The improvement in properties of polyester resin-based composites using a new type of silane coupling agent

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Abstract: Adhesion between the polymer matrix and fillers is an important factor influencing the properties of the obtained composites. One way to improve interactions at the interface is to modify the filler with coupling agents, *e.g.*, silanes. The article presents the effect of modifying the surface of the mineral filler with a new type of silane [triethoxy(ketoimino)silane] on the mechanical properties of polyester resin based composites. Composites with triethoxy(ketoimino)silane-modified filler had similar mechanical properties to composites obtained with commercial silanes, with slightly lower water absorption.

Keywords: polyester resin, silanes, composites, mechanical properties.

Modyfikacja właściwości kompozytów na bazie żywicy poliestrowej z użyciem nowego rodzaju silanu

Streszczenie: Adhezja między osnową polimerową i napełniaczami jest istotnym czynnikiem wpływającym na właściwości otrzymanych kompozytów. Jednym ze sposobów poprawy oddziaływań na granicy faz jest modyfikacja napełniacza środkami sprzęgającymi, np. silanami. W artykule przedstawiono wpływ modyfikacji powierzchni napełniacza mineralnego przy użyciu nowego typu silanu [trietoksy(ketoimino)silan] na właściwości mechaniczne kompozytów na bazie żywicy poliestrowej. Kompozyty z udziałem napełniacza modyfikowanego trietoksy(ketoimino)silanem miały podobne właściwości mechaniczne do kompozytów otrzymanych z udziałem silanów handlowych, przy nieco mniejszej chłonności wody.

Słowa kluczowe: żywice poliestrowe, silany, kompozyty, właściwości mechaniczne.

The technological process of obtaining highly filled cast composites is known and is commonly used to obtain polymer concretes intended for elements of building structures and for the manufacture of sanitary fittings, for example, sinks. The process consists of mixing liquid chemically cured resins, usually polyester or epoxy resin, with a mineral filler followed by chemical hardening after placing such a mixture in a suitable form [1–3].

The resin is a binder, with the main strength properties of the composite provided by the filler. Fillers, most often crushed dolomite, quartz powder, silica, and ground granite, are selected in terms of grain size to obtain the highest possible degree of packing. In line with the increasing demand for composite materials, improving their properties and methods of manufacturing are still desirable [4–7].

Most known solutions for polymer concretes focus on the appropriate selection of the composition and grain size of the filler or the appropriate selection of resin additives. The strength of the composite can also be improved by strengthening the bond between the resin and the filler. This is achieved most often by modifying the surface of the filler with organosilicon compounds (silane coupling agents).

The most widely used organosilanes have one organic substituent and three hydrolyzable substituents [8] (Figure 1).

Through their dual reactivity, organosilanes serve as coupling agents between inorganic substrates (such as minerals, fillers) and an organic polymeric matrix (such as rubber, thermoplastics, or thermosets) and can dramatically improve the adhesion between them [9–15].

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[2)] Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznan, Poland.

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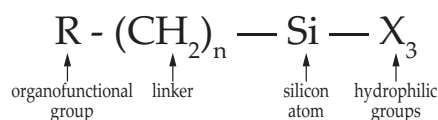*) Author for correspondence: dominik.paukszta@put.poznan.pl

$$R - (CH_2)_n — Si — X_3$$

organofunctional group — linker — silicon atom — hydrophilic groups

Fig. 1. The basic structure of silanes [8]

– **X, a non-hydrolysable organic substituent. This moiety can be reactive toward another chemical (*e.g.*, amino, epoxy, vinyl, methacrylate, sulfur) or nonreactive (*e.g.*, alkyl).**

– **Si-OR' – a hydrolyzable group, such as an alkoxy group (*e.g.*, methoxy, ethoxy, isopropoxy) or an acetoxy group that can react with various forms of hydroxyl groups present in mineral fillers.**

– **(CH)$_n$ – a spacer, which can be an alkyl chain, typically propyl (n = 3).**

Fig. 2. The structure of triethoxy(ketoimino)silane

According to the well-established information contained in the scientific literature, in most surface treatment applications, the alkoxy groups of trialkoxysilanes are hydrolyzed to form species that can react with various forms of hydroxyl groups present in mineral fillers, and a covalent siloxane linkage is formed [16–18].

