



Preparation and characterisation of montmorillonite-ammonium silane surface layers promoting adhesion between steel and a polyurethane adhesive



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ABSTRACT

Novel pro-adhesive surface layers on a steel substrate were created via electrostatic adsorption of montmorillonite platelets on ammonium silane layers based on (3-aminopropyl)trimethoxysilane. Morphology of the mentioned montmorillonite-ammonium silane surface layers (MSL) (prepared using clays with calcium, strontium and diisopropylammonium exchangeable cations) was analysed by means of SEM, EDX and XRD techniques. The MSL significantly reduced dipropylene glycol contact angle (-14°) and roughness (-38%) of the steel substrate as well as increased its corrosion rate ($+160\%$) and shear strength of joints prepared using a commercial 2 K polyurethane adhesive ($+77\%$). Additionally, the steel samples with MSL created by means of Ca- or Sr-montmorillonite exhibited markedly higher shear strength after their exposition in a salts spray chamber ($+316\%$ and $+311\%$, respectively) in relation to untreated samples.

1. Introduction

Silanes belong to the most attractive compounds for surface modification of many inorganic and organic substrates. Hydrolysis of mono-, di-, and trichlorosilanes, acetoxysilanes and alkoxysilanes and following condensation of generated silanols with hydroxyl groups located on surfaces of a glass [1,2], mineral (e.g. quartz, mica) and synthetic fillers (titanium dioxide, carbon black), plastics, ferrous and non-ferrous metals and alloys (iron, steel, duralumin, zinc, copper) lead to creation of unreactive or reactive siloxane layers [3,4]. In the case of fillers, an application of the silanes (bearing auxiliary epoxy, amine or unsaturated groups) allows chemical bonding of the powders with polymeric matrices [2,5], but also improves their dispersibility in the compositions during their production process [2]. Treatment of plastics, aluminium and its alloys as well as steel substrates by silanes has resulted in higher adhesion of coatings and adhesives [6–10]; its positive influence on anticorrosive protection of metallic elements has also been observed and discussed in the literature [9,11,12].

An addition of natural nanofillers, e.g. montmorillonite (MMT) markedly improves a few parameters of organic coatings (adhesion to steel substrates, hardness, scratch resistance [13], impact resistance [14], barrier properties [13,14]), adhesives (shear strength [15,16],

Young's modulus [17]) and cast polymeric materials (flexural strength, softening temperature, thermal stability [18]). Due to limited compatibility of the raw clay with thermoplastic and thermosetting polymers its modification/organophilisation should be made; ammonium salts bearing different organic substituents are usually used in that process [13,14,16–18], however, MMT modification by means of silanes are described in the literature as well [19,20]. It should be noted that organophilisation of MMT is realised via electrostatic adsorption (onium salts) or covalent bonding of a modifier by hydroxyl groups located on the surfaces of the clay particles (silanes). In the presented work, the electrostatic adsorption process of natural or modified montmorillonites on an ammonium silane layer (based on (3-aminopropyl)trimethoxysilane) was applied to the preparation of novel pro-adhesive surface layers on a steel substrate. Samples with the montmorillonite – ammonium silane surface structures were tested using a commercial 2K polyurethane adhesive; that binder was selected considering limited adhesion of polyurethane compounds to steel substrates (in relation to e.g. epoxy systems). To the best of our knowledge, surface layers based on ammonium silanes and aluminosilicates have not been investigated and described in the literature.

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2. Experimental

2.1. Materials

The following components were used for adhesion promoting layer preparation:

- (3-aminopropyl)trimethoxysilane (APTMS), molecular weight 179.3 g/mol, purity 99% (Innosil, Poland);
- solvents: methanol (purity 97%) and propan-2-ol (97%; Chempur, Poland);
- acetic acid (99%; Chempur);
- water slurry of calcium montmorillonite (MMT-Ca) with cation exchange capacity (CEC) ca. 86 mmol/100 g, 4.4 wt% of solids (Bentonit SN; Z.G.M. Zębiec, Poland);
- water slurry of strontium montmorillonite (MMT-Sr), CEC ca. 94 mmol/100 g, 7.1 wt% of solids (oMMT-6; ZUT, Poland);
- water slurry of a montmorillonite modified with protonated diisopropylamine (MMT-DIPA), 6.3 wt% of solids (oMMT-12; ZUT).

Adhesive joints were prepared using:

- 2K polyurethane adhesive (PUR) based on methylene diphenyl diisocyanate and a polyols mixture, density ca. 1.12 g/cm³, viscosity 30 Pa.s (Multibond 3645; AM Technologia, Poland);
- low-carbon steel panels, CRS SAE 1008/1010, 102 × 25 × 1.5 mm (RS14; Q-Lab, Germany) (for overlap shear strength tests);
- low-carbon steel panels, CRS SAE 1008/1010, 120 × 76 × 0.8 mm (S-36; Q-Lab) (for pull-off adhesion and other tests).

Dipropylene glycol (DPG) (99%; Acros Organics, Belgium) was utilised in substrate wetting tests.

2.2. Silanisation of steel substrates

APTMS (0.001 wt. part), methanol (50 wt. parts) and distilled water (10 wt. parts) were mixed and stored at room temperature for 4 h. Then, the system was mixed with propan-2-ol (40 wt. parts) and applied onto steel substrates (washed using acetone, activated by their immersion in distilled water for 2 min and drying using acetone) by means of a brush and dried in a laboratory oven for 30 min (RT), 4 h (95 °C) and 2 h (125 °C). The aminosilane coated steel samples were abbreviated to ST-SiN while untreated steel panels were described as ST-0.

