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Optimisation of wet chemical silane deposition to improve the interfacial strength of stainless steel/epoxy

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ABSTRACT

The evaluation of various wet chemical deposition conditions of γ-aminopropyltriethoxysilane (APS) on stainless steel resulted in stainless steel/epoxy hybrids with improved interfacial strength. Nuclear magnetic resonance spectroscopy (NMR) revealed the working window of the silane solution used, while scanning electron microscopy (SEM) and spectroscopic ellipsometry (SE) served at characterising the final APS film structural properties. With pull-off testing the interfacial strength of surface treated steel plates in contact with an epoxy resin was determined. Fracture surface morphological features allowed identifying the failure mode. Optimisation of the different silane deposition conditions led to a doubling of the interfacial strength compared to non-treated samples. The fracture strength value of more than 60 MPa by far exceeds values currently found in literature and approaches the epoxy fracture strength by which the original adhesive failure mode converts into a more cohesive failure mode.

1. Introduction

Stainless steel (SS)/polymer hybrids are a new class of materials recently explored for composite applications in the form of either fibre reinforced composites [1–3] or sandwich panels (laminated steel plates) [4–6]. These hybrid materials combine the high stiffness and strength of stainless steel with the low density and other functionalities of the polymer, thereby offering a higher strength-to-weight ratio, improved corrosion and impact resistance, better dimensional stability and more design freedom [5,6]. However, the typical combination of high stiffness with high ductility of stainless steel has not been exploited to its full extend in composite applications, as steel combined with a polymer matrix generally suffers from a low interfacial strength [2,7,8]. The reported interfacial strength of native SS/epoxy is around 30 MPa with an adhesive failure pattern [8]. In combination with mild steel the interfacial strength is about 37 MPa before and 45 MPa after silane application [9]. Clearly, enhancing the interfacial strength for real life applications is mandatory [10,11]. This can be done in different ways [10–12]. First, one can increase mechanical interlocking with the matrix by increasing the substrate surface roughness through e.g. grit blasting [13], sand blasting [14], chemical etching or a combination thereof [7,14]. Another approach involves chemical modification of the surface [7,10–12] by e.g. the introduction of a coupling agent [7,11,14–19] which facilitates chemical bonding. The coupling agent acts as a molecular bridge between substrate and matrix, being able to establish covalent chemical bonds or physical interactions with both sides, in this way increasing adhesion [16]. Among the different adhesion promoters, especially silane-based molecules are frequently used [17,18]. In addition, silanes may increase corrosion protection and improve the composite thermal and mechanical properties as well as its chemical or moisture resistance [16,19]. Functional organosilane coupling agents have X_n–Si–$(R$–$Y)_{4-n}$ as general structure, in which X represents a hydrolysable group, mostly alkoxy or chlorine, R a spacer or linker group and Y the organofunctional group. After hydrolysis, the formed hydroxyl groups can react with the steel surface, while the organofunctional group remains available to react with the polymer matrix later on. Generally, silanes are attached to the substrate before matrix application. The wet deposition of silanes requires different steps, the first one being its hydrolysis in an (aqueous) solution to form active silanol (Si–OH) groups (Fig. 1a (left)). Second, these hydrolysed molecules are applied onto the steel surface

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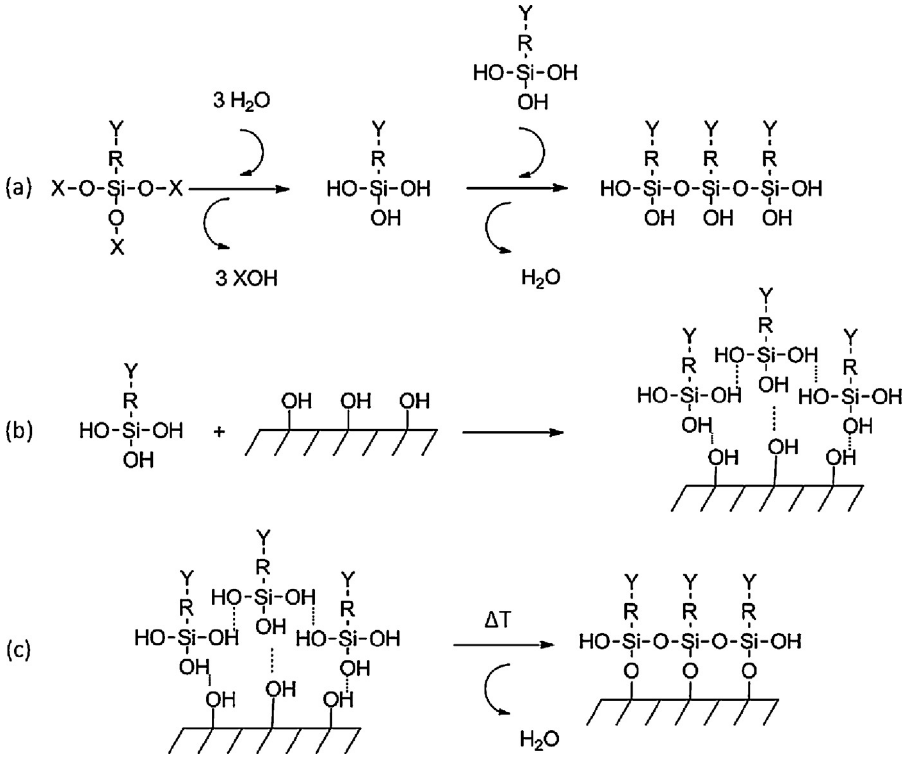

