Dipodal Silanes: Important Tool for Surface Modification to Improve Durability

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ABSTRACT

Dipodal silanes possess two silicon atoms that can covalently bond to a surface. They offer a distinctive advantage over conventional silanes in terms of maintaining the integrity of surface coatings, adhesive primers and composites in aqueous and aggressive environments. The improved durability of such dipodal silanes is associated with an increased crosslink density of the interphase and the inherent resistance to hydrolysis, as they can form six, rather than three, Si-O bonds to the substrate. This study examines dipodal silanes with hydrophobic alkyl functionality and compares them with similar functionality on conventional silane coupling agents. It also introduces new structural dipodal silanes containing “pendant” and “bridged” functionality and then examines their stability in aqueous environments. In strongly acidic and brine environments, dipodal silanes clearly demonstrate improved resistance to hydrolysis compared to conventional silane coupling agents.

INTRODUCTION

Silane surface modification [1-3] is an important tool to improve and/or change the properties of various substrates and is applied by various industries involved with medical devices, transportation, construction, energy, biotechnology etc. Maintaining the integrity of the treated surface is therefore very important to the longevity and performance of the resultant coating. However such performance is strongly affected by the wetting at the interface.

Figure 1: Covalent bonding to a hydroxylated surface by (a) conventional and (b) dipodal silane.

Dipodal silanes [4] have two silicon atoms that can covalently bond to a surface unlike conventional silane coupling agents, which have one such silicon atom for surface attachment (figure 1). In this way dipodal silanes offer a distinctive advantage as this extra point of surface attachment helps maintain the integrity of the resultant surface coatings, adhesive primers and composites in aqueous environments through improved ‘wet’ durability. Such improved durability is also associated with an increased crosslink density of the dipodal silane interphase as it also extends out from the surface, providing further resistance to hydrolysis. Calculations based on the equilibrium constant for $\equiv Si-O-Si\equiv$ dissociation to silanols indicate that dipodal silanes have 10,000 times greater resistance to hydrolysis than conventional silanes. We
therefore examine the experimental hydrolytic stability for several hydrophobic dipodal silanes as compared to conventional silanes. Structurally different dipodal silanes with either “pendant” or “bridged” functionality are also examined. Significantly, we probe resistance to hydrolysis in acidic and brine environments, where dipodal silanes clearly demonstrate the best performance.

EXPERIMENTAL

Silanes

1,2-Bis(trimethoxysilyl)decane (B, Product code SIB1829.0) was prepared according to the method earlier reported [5]. N-Decyltriethoxysilane (A, Product code SID2665.0), 1,1,1,3,3-Pentamethoxy-1,3-disilaundecane (C), 1,10-Bis(trimethoxysilyl)decane (D) were synthesized by Gelest and are available commercially. The synthetic details for the silanes will be presented in a later publication.

Sample preparation

Borosilicate glass slides (Schott North America, Inc.) were acid etched before silane treatment by dipping in 4 wt% HCl for 45 min before washing with (i) deionized water (5 mL), (ii) ethanol (5 mL) and (iii) acetone (5 mL). The slides were dried under N₂ and treated with the various silanes immediately.

A 2 wt% solution of n-decyltriethoxysilane (A) was prepared in cyclohexane and a small amount of deionized water (less than 0.5 wt%; containing enough glacial acetic acid so that the pH = 3-5) was added with stirring. The stirred silane solution was allowed to hydrolyze for 5 h prior to dipping the cleaned glass slides into the stirred solution. After 20 h the glass slides were removed and rinsed with cyclohexane, dried under N₂ before being put into an oven at 110 °C for 30 min. The glass slides were allowed cooled to room temperature in a desiccator and the water contact angles were measured. The contact angle measurements were carried out on a Ramé-Hart 100 goniometer. Multiple sessile drop contact angle (advancing and receding) measurements were carried out for each silane and the average numbers (minimum of 6 measurements) are reported. Glass slides were also prepared for silanes B-D and the respective water contact angles were measured following the same procedure.

Durability of silanes

The durability of the silane coating was assessed by static immersion tests in both 6 M HCl and 3.5 wt% aqueous NaCl. When each slide was then taken out of its solution, it was rinsed with water, dried under N₂ before being put into an oven at 110 °C for 30 min. On cooling to room temperature the water contact angles were measured. After each contact angle measurement the treated slides were re-immersed in their 6 M HCl or 3.5 wt% aq. NaCl. The process was repeated for all the samples at specified intervals for ~75 days in 6 M HCl and ~45 days in 3.5 wt% NaCl.

