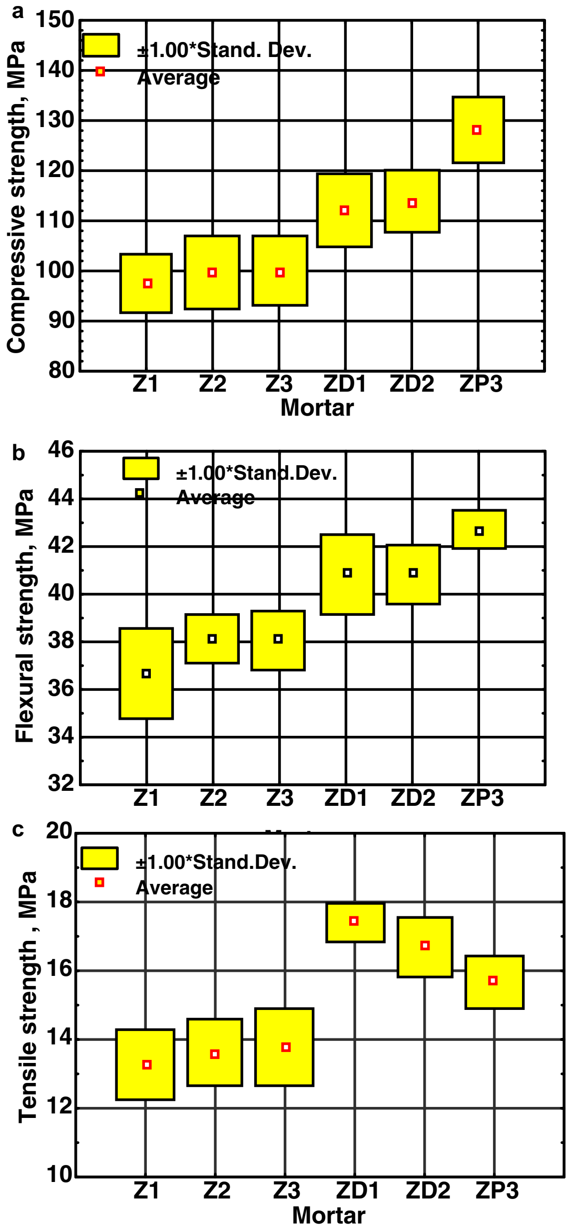

Fig. 5. Compressive (a), flexural (b) and tensile (c) strengths of vinylester resin modified with MTS silane (ZD1, ZD2, ZP3) and unmodified (Z1, Z2, Z3).

and in ZP3 filler to resin ratio) takes up the place between them.

In order to evaluate the fracture properties of the mortars the wedge splitting test was performed. It was found that MTS silane addition increases the maximum splitting force (P_h) (Fig. 6). Stress intensity factors (Table 6) calculated on that basis indicate that mortar with silane pre-treated silica flour has the highest value of K_{IC} – 20% higher than the unmodified mortars. Lower values of K_{IC} were found for the mortars modified by silane addition to the resin, but they were 12% higher than for the unmodified mortars. Modulus of elasticity of the mortars does not differ significantly. Taking into account the area under the splitting force–CMOD curve (Fig. 6) and ligament area of the sample, the fracture energy G_F was calculated. It was found that silane modification increases the fracture energy; the most effective modification was done by the use of silane pre-treated silica flour. Changes in the material brittleness described by its characteristic length l_{ch} (Table 6) indicate, that the modification by the silane direct addition to the resin causes increase in brittleness of the mortar in comparison with the unmodified one (smaller l_{ch}). Unlike in previous case, when silane was introduced to the mortar through the surface of pre-treated silica flour, the decrease in brittleness (increase of l_{ch}), can be observed.

5. Discussion

The silanes have moderate influence on resin viscosity however, in the case of the resin–silane–silica flour mixture, 70% decrease in viscosity is observed. The investigated admixtures extend the gelation time. The highest hardening temperature (higher than for pure resin) was detected when MTS was added to the resin.

The increase in silanes concentration in the resin causes slight decrease of glass transition temperature of "micro-mortars", measured by the changes of lost tangent with temperature. It indicates lower degree of crosslinking. However, a stronger exothermic effect of curing (e.g. when MTS added) can minimise this effect for mixture cured at ambient temperature. The results indicate that the presence of silanes in the resin binder can change the temperature and kinetics of resin hardening.

Comparison of silane modified and unmodified mortars, it revealed that in general modification results in increase of fracture stresses. The effect of modification depends on the method of silane addition to the composite. In case when silane admixture was added directly to the resin binder there was an increase in both the tensile strength (ca. 25%) and brittleness (more than 30%) of the composite. For mortar containing the silica flour pre-treated with silane, the fracture energy and fracture intensity factor increased by 60% and 20%, respectively. The modified mortar samples are also significantly less brittle than the unmodified ones. The modulus of elasticity of the mortar shows insignificant changes after modifications.