Fig. 1. Silane reaction scheme and working principle.

from solution, with the silane hydroxyl groups adsorbing through hydrogen bonding with the metal hydroxyl groups (Fig. 1b) [18,19]. Next, condensation takes place during a drying operation where silanol groups further covalently link with each other (Fig. 1a (right)) and with the substrate surface (Fig. 1c), forming, respectively, a siloxane network (Si—O—Si) and metal–siloxane (Si—O—M) bonds [11,16,18]. It is understood that the self-condensation of the reactive silanol groups in the solution prior to application on the metal substrate should be avoided as much as possible as this consumes hydroxyl groups, necessary for coupling to the steel surface. Moreover this can lead to the adsorption of oligomeric siloxane species on the steel surface, leading to weak points in the resulting polymer-metal hybrids. [16,18,20].

The properties and quality of siloxane layers, including its adhesion properties, strongly depend on the silane solution composition as well as on the deposition and condensation conditions (vacuum, temperature and time) [16,21]. The solution composition influences the silane hydrolysis, (self-)condensation and transetherification not only during the actual wet deposition but also during storage of the solution [16,22]. Typical solvents include water, alcohol or a mixture of both [16–19,23]. For solvent mixtures also the exact solvent ratio used influences the rates of the mentioned reactions and hence the solution stability and performance [16,22]. The solution pH affects the molecular orientation after deposition [16,21,24]. The silane concentration is often kept low to suppress self-condensation and limit the siloxane layer thickness after deposition [16,18,19,25]. Literature generally reports that the final film thickness (linearly) increases with the solution concentration, while the uniformity decreases [25–27]. As a result the interfacial strength often decreases when higher silane concentrations are used [19]. Siloxane monolayers most efficiently strengthen the interface in case of a perfectly flat and clean substrate [19], although in practice the optimum thickness depends on the type of substrate and its surface topography [19]. Deposition conditions such as dipping time and subsequent rinsing also have an effect on the siloxane layer formed. Longer dipping times increase the amount of silane adsorbed onto the steel surface, while rinsing removes loosely bound molecules, thereby improving the film uniformity [16]. Finally, the drying conditions affect the condensation degree, the amount of solvent evaporation and water release during condensation. All of this in turn affects the siloxane film properties and hence the performance of the envisaged hybrid.

This work uses γ-aminopropyltriethoxysilane as a coupling agent, given its ease of use and amino functional group (NH_2), which is reactive with the epoxy matrix [16,28,29]. The wet chemical deposition process is optimised for maximising the final interfacial strength of the surface treated SS/epoxy hybrid. The interfacial strength is evaluated by pull-off testing (dolly testing). Optimised parameters include the concentration and solvent composition of the silane solution, the dipping and rinsing time besides the time, temperature and use of vacuum during the drying and condensation of the silane layer. Ageing effects of the silane solution and of the treated surface on the interfacial strength are also considered.

2. Experimental

2.1. Materials

Bright annealed stainless steel (SS) plates type 304 with a thickness of 0.8 mm (OCAS, Belgium) were used as substrate for the silane surface treatment. SS plates were cut into pieces of 30 mm × 30 mm and cleaned ultrasonically in ethanol (3510 BRANSON ultrasonicator, 70 W) for 15 min immediately before silane deposition. After cleaning, the presence of hydroxyl (—OH) functionalities at the surface of the SS plates was confirmed by X-ray photoelectron spectroscopy (for more details see the Supplementary data, Fig. S.7).

γ-Aminopropyltriethoxysilane (APS) (≥99% purity) was supplied by Sigma-Aldrich (Belgium). The epoxy resin formulation was a stoichiometric combination of a diglycidyl ether of bisphenol A (DGEBA) based epoxy (EPIKOTE 828 LVEL) with an equivalent weight of 185 g/mol, supplied by Momentive Specialty Chemicals