RESULTS AND DISCUSSION

The structure of the various silanes is shown in figure 2. N-Decyltriethoxysilane is a conventional silane coupling agent with one silicon atom available for bonding to a substrate. The three dipodal silanes, 1,2-Bis(trimethoxysilyl)decane, 1,1,1,3,3-Pentamethoxy-1,3-
disilaundecane and 1,10-Bis(trimethoxysilyl)decane, have two silicon atoms with unique locations on the alkyl chain in each silane. The presence of two silicon surface attachment sites gives these dipodal silanes an increased cross-linked density at the glass surface, which increases the adhesive strength and the durability of the coated surfaces. All the dipodals listed above are structurally different, which affects their wetting behavior. 1,2-Bis(trimethoxysilyl)decane has two carbons between the trimethoxysilane centers (one located β to the terminal silane center, and pendant to the main alkyl chain), while 1,1,1,3,3-Pentamethoxy-1,3-disilaundecane only has one carbon atom between the di- and tri-methoxysilyl centers with both located within the alkyl chain. 1,10-Bis(trimethoxysilyl)decane with the silicon atoms located at each end of the alkyl chain, in a sense ‘bridging’ the alkyl chain. The structural variations affect how each dipodal silane can bond to the glass surface hydroxyls. A variation in the structure does not affect the method of deposition as the mechanism is only dependent upon the hydrolysis of the alkoxy groups –Si–(OR)$_3$.

![Figure 2: Structure of the Various Silanes](image)

**Silane treatment and durability**

The initial sessile, contact angle measurements (advancing and receding) for the various silanes (A)-(D) above after undergoing a 5 h hydrolysis and 20 h treatment time is listed in table I. All the silanes, but 1,10-Bis(trimethoxysilyl)decane, show sessile water contact angles (CA) ≥90°. All the silane coatings show a hysteresis (advancing CA – receding CA) >10° generally indicative of surface defects or inhomogeneities, but after examination by SEM (scanning electron microscopy), the samples revealed a smooth homogeneous coating (data not shown).

The silanes investigated in this manuscript have long alkyl chains and are therefore expected to exhibit water contact angles (CA) in the hydrophobic region (>90°) [6]. 1,10-Bis(trimethoxysilyl)decane has its two trialkoxy silicon groups bridged by a long alkyl chain. It does not have any free terminal methyl groups able to contribute towards its hydrophobic behavior. Even though it does have the capability to produce a highly cross-linked structure, absence of any free methyl groups leads to a consistently <90° water CA for this silane (Table I). All other silanes have long alkyl chains having methyl terminal groups extending out into the contact water drop so leading to sessile water CA >90°.
The positioning of silicon bonding sites plays a very important role in the self-assembly of such dipodal silane coupling agents. Figure 3 illustrates a very simplistic model of how the various silanes can assemble onto a hydroxyl rich borosilicate glass surface. N-Decyltriethoxysilane, 1,2-Bis(trimethoxysilyl)decane, and 1,1,1,3,3-Pentamethoxy-1,3-disilaundecane assemble onto the glass surface to closely resemble a self-assembled mono-layer structure [7]. Both 1,2-Bis(trimethoxysilyl)decane, and 1,1,1,3,3-Pentamethoxy-1,3-disilaundecane can form a more crosslinked interface compared to N-decyltriethoxysilane. Such additional linkages to the surface should significantly influence the longevity of the coating.

1,10-Bis(trimethoxysilyl)decane with bonding silicon atoms at both ends can do a variety of things – (i) the molecule can lay flat/loop on the surface occupying a lot of area but not satisfying all the surface hydroxyls, (ii) it can stand up and condense with neighboring terminal – Si(OCH\textsubscript{3})\textsubscript{3} creating a ≡Si–O–Si≡ network which leaves some hydrophilic groups at the outer surface. This silane however can still create a densely cross-linked structure similar to the other dipodal silanes used.