2.3. MMT adsorption on silane layers

Aminosilane-treated steel panels (ST-SiN) were immersed in an aqueous solution of acetic acid (2.5 wt%) for 15 s, gently washed using distilled water and immersed in a water slurry of montmorillonite clay (0.5 wt% of MMT-Ca, MMT-Sr or MMT-DIPA; 1 min). Next, the samples were washed using tap water, distilled water and subsequently acetone and dried in a laboratory oven at 75 °C for 30 min. Prepared samples were abbreviated to ST-SiN/Ca (MMT-Ca), ST-SiN/Sr (MMT-Sr) and ST-SiN/DIPA (MMT-DIPA).

2.4. Polyurethane joints preparation

Samples for overlap shear strength tests: the PUR adhesive (containing 0.1 wt% of glass beads with a diameter of 0.5 mm as internal spacers) was applied onto steel substrates and cured (under a constant pressure of 80 Pa) at RT for 24 h. Then, the samples were heated at 45 °C (15 h) and 75 °C (1 h). Dimensions of the joints were 25 × 25 mm.

Samples for pull-off adhesion tests: sandblasted steel dollies (ø20 mm) were covered with the PUR adhesive, placed onto steel substrates and cured at RT (24 h), 45 °C (15 h) and 75 °C (1 h).

2.5. Methods

The particle size distributions of montmorillonites in their water slurries (0.0025 wt% of solids) were analysed using a light scattering technique (Zetasizer Nano; Malvern, UK). Wettability of untreated and surface-treated steel samples by water and dipropylene glycol (DPG) was considered in relation to static contact angle values determined (at 23 °C, three measurements for each sample) by means of the drop shape analyzer (DSA100; Krüss, Germany). The surface roughness (R_a parameter) of the samples was assessed using a laser scanning microscope VK-9700 (three measurements for each sample; Keyence, USA). X-ray diffraction (XRD) patterns for the steel substrates and MMT-Ca (powdered) were obtained with the X'Pert PRO Philips diffractometer (Cu $K\alpha$, 1–25 °2 θ) equipped with the X'Pert PRO High Score Philips software. Transmission electron microscopy analysis of the steel samples was performed using the Hitachi SU-70 microscope (Hitachi, Japan) equipped with the EDX analyzer (Thermo Scientific, USA).

The Tafel experiments (± 250 mV in relation to OCP, scan rate 0.25 mV/s) for steel samples were performed using the DC105 software and FAS2 femtostat (Gamry, USA). As a result, corrosion potential, corrosion current density as well as a corrosion rate was determined using the Echem Analyst software (Gamry). The tests were carried out after 2 min of a glass cell filling with the electrolyte (3.5 wt% NaCl aqueous solution).

The salt spray test was performed for 480 h in CorrosionBox 400 (Co.Fo.Me.Gra., Italy) using an aqueous NaCl solution (concentration of 50 \pm 5 g/l) sprayed with compressed oil-free air (100 kPa). Samples (except PUR joints) were protected with a special pressure adhesive tape (TESA Tape, USA) and mounted at an angle of 20° vertically. The temperature in the spray cabinet was maintained at 35 °C.

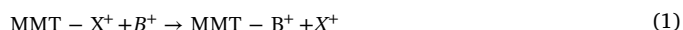
Samples were exposed in the climatic chamber for 480 h (10 cycles comprising exposition for 24 h at -20 °C and 24 h at 35 °C and 95% RH; Espec, Japan).

The overlap shear strength of joints (before and after their exposition in the salt spray chamber or in the climatic chamber; seven samples of each system) was measured according to PN-ISO 4587 standard at room temperature by means of the Instron 5982 machine (tensile velocity of 10 mm/min; Instron, USA). Pull-off adhesion of the PUR adhesive to steel substrates was evaluated acc. to PN-EN ISO 4624 using the Elcometer 510 T hydraulic apparatus (tensile stress increment of 1 MPa/s, six measurements for each sample; Elcometer, UK).

3. Results and discussion

Preparation process of montmorillonite-ammonium silane layers (MSL) consisted of (i) hydrolysis of the aminoalkoxysilane (APTMS), (ii) condensation of generated aminosilanols on a steel surface, (iii) protonation of amine groups of condensed aminosilanols (i.e. aminosilane layer) using acetic acid, and (iv) electrostatic adsorption of montmorillonite platelets (from its aqueous suspension) on the created ammonium silane layer (Fig. 1).

The mentioned electrostatic adsorption of the MMT on the steel substrate was caused by cation exchange reactions (CER) between ammonium groups of the silane layer and exchangeable cations (calcium, strontium or ammonium) located on a surface of the clay. As described in the literature [21] CER can be observed for MMT treated by a modifier with higher value of dissociation/ionisation constant (pK_a) than cations initially adsorbed by the MMT. Generally, CER can be presented as:



where: X^+ represents an exchangeable cation initially adsorbed on a MMT and B^+ represents a surface modifier of the MMT.

Considering pK_a values for Ca^{2+} (1.1–1.5), Sr^{2+} (0.8–1.0) [22] and APTMS (ca. 10.6) [23] CER between MMT-Ca (or MMT-Sr) and protonated aminosilane should be effectively realised. This phenomenon

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