The silane to filler ratio depends closely on the average particle size of the inorganic material and the specific surface area. The typical amount of silane used is between 0.1 and 1.5% with respect to the treated filler weight and allows for a monolayer coating of the material. Fillers that can be efficiently coated with silanes are, for example, silica, quartz, aluminum hydroxide, talc, calcium carbonates, inorganic oxides and many more [19–21].

Unmodified mineral fillers are usually highly hydrophilic. Surface modification with silanes typically renders the surface hydrophobic. In the case of composites, this is particularly advantageous as it reduces the water absorption of the composite, resulting in blocking water from penetrating the boundary space between the filler and the resin. Usually, the modified surface is better wetted by the resin, which improves the processing properties, especially the miscibility of uncured composites.

Currently, many different types of organosilicon compounds are produced, which allows shaping of the filler's features over a very wide range to obtain the best final effect [18–21].

In the case of polyester resins, silanes with a vinyl or methacrylic group are the most used, while glycidoxysilanes are most often used for epoxy resins, obtaining composites with very good water resistance and good strength parameters [22]. Significant improvement of strength is also obtained by using silanes with an amino group, which are among the most available, universal, and cheap adhesion promoters. On the other hand, composites with silane-modified fillers with an amino group, because of the hydrophilic nature of this group, usually show increased water absorption, even compared to unmodified fillers, which eliminates them from some applications. In this work, we present the possibilities of modifying typical commercial adhesion promoters to improve some of their prop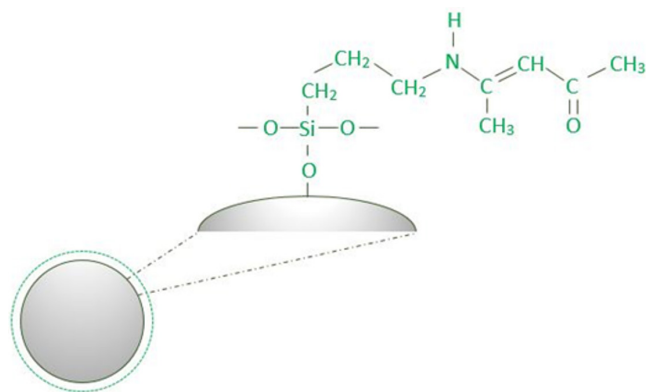erties. In our research, we focus on the use of a new type of silane with a ketoimine group to modify the mineral filler used in polyester-based polymer concretes and compared to known trade compounds.

The organosilanes modified filler with a ketoimine group, shown in Figure 2, can be obtained by two methods. First, an organosilicon compound with a ketoimine group is produced by reacting an aminosilane with acetylacetone, and the surface of the filler is modified with the silane thus obtained. The second way is to modify the filler with an aminosilane, and then the surface-bound amino groups are converted to ketoimine groups by the reaction with the excess acetylacetone ions.

In both cases, the filler surface is modified, as shown in Figure 2, and the properties of the fillers in both cases are identical.

EXPERIMENTAL PART

Materials

Polyester resin with a max. acid number 26 mg KOH/g, styrene content 36-38%, viscosity 450-600 mPa·s, gelling time 5-7 min was purchased from Connector.pl Ltd (Poland). Mixture of minerals and crushed stone, containing calcite (CaCO$_3$), silicon dioxide (SiO$_2$) and tiny amounts of various mineral compounds (Connector.pl Ltd, Poland) was used as a filler. Vinyltrimethoxysilane (Geniosil® XL10) and 3-aminopropyltriethoxysilane (Unisil U-13) were supplied by Wacker Chemie (Germany) and Unisil Ltd (Poland), respectively. 3-triethoxy(ketoimino)silane was synthesized according to the procedure described in the next section. Acetylacetone (2,4-pentanedione) was supplied by Merck (Germany). Methyl ethyl ketone peroxide (Butanox M-50) was the product of AkzoNobel (The Netherlands). Cobalt 2-ethylhexanoate was supplied by Henan Tianfu Chemical Co., Ltd (China) and used as a catalyst.