The static immersion durability tests were conducted in 6 M HCl and 3.5 wt% aq. NaCl, both of which are very harsh. The ≡Si–O–Si≡ linkage is very susceptible to hydrolysis at pH < 3 and 6 M HCl has a pH of -0.78. 3.5 wt% aq. NaCl, which is a brine solution, mimics sea water concentration and is a known nuisance to maintaining the integrity of coatings. The integrity of the coating is directly related to the water CA measured on the substrates. Figure 4 (a,b) shows the progression of the sessile water CA with time for the glass substrates coated with various silanes (A)-(D) above for static immersion tests in (a) 6 M HCl and (b) 3.5 wt% aq. NaCl. In figure 4, it is clear that all the silane treatments except 1,10-bis(trimethoxysilyl)decane start well within the hydrophobic region (water CA>90°). 1,2-Bis(trimethoxyxil)decane, and 1,1,1,3,3-pentamethoxy-1,3-disilaundecane form the most rigid and durable coatings as the static water CA after 75 days in HCl is 85±1.6° and 99±0.9° respectively. The conventional silane, n-decyltriethoxysilane, and the pendant dipodal, 1,2-bis(trimethoxysilyl)decane, CAs follow each other very closely up to day 28, after which the conventional silane coating starts to degrade significantly. The CAs drop from 102±1.1° on day zero to 63±4.5° on day 75 for n-decyltriethoxysilane. Similar behavior is seen for the static immersion tests in 3.5 wt% aq. NaCl (carried out over a period of ~ 45 days), where the conventional silane (A) starts to degrade as

<table>
<thead>
<tr>
<th>Silane</th>
<th>Water Contact Angle (°)</th>
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<tbody>
<tr>
<td></td>
<td>Sessile</td>
</tr>
<tr>
<td>N-Decyltriethoxysilane (A)</td>
<td>94±0.6</td>
</tr>
<tr>
<td>1,2-Bis(trimethoxysilyl)decane (B)</td>
<td>102±1.1</td>
</tr>
<tr>
<td>1,1,1,3,3-Pentamethoxy-1,3-disilaundecane (C)</td>
<td>104±1.5</td>
</tr>
<tr>
<td>1,10-Bis(trimethoxysilyl)decane (D)</td>
<td>78±2.4</td>
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early as day 15. The coatings with dipodal silanes (B-D) show minimal effect of the brine solution.

![Figure 3: A simplistic representation of how the various decyl silanes assemble on glass (a) n-Decyltriethoxysilane (A), (b) 1,2-Bis(trimethoxysilyl)decane (B), (c) 1,1,3,3-Pentamethoxy-1,3-disilaundecane (C) and (d) 1,10-bis(trimethoxysilyl)decane (D).](image)

![Figure 4: Sessile water contact angle measurements for (a) 6 M HCl and (b) 3.5 wt% NaCl. Data for an untreated “control” slide is also shown in both the graphs.](image)
Dipodal silanes have also been reported to be used as additives to improve the mechanical and adhesive strength of coatings [1,4,8-9]. The durability studies in 6 M HCl and 3.5 wt% aq. NaCl clearly indicate the advantages of using a dipodal silane over the analogous conventional silane coupling agent. These studies conducted over ~75 day period are being continued for at least 6 months (180 days) to assess the progression of the dipodal coating durability under these conditions. The dipodals silanes form a highly crosslinked interphase making it difficult for the 6 M HCl acid used, to degrade the coating and promotes longevity of the surface treatment. We are also assessing the durability of these coatings in deionized water and under strong basic conditions. Silanes are known to have least tolerance towards solutions where the pH >12, so these new durability studies will be very revealing.

CONCLUSIONS

Novel dipodal silanes with various structures were successfully synthesized and deposited on the hydroxyl rich surfaces. A variation in the structure does not affect the method of deposition as the mechanism is only dependent upon the hydrolysis of the alkoxy groups –Si–(OR). The structural differences, however do affect the nature of the coating where a dipodal containing silane alkoxy groups at each end of a long alkyl chain creates a surface, which is not as hydrophobic as those silanes where free alkyl chains with terminal methyl groups extend out into a water drop. Static immersion studies under highly acidic and brine conditions over a period of ~75 days reveal that dipodal silanes do form a highly cross-linked network that outlasts the conventional alkylsilane coupling agent. These studies will be continued to assess the long term durability of the dipodal silanes. We plan to extend such durability studies to include immersion in deionized water and basic pH solution.

REFERENCES