IMPROVING THE PROPERTIES OF POLYMER-STEEL COMPOSITES BY USING SILANE COUPLING AGENTS

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Introduction

Polymer-steel hybrids may offer excellent properties for structural applications, since they can give rise to light weight and multifunctional composites. However exploiting these properties to the fullest requires sufficient adhesion at the interface, which can be obtained by taking advantage of silane coupling agents, which form a covalent chemical bridge between the two constituents. The type of coupling agent is polymer matrix specific and deposition can occur by dipping a steel substrate into an alkoxysilane solution in a water/alcohol mixture. The initial cleaning and quality of the steel surface as well as the solution properties play an important role. In order to obtain good coverage of the steel surface, the silane solution should wet it sufficiently, which can be achieved by maximizing the surface energy while decreasing the solution's surface tension. Furthermore the alkoxysilane molecules in solution need to be (sufficiently) hydrolysed before they can attach to the steel surface by condensation of hydroxyl groups, while self-condensation in solution should be minimized (Figure 1).
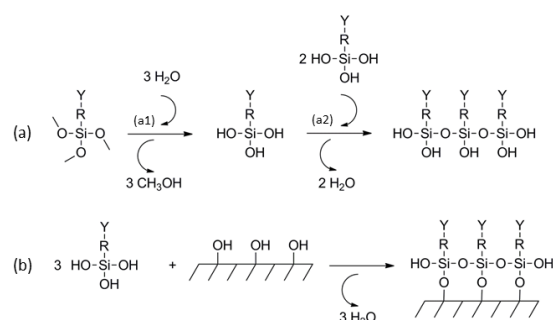

Figure 1(a) Alkoxysilane Hydrolysis (a1) and Self-Condensation (a2). (b) Condensation to the Surface

Experimental

1. Materials

Silanes used are shown in Figure 2: 3-Aminopropyl-triethoxysilane (APS) (a) and 3-glycidoxypropyltrimethoxysilane (GPS) (b) were pur-chased from Acros Organics, 1,2-bis(triethoxysilyl)ethane (BTSE) (c), acetic acid and deuterated solvents for NMR measurements from Aldrich, and ethanol from Chem-Lab. Unless mentioned otherwise, deionized water was used. Steel plates (stainless steel 304) were kindly provided by OCAS, Belgium, ultrathin fibers by Bekaert, Belgium.
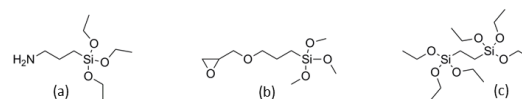
Figure 2 Silanes Used: APS (a), GPS (b) and BTSE (c)

2. Steel Substrate cleaning

Three different cleaning methods were used: Gently wiping the substrate with a paper tissue after the application of ethanol (method 1); Ultrasonic cleaning involvd 5 min of degassing followed by 10 min of ultrasonic cleaning (method 2); Alkaline cleaning concerned the use of industrially used Ridoline C72 (10 g/L, 3 s dipping) (method 3). After cleaning substrates are dipped in deionized water and, for tensiometry experiments, blown dry with filtered compressed air.

3. Silane deposition

First a silane solution was prepared from a water/alcohol mixture with a predefined ratio (v/v) to which the appropriate silane was added (and also acetic acid if needed). While stirring this solution for a certain time, the steel substrate was cleaned. After this, the cleaned substrate was dipped into the solution (silane/water/alcohol (v/v/v)) for 30 s, potentially rinsed in ethanol, followed by condensation of the silane to the surface in an oven at 90°C in the presence or absence of vacuum.

4. Experimental techniques

Dynamic tensiometry (steel plates) was performed using a Krüss K100 device with a measuring speed of 2 mm/min. Contact angles (steel plates) were measured in milli-Q water. To obtain surface energies, calculated by the Owens-Wendt theory, also dijodomethane and ethyleneglycol were used as measuring liquid.

XPS data (coated steel plates) were obtained with a VG S-Probe monochromatized XPS spectrometer with an $Al_{K\alpha}$ source.

^1H NMR and ^{13}C NMR measurements were done with a Bruker Avance 400, ^{29}Si NMR with the 600 type.

Results and Discussion

Contact angles reveal information on the surface energy of a substrate and hence on its wettability. A lower contact angle is related to a higher surface energy, which generally means a higher wettability (although also the surface tension of the liquid to spread influences the wettability). Dynamic tensiometry (Figure 4) clearly illustrates the effect of cleaning steel plates on the water contact angle. Method 1 seems to barely reduce the contact angle compared to the uncleaned specimen. Method 2 lowers the equilibrium contact angle, especially because of the receding part of the contact angle, which is related to the high energy, polar part of the surface, and points at the appearance of oxide groups [1]. Alkaline cleaning (method 3) lowers the contact angle still more, and influences also the advancing angle, related to the apolar part of the surface. This effect suggests more efficient removal of apolar contaminants. Comparing the oxygen peak composition of these samples, as measured by XPS, confirms these findings (Figure 4). While decreasing the contribution of (apolar organic) contaminants, cleaning increases the total oxygen content, by increasing the contribution of hydroxides and oxides, which are transformed into hydroxides after contact with the aqueous solution.