Synthesis of triethoxy(ketoimino)silane

To synthesize the triethoxy(ketoimino)silane, 22.14 g of 3-aminopropyl-triethoxysilane, 11.0 g of acetylacetone and 100 cm³ dried toluene was injected into a Dean-Stark

apparatus. The mixture was kept at the boiling temperature for the azeotropic distillation of water. After 60 minutes, when about 1.8 cm^3 of distilled water had separated from the mixture, the remaining solvent and residues of the used acetylacetone were left.

The UV-Visible absorbance spectrum of the obtained compound showed a strong band in the range of about 277 nm, characteristic of the ketoimine group. There was no signal in the 210 nm range, which is characteristic of the amino group. This indicates that a chemical compound has formed, characterized by the composition: $(CH_3CH_2O)_3SiCH_2CH_2CH_2N=C(CH_3)CH_2COCH_3$, and the structure presented in Figure 3. The compound can coexist in three tautomeric forms, similarly to the amino-ketone derivatives of acetylacetone [21, 23–24].
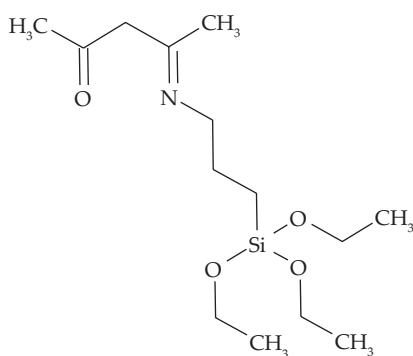
Fig. 3. The structure of triethoxy(ketoimino)silane

Silanization of the inorganic filler

As a filler, a commercial mixture of crushed stone (dolomite) was used, with an even grain size in the range of 0.025–1.0 mm, mainly 0.125–0.5 *mm*, ensuring maximum grain density and a specific surface area of approximately 4.0 ± 0.5 m²/g, containing calcite ($CaCO_3$), silicon dioxide (SiO_2), quartz powder, and small amounts of various mineral compounds.

Silanization was performed in a standard laboratory rotary evaporator. In a spectroscopy round bottom flask, 100 g of filler and 150 cm^3 of a 1:1 mixture of methanol and acetone (in the case of vinylsilane and ketoiminosilane) or water (in the case of aminosilane) were placed, to which 150 mmol of silane was added.

After the flask was mounted on the evaporator, rotary mixing was turned on for 60 minutes (flask rotation about 10–30 rpm) without applying a vacuum. After 60 minutes, the water bath heater was turned on and
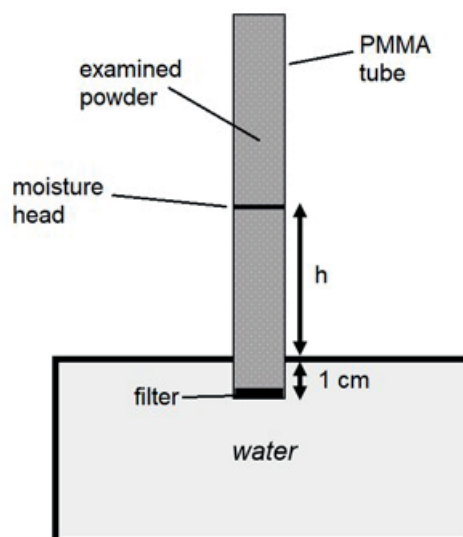
Fig. 4. The capillary rise test scheme

stirring continued while the solvent was slowly distilled (approx.120 min). Then a vacuum was applied to completely remove the solvent. The modified fillers obtained in this way were ready for further research.