Silane addition improves adhesion between mineral grains and the resin binder. It is due to the synergetic effect between silica flour and silane admixture as well as high specific surface of silica flour [15]. The presence of silane changed in a spectacular way the fracture surface of the mortar (Fig. 7). The flat, uniform surface is observed for unmodified composite (Fig. 7a). Characteristic polygons structures are observed for composite with silane added directly to the resin (Fig. 7b and c). Similar structure, known as Giant's Causeway in Ireland, was formed during unstable equilibrium of volcanic lava's consolidation (Fig. 7d).

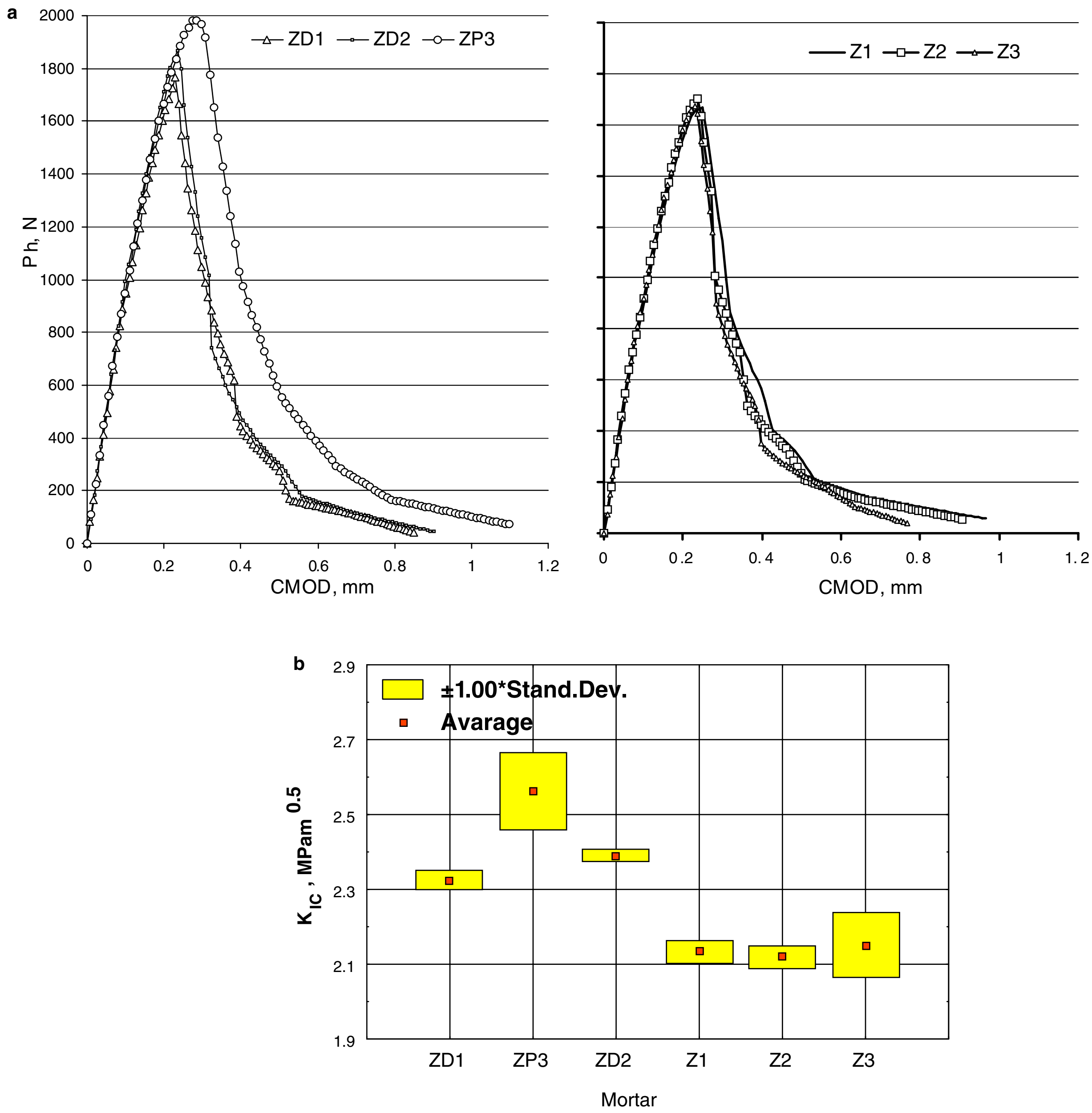

Fig. 6. Relationship between average value of horizontal component of splitting force (P_h) and CMOD (a) and average values of stress intensity factor K_{IC} (b) for MTS modified (ZD1, ZD2, ZP3) and unmodified (Z1, Z2, Z3) vinylester mortars.

