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Full Length Article

# Organosilane grafted silica: Quantitative correlation of microscopic surface characters and macroscopic surface properties

Tuo Ji[a], Chi Ma[b], Logan Brisbin[a], Liwen Mu[a], Christopher G. Robertson[c], Yalin Dong[b], Jiahua Zhu[a,*]

[a] Intelligent Composites Laboratory, Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, OH 44325 USA
[b] Department of Mechanical Engineering, The University of Akron, Akron, OH 44325 USA
[c] Eastman Chemical Company, 260 Springside Dr, Akron, OH 44333, USA

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ABSTRACT

In polymer composites, organosilanes are often used to modify the surface property of silica nanoparticles and improve the interfacial properties. Surface properties of the modified silica, such as grafting density and consequent surface energy, largely depend on the molecular structure of the silane. Achieving maximum interfacial bonding between the filler and polymer requires precise control of silica surface property. In this work, four silanes with similar molecular structure but different alkyl chain lengths, trimethoxy(propyl)silane, trimethoxy(octyl)silane, hexadecyltrimethoxysilane and trimethoxy(octadecyl)silane, are selected as model agents to study their roles in influencing silica surface property. The grafting density of silane on the silica is well controlled by regulating the reaction conditions. Three main surface characters, silane grafting density, surface energy and surface potential, are measured. More importantly, a linear relationship has been correlated when plotting grafting density vs. surface energy and grafting density vs. surface potential. Utilizing these relationships, a linear model has been developed to predict grafting density and surface energy by simply measuring surface potential. This model has been validated by both commercial silica and synthesized silica particles of different sizes.


## 1. Introduction

Surface functionalization of silica nanoparticles has become an essential for its numerous successful applications, such as drug delivery, support of heterogeneous catalyst, reinforcing filler and etc [1–6]. Organosilane, abbreviated as silane in this work, is the most widely used chemical agent for silica surface modification. Silane molecules are typically comprised of two functional parts, one part reacts with the silica surface to form covalent bond and the other forms physical/chemical interactions with the surrounding materials. The wide variety of silane structures, including alkyl chain length, terminal functional groups and number of reactive sites [7], provides a great platform to design silica surface functionalities. Numerous work has been reported on the assembling behavior and patterning of silane molecules on different substrates [8–11]. Silane grafting has resulted in a variety of practical benefits in terms of material performance. For instance, bis(triethoxysilylpropyl) tetrasulfane can enhance the dispersion and compatibility of silica nanoparticles in the dense membrane of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), which affects methanol diffusion selectivity in the liquid [12]. Also, it is possible to design nanoparticles with superhydrophobic properties [13,14]. Indeed, the silane molecule structure determines the subsequent surface properties to a great extent, but it is not the only factor since silane patterning and surface coverage also govern surface properties in most cases [7,15]. Therefore, the silane's molecular structure and surface coverage are equally important to achieve the desired surface properties.

The determination of interfacial bonding and quantification of silane grafting density have been studied by using different characterization techniques [16–18]. For example, nuclear magnetic resonance (NMR) and flourier transform infrared (FT-IR) are very useful qualitative tools to identify covalent bond formation, surface group species and cross-linking [18,19]. To further quantify the amount of grafted molecules, thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) were used to provide specific surface information on loading, atomic ratio of different elements, and grafting coverage, respectively [16,20–22]. A microscopic understanding of silane function requires a precise quantification of silane grafting density (or

* Corresponding author.
*E-mail addresses:* jzhu1@uakron.edu, jhzhu.yzu@gmail.com (J. Zhu).

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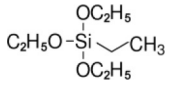
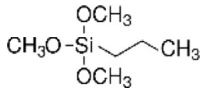
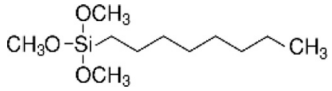
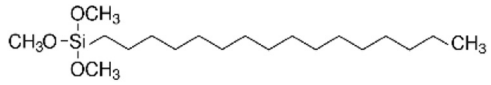
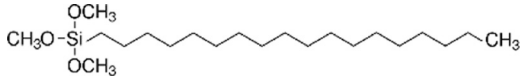
**Table 1**
Detailed information of silanes used in this work.

| Silane | Structure | Molecular formula | Mw (g mol$^{-1}$) | $r_{a/s}$ |
|---|---|---|---|---|
| TEES |  | $C_8H_{20}O_3Si$ | 192.3 | 0.15 |
| TMPS |  | $C_6H_{16}O_4Si$ | 164.3 | 0.26 |
| TMOS |  | $C_{11}H_{26}O_3Si$ | 234.4 | 0.48 |
| HDTMS |  | $C_{19}H_{42}O_3Si$ | 346.6 | 0.65 |
| OTMS |  | $C_{21}H_{48}O_3Si$ | 374.7 | 0.68 |