This clearly illustrates that cleaning is necessary to (a) remove contaminants, (b) generate/set free hydroxyl groups needed for an efficient coupling to silane hydroxyl groups and (c) to increase the surface energy, which facilitates spreading of the silane solution.
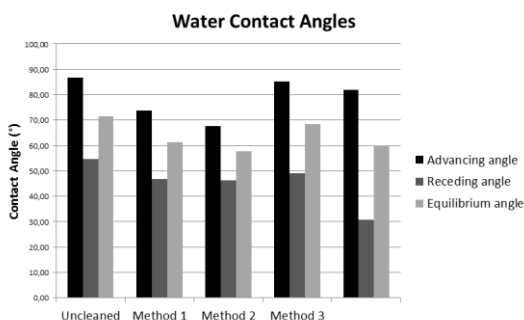

Figure 3 Water Contact Angle after Different Cleaning Methods
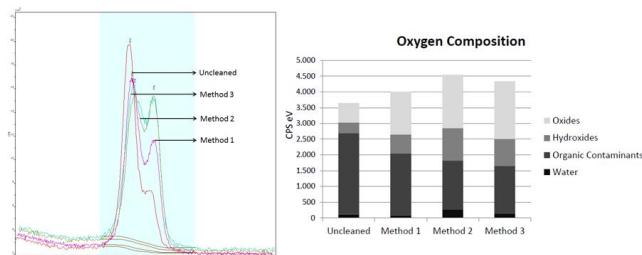
Figure 4 Oxygen Peak as Measured by XPS (left) and Consequential Oxygen Composition (right)

The requirement for maximum hydrolysis and minimum self-condensation of the silane molecules within solution justifies setting up a working window for silane deposition. The hydrolysis time was monitored by ^1H NMR. For APS mixtures complete hydrolysis takes only 5 min in 100% water and takes less than an hour in a 50/50 (water/alcohol) mixture (Figure 5). Adding acid increases this time up to 4 hours, probably due to an inhibition of the self-catalytic effect of the amine groups. For non-acidified GPS solutions, full hydrolysis takes at least 7 days for water solutions, and lasts up to one month in a 50/50 mixture. Due to the catalytic acid effect, hydrolysis is completed in less than 3 min when adding acetic acid. Importantly, the epoxy functionality is left intact in this case for at least 8 hours (as determined by ^{13}C NMR). For BTSE at least 50% alcohol and the addition of acetic acid are required to ensure BTSE solubility. Under these conditions full hydrolysis only takes a few min for 1.3% of acetic acid in combination with water and alcohol, which decreases when using more acid.
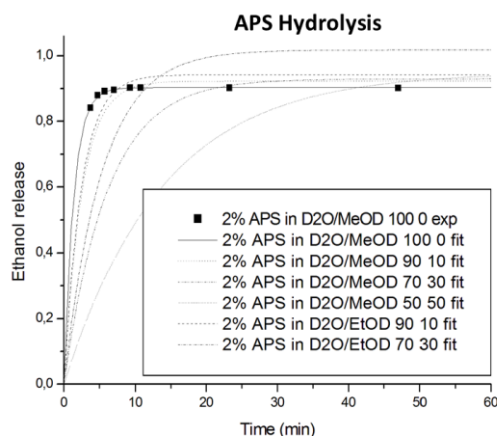

Figure 5 Hydrolysis of APS

Self-condensation times are determined by ^{29}Si NMR for the 90/10 solutions. This solvent ratio is selected as hydrolysis is faster when less alcohol is used, while a small amount of alcohol (10%) benefits wetting the substrate in the deposition step. For APS a considerable amount of self-condensation is found only after more than 13 h, while this time decreases to 9 h after the addition of acid. For both solutions the working window thus spans a few hours. The GPS self-condensation becomes prominent after 9 h for the acidified solution, while only after 12 to 14 hour for

the non-acidified solution. BTSE this time amounts at least 18 h. Except for the non-acidified GPS, these measurements reveal a working window of a few hours to deposit the silanes in their hydrolyzed but relatively uncondensed state onto the steel substrate.