The aminosilane-modified filler was additionally reacted with acetylacetone in the same manner as the silane modification, using a solution of acetylacetone in acetone in an amount corresponding to a 50% molar excess in relation to the amino groups.

The modified filler was analyzed using reflective UV-Vis spectroscopy, which confirmed the presence of ketoimine groups on the surface (strong absorption maximum in the range of approximately 277 nm), which confirms that the amino groups reacted with the acetylacetone.

To evaluate the effects of modification of the filler surface, a modified procedure was used to evaluate the capillary rise in soils [25]. On this basis, the level of wettability of the filler by water was determined.

Measurements were made in poly(methyl methacrylate) (PMMA) tubes, 100 cm long with an internal diameter of 10 mm. The capillary rise was determined after 10 min based on the measurement of the height of the moisture front, visible as a change in filler color.

Preparation of composites

To obtain the composites, the compositions were prepared with filler in constant proportions: filler to resin

T a b l e 1. The characteristic of composites

Sample name	Silane active group	Filler capillary rise, cm	Composite water absorption, %
REF	Without	4.0	0.26
VINYL	Vinyl	1.0	0.05
AMIN	Amino	7.0	0.32
K-IM	Ketoimino	2.2	0.03

75:25 wt%, with the addition of catalyst (approx. 2 cm³). The materials are characterized by silane active group type (Table 1); e.g., the compound indicated as VINYL contains 75 wt% of inorganic filler, modified using 0.3 wt % of trimethoxvvinylsilane.

The filler and a mixture of polyester resin with a hardener (methyl ethyl ketone peroxide – 1.5% in relation to the resin) and an accelerator (cobalt 2-ethylhexanoate – 1% in relation to the hardener) were mechanically mixed until a homogeneous composition was obtained, then vented under vacuum and poured into molds to give the appropriate shape and dimensions to the samples for mechanical tests.

Methods

UV-Visible spectroscopy was applied to characterize the chemical structure of the obtained silane and modified filler. The spectra were obtained using a double-beam spectrophotometer (Lambda 12 UV/VIS, Perkin Elmer, USA). The scanning mode was applied, and the spectra were achieved in the wavelength region of 200 to 700 nm. Young's modulus, tensile strength, elongation at maximum strength, strength at the break, elongation at the break, strength at a yield of 0.2% at a constant speed of 10 mm/min were evaluated according to ISO 527 using a Zwick-Roell Z020 testing machine. The size of each sample was 150 mm × 10 mm × 4 mm. Impact strength was determined according to ISO 179 using an Instron CEAST 9050 Charpy hammer. The water absorption was measured according to EN ISO 62. The method consists of determining the amount of water absorbed by plastic samples of specific dimensions immersed in water. The samples were evaluated after soaking in water for 336 hours (14 days).

RESULTS AND DISCUSSION

The results of the capillary rise tests and water absorption are summarized in Table 1. The values obtained for the filler modified with silane containing ketoimino groups, regardless of the modification method, were identical. Moreover, composites with a silane-modified filler with vinyl and ketoimino groups showed the lowest water absorption, which was much lower than that of the composite with unmodified filler.