$r_{a/s}$: Molecular weight ratio of alkyl chain to whole silane molecule.

coverage) on silica surface. Traditionally, only a partial surface property can be accessed by using single characterization technique, which provides only limited information and it is difficult to correlate the macroscopic surface properties. Therefore, tremendous research efforts have been devoted to obtain quantitative information on surface functional groups by combining different techniques [23]. For example, Fischer et al. found the relationship between fluorescence and XPS signals, which allows a direct correlation between an analysis of fluorescence and quantification of XPS [20]. However, it met significant challenges to quantify the grafting density of silane without nitrogen element such as silanes with aliphatic chains [24]. Rostami et al. utilized tensile strain experiments and dynamic mechanical thermal analysis to provide information on interfacial adhesion. By controlling the loading of silane-treated silica, it was shown that interfacial interactions were directly proportional to the amino silane content on silica nanoparticles [25]. Those methods mentioned above require lengthy sample preparation and skillful operation of expensive instruments, which greatly restricts their use in practical applications.

Besides the techniques mentioned above, some other macroscopic surface properties, such as surface potential, wettability and surface energy [26,27] can be used to quickly index the surface property as well. However, a quantitative correlation between microscopic information and macroscopic surface properties is not available right now. Once a mathematical model between microscopic surface information and macroscopic surface properties can be built, then, the microscopic information can be directly speculated by macroscopic surface properties without involving lengthy sample preparation and expensive instrumental analysis.

In this work, we selected four different silanes with similar molecular structure but different alkyl chain lengths to modify the silica surface. By controlling the silane grafting density across a wide range, different surface properties including surface energy and surface potential can be obtained. The relationship among silane grafting density, surface energy and surface potential on both commercial silica and synthesized silica are explored. A linear model is built and validated to predict the silane grafting density and silica surface energy from zeta potential. Comparing with conventional quantification methods, like NMR, XPS, this method provides obvious advantages of convenient sample preparation and short testing time.

## 2. Experimental

### 2.1. Materials

Triethoxy(ethyl)silane (TEES, 99%), trimethoxy(propyl)silane (TMPS, 97%), trimethoxy(octyl)silane (TMOS, 96%), hexadecyltrimethoxysilane (HDTMS, 85%), trimethoxy(octadecyl)silane (OTMS, 90%), methanol (≥99.8%), commercial silica nanoparticles (c-$SiO_2$, ~16 nm) and tetraethyl orthosilicate (TEOS, 98%) were purchased from Sigma Aldrich. Formic acid (97%) was purchased from Acros Organics. Ammonium hydroxide (28%) was purchased from BDH chemicals. Ethanol was purchased from Decon Labs. Inc. The structural and compositional information of silane molecules are provided in Table 1. All chemicals were used as received without further purification. Deionized water (Millipore) was used throughout the experiment.

### 2.2. Silica surface modification by silanes

One unit of silane was sonicated in 10.0 g of methanol:water (90:10) for 10 min and 1.0 g of formic acid was added into the mixture solution. After 30 min, 0.5 g of c-$SiO_2$ powder was added to above mixture solution and then reacted at 65 °C for 24 h. The ratio of silane/silica is 2.0, 2.5, 3.0, 3.5 and 4.0 mol% for TMPS, and the ratio is controlled at 0.5, 1.0, 2.0, 3.0 and 4.0 mol% for TMOS, HDTMS and OTMS. The resulting samples were separated and rinsed with 200 mL methanol. The samples were then dried at 80 °C for 12 h. The modified silica particles were named in the format of "silane-#". "silane" represents the five selected silanes in this work, *i.e.* TEES, TMPS, TMOS, HDTMS and OTMS. "#" means the mole percentage of silane used to modify the silica nanoparticles. For example, TMPS-2, TMPS-2.5, TMPS-3, TMPS-3.5 and TMPS-4 were named for c-$SiO_2$ grafted by 2, 2.5, 3, 3.5 and 4 mol% of TMPS.

### 2.3. Synthesis of silica particles

Silica particles with different sizes were prepared following the well-known Stöber method [28]. Firstly, ethanol and deionized water were mixed and kept in a sonication bath. Then, TEOS was dropwise added into the mixture and kept sonicating for 20 min. At last, ammonium hydroxide was added into the mixture and kept sonication for another hour. A white turbid suspension was formed