Next the influence of rinsing after dipping a cleaned (method 2) steel plate in silane solution and the influence of a vacuum during high temperature silane condensation on the contact angle is studied for APS coated steel plates (Figure 6). After deposition and condensation of the silane layer the contact angle increases as a consequence of the disappearance of the freshly cleaned steel surface with an inherent high surface energy (related to cohesive forces always present in these type of specimen). Ethanol rinsing prior to high temperature condensation does not influence the contact angle, although thickness measurements show that definitely rinse off some of the silane, so it seems that rinsing at least leaves a monolayer. In contrast, the use of vacuum during high temperature condensation increases the contact angle, which may be due to the evacuation of water out of the silane layer in a vacuum.
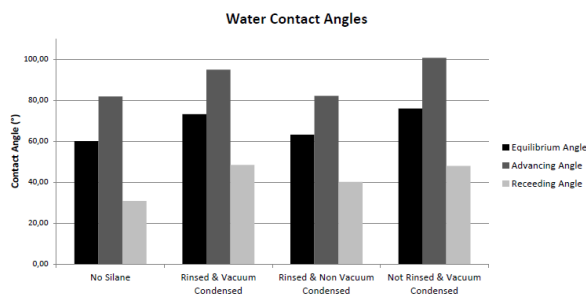

Figure 6 Influence of Condensation Parameters

When determining the surface energy for different samples, it is again clear that deposition of the silane decreases the surface energy (Figure 7). APS and GPS result in higher surface energies compared to BTSE, which is probably due to the lack of a functional group and larger apolarity of BTSE. When depositing APS subsequently to BTSE, it is clear there is still an influence of the underlying BTSE layer, as the surface energy is intermediate. Parallel deposition of these molecules by plasma techniques [2] leads to higher surface energies for these samples, probably due to remainders of highly reactive intermediates and the absence of a high temperature surface condensation step in a later stage. XPS also points at the destruction of silane molecules, indicating plasma deposition parameters were not ideal. Wet chemistry deposition results in thinner silane films, as clearly demonstrated by the iron signal (from the substrate) visible in XPS spectra of these samples. Thinner layers are preferred for a better coupling to the polymer matrix in a next stage.
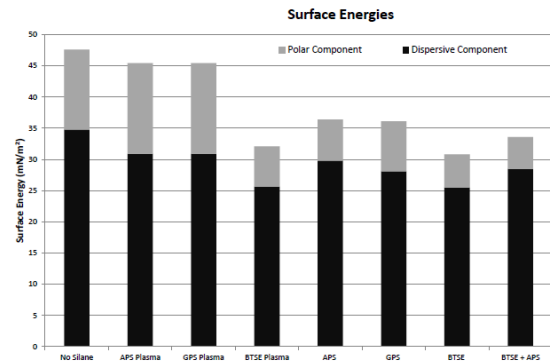
Figure 7 Surface Energy of Different Samples

Preliminary 3-point bending tests (in transverse direction) on quasi UD-composites of steel fibers in an epoxy matrix confirm the usefulness of a silane coupling layer (Figure 8) [3]. APS and GPS reveal a significant improvement of the composite strength, while the combination of BTSE and APS seems detrimental for the adhesion strength. This can be due to the lower surface energy and hence the poorer spreading of the epoxy on the coated surface, to poorer orientation and hence less availability of the amine functionalities, decreasing coupling and hence adhesion to the epoxy matrix, or potentially to the BTSE-APS phase being rather weak as a result of its thickness.
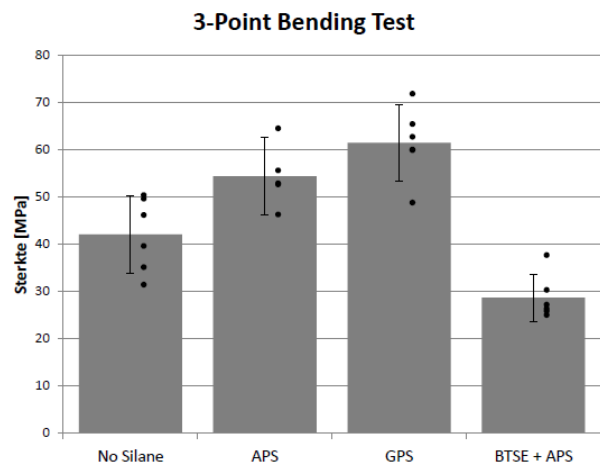
Figure 8 Strength of Quasi-UD epoxy-steel fiber composites as Determined from 3-Point Bending Tests

Conclusions

This work clearly demonstrates the need for appropriate (alkaline or ultrasonic) cleaning of steel surfaces prior to silane deposition. Ideal silane solutions can be prepared that combine wettability, maximized silane hydrolysis and minimum self-condensation over a reasonable time window. Rinsing of dipped steel samples before high temperature silane-steel condensation leaves at least a silane monolayer on the steel surface. Adverse effects are seen when the high temperature condensation is executed under vacuum. Epoxy-steel fiber composites display enhanced

mechanical properties when the fibers are silane coated. The presence of too thick silane layers or layers with a too low concentration of available functional groups may, however, lead to poorer mechanical properties.

Acknowledgements

References

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