Table 6
Characteristic of fracture of vinylester mortars unmodified and modified by MTS silane, where: G_F – fracture energy, K_{IC} – stress intensity factor, E – Young's modulus, l_{ch} – characteristic length, f_t – tensile strength

Mortars	f_t (MPa)		G_F (N/m)		K_{IC} (MPa $m^{0.5}$)	E (GPa)		l_{ch} (mm)
Z1	13.3	13.6	248	232	2.13	24.7	25.1	31.5
Z2	13.6		225		2.12	25.7		
Z3	13.9		224		2.15	24.9		
ZD1	17.4	17.0	241	241	2.32	22.8	23.3	19.4
ZD2	16.7		241		2.39	23.8		
ZP3	15.7	15.7	381	381	2.56	25.9	25.9	40.0

One may say that the presence of silane in the interfacial transition zone between mineral grain and resin binder joins both materials by chemical bonds. Consequently, the tensile strength increases. However, the increase of exothermic effect of the curing process and finally, the increase of shrinkage when silane is added directly to the resin, causes the stress concentration and cracks along the grain's surface. Silane particles deposited on the surface of pre-treated silica flour modify whole matrix more uniformly as compared to the composite with silane added to the resin. In that case the kinetics of the hardening process does not change significantly. The increase in fracture energy as well as decrease in brittleness can be observed.

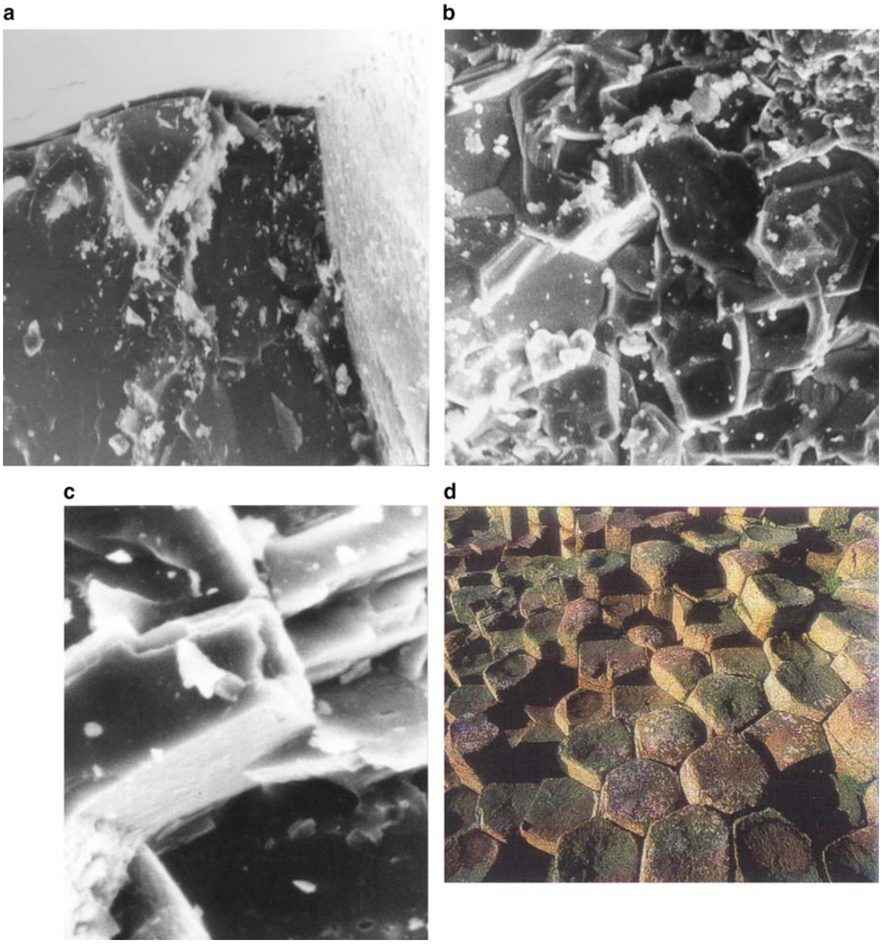

Fig. 7. View of fracture surfaces of vinylester mortars with resin binder: (a) unmodified, (b) modified with 2% MTS silane added to the resin (×1000) (c) the same as in "b" (×5000) (d) Giant's Causeway.

6. Conclusions

The results allow the authors to conclude that the silane modification of the resin mortar depends on the method of modification. It was found out, that the silane modification:

- decreases resin–silica flour mixture viscosity,
- influences the resin hardening process,
- increases the compressive, flexural and tensile strength,
- increases fracture toughness and fracture energy,
- decreases composite brittleness, when the silane is added into the mixture through the silica flour's surface.

Silanes are very useful modifiers of polymer mortars. However, their efficiency should be carefully checked for each resin–silane system in order to establish the influence of the admixture on resin hardening as well as on the final effects.

Acknowledgement

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