As can be seen in Figure 5a, the maximum value of Young's modulus was observed for the composite filled with (3-aminopropyl) triethoxysilane-modified filler. The use of triethoxy(ketoimino)silane or trimethoxvvinylsilane increases this parameter compared to the composite with unmodified filler. The increase is significant (about 200%). Filler silanization improves adhesion at the filler-polymer matrix interface resulting in higher composite's stiffness. A similar tendency can be observed for the tensile strength (Fig. 5b) with the highest value for the composite containing (3-aminopropyl)triethoxysilane-modi-
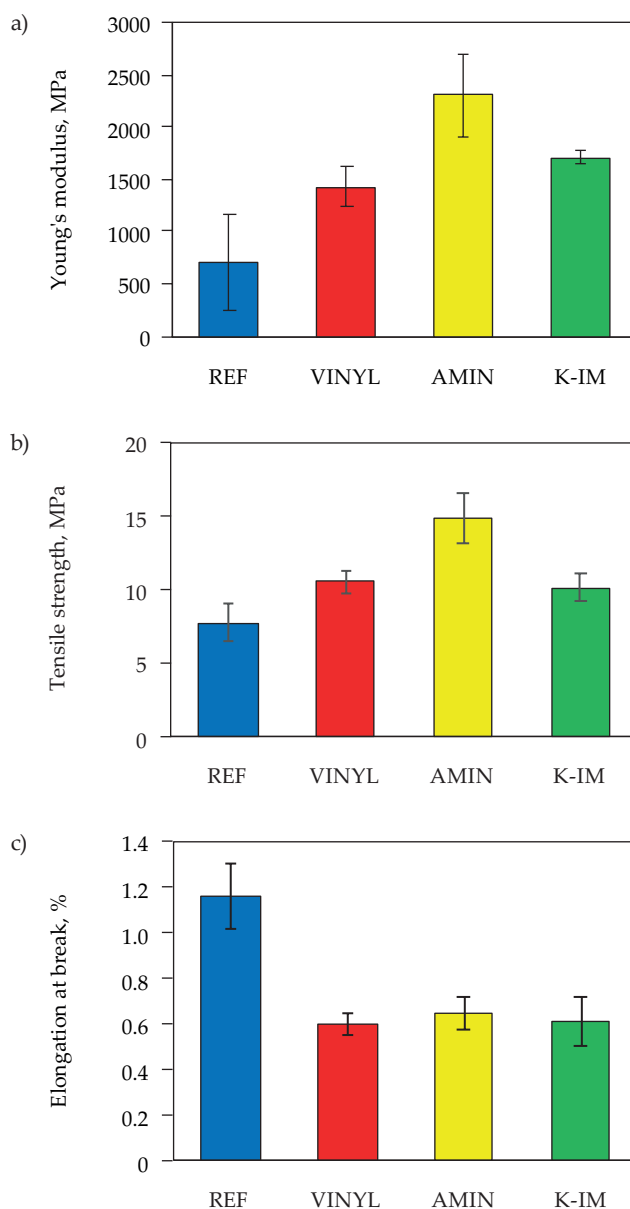

Fig. 5. Mechanical properties of the composites: a) Young's modulus, b) tensile strength, c) elongation at break

fied filler (about 15%). The tensile strength is similar for the VINYL and K-IM composites (about 12%), and lower than for the AMIN composite, as is the Young's modulus distribution.

However, the improvement in tensile strength (from unmodified filler-filled composites to silane-modified filler-filled composites) is less significant than for Young's modulus. The reason for this phenomenon may be better adhesion (when using silanes) and an increase in the force needed to break the material. Analyzing Figure 5c, it can be observed the same elongation at the break (about 0.6%) for all composites with modified filler. However, the elongation for the composite with unmodified filler is higher. It should be emphasized that the composites used for the production of sinks should be characterized by high rigidity and not undergo plastic deformation.

CONCLUSIONS

A new triethoxy(ketoimino)silane was synthesized and used as a surface modifier of a polar inorganic filler. Additionally, the filler was modified with aminosilane and then with acetylacetone. The advantage of this modification is the possibility of using an aqueous solution to modify the aminosilane with hydrocarbons. During the two-stage modification with a slight excess of acetylacetone, dusting of the filler during dosing to the resin and production of the cast composite was significantly reduced, without significantly affecting strength and water absorption. The selected properties of polyester resin-based composites with triethoxy(ketoimino) silane-modified filler were examined and compared to the composites with commercial silanes [(3-aminopropyl)triethoxysilane and vinylsilane]. The use of silanes increases the adhesion of the filler to the matrix, which is associated with better mechanical properties. This effect depended on the structure of the silane used. The silane-modified filler increased the stiffness and reduced the susceptibility to plastic deformation of the composites. The new modifier, triethoxy(ketoimino)silane, is as effective as other commercial modifiers.

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