



Investigation of hydrophobic coatings on cellulose-fiber substrates with in-situ polymerization of silane/siloxane mixtures



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ARTICLE INFO

Keywords:

Cellulose
Micro-roughness
Silanization
Contact angles
Hydrophobicity

ABSTRACT

The purpose of this study was to investigate the interfacial interactions of SilRes BS290, a mixture of silanes and siloxanes, upon in-situ polymerization and curing over cellulose substrates (40 and 110 °C), and to further investigate the influence of these chemical interactions with hydrophobic development of the film. SilRes solutions (7 wt%) were prepared in n-heptane and roll-coated over pure cellulose substrates (Whatman). The bond development with time was monitored with FTIR, and was compared with surface hydrophobic development, monitored with contact angle analysis using deionized water droplets. It was found that the bond development was completed well before the onset of surface hydrophobicity in both the low and high temperature curing cases, with superhydrophobicity being observed for the high temperature preparations. Hydrophobic development tended to be influenced more strongly by surface topology resulting from the appearance of 300 nm-size polysiloxane beads on the fiber surface. Film porosity was also observed in some cases which additionally improved the hydrophobic outcome of the surface. While the hydrophobic behavior did not appear to coincide with the interfacial bond development of the in-situ polymerized film, damage to the surface hydrophobic layer via mechanical action decreased the hydrophobic performance in some cases. This was mainly due to a reduction in vibrational activity of the surface hydrophobic groups. High temperature curing maintained hydrophobic performance despite similar damage to chemical bonding, perhaps as a result of higher levels of covalent bonding to the substrate. Therefore, although the hydrophobic surface requires roughness and porosity to fully form, the chemical hydrophobicity created from polymerization also ultimately contributes to the overall hydrophobicity observed.

1. Introduction

Organosilanes, first discovered in the 1940s [1], are frequently used as coupling agents to adhere polymeric substances with specific properties to inorganic substrates, such as metals, glass, or other inorganic minerals [2–4]. The general form of silanes is $R'-Si-(OR)_3$, and the R' group is often a functional organic group (e.g. amino, chloro, etc.) that can react with a polymer identified for attachment to a substrate. The OR groups are often methoxy or ethoxy groups, and are easily hydrolysed to form silanols [1,2]. The silanols may react with themselves, forming a siloxane oligomer, with a characteristic $-Si-O-Si-$ linkage [1,2,5–7], and can also attach to the substrate in one of two methods, depending on conditions and the balance between hydrolysis and condensation. Covalent bonding of polysiloxanes onto the substrate is often observed at high thermal curing temperatures (at least 110 °C) where a condensation reaction occurs. At lower temperatures (room or 40 °C), it is more likely hydrogen-bonding that occurs between the

polysiloxanes and substrate [6]. This has been confirmed with FTIR studies [8–10] and soxhlet extraction methods [11].

While the polysiloxanes may be used as a bridge between polymeric substances and a given substrate, silanes themselves have useful hydrophobic properties if the R' group is a hydrocarbon chain, and these may be exploited without the need for attaching additional polymeric content.

Silane coupling agents were initially applied to inorganic substrates, however more recent research has focused on opportunities to modify cellulose fibers with polymeric substances for added strength, primarily for applications in reinforced fiber materials [7–13]. Fewer studies have exploited the hydrophobic properties of stand-alone silanes on paper substrates as coating applications. One study by Karapanagiotis et al. [5] utilized silica nanoparticles dissolved in silane/siloxane mixtures that were brushed onto paper substrates. The silane/siloxane mixture polymerized in-situ over the substrate forming a film, and the resulting surface was superhydrophobic, confirmed with contact angle (CA)

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analysis. Without the nanoparticles, the CA was still hydrophobic, averaging 125°. The surface chemistry of the films with and without silica nanoparticles was deemed similar, but it was the surface roughness that accounted for the difference in wettability. High resolution Scanning Electron Microscope (SEM) images showed a ‘beaded development’ of siloxane over the paper fibers, while the nanoparticles showed additional flower-like aggregation on the surface. In another study, Matin et al. [14] applied 0.2 M octadecyltrichlorosilane (ODTS)/hexane solutions directly onto plasma-cleaned glass and plastic substrates pre-hydroxylated with DI water, with overnight drying at ambient conditions. SEM analysis showed a somewhat surprising ‘dual-scale’ roughness of the ODTS film over the substrate. This type of structure has been known to occur in the presence of sufficient moisture, where vertical polymerization of the siloxanes occurs in addition to horizontal polymerization across a surface with hydroxyl groups. CA analysis consistently showed CA well in excess of 150° and a contact angle hysteresis (CAH) of around 10°, thereby exhibiting self-cleaning properties.

The ability of silanes to strongly attach to –OH groups on cellulose fibers represents an opportunity to modify paper or paperboard for packaging applications. Traditionally, paperboard packaging has been hydrophobized using paraffin coatings, which represents a simple, inexpensive method for transporting meat, fish and other ‘wet’ produce by providing an excellent water-proof barrier [15]. The method of attachment is more likely to be entanglement between the long paraffin chains and the highly porous nature of the cellulose substrate, as well as possible diffusion of the wax through the pores [16]. Unfortunately, wax cannot be recycled due to fouling issues from the wax in recycling machines, and traditional wax coatings are being phased out in favor of more eco-friendly recyclable wax alternatives [17]. Statistics from 2013 show a 653% increase in usage of recyclable wax alternatives since 2002, which include natural waxes such as beeswax [18] or biopolymers [19]. Therefore, alternative and safer options for hydrophobizing paperboard are becoming popular, and the required research to fully understand the performance of these new alternatives is growing along with the developments. The stronger, more permanent attachment of silanes onto cellulose substrates will assist in reducing coating or film damage upon mechanical action, and, given that they are ecofriendly [2], could be introduced either into a typical paper coating formulation or used solely.

The overall goal of this work is to demonstrate that silane coatings on cellulose substrates represent an effective option for hydrophobic promotion, and that their strong attachment to the substrate enables them to better withstand mechanical stress without compromising their performance. The relative dominance between topology of the silane film; chemical nature of the film surface; curing temperature; and interfacial bond formations between film and substrate will be ascertained to understand the conditions that best promote a hydrophobic film. This will be achieved through analysis of SEM, CA and Fourier Transform Infrared (FTIR) measurements. Secondly, changes in chemical bonding attachment of the silane film to the substrate upon mechanical deformation (in the form of folding), and its effect on hydrophobic performance, will be studied.

2. Experimental

2.1. Materials

SilRes BS290, a mixture of vinyltrimethoxysilane, its siloxane, and others with varying-length hydrocarbon backbones, was kindly donated from Wacker and used without further modification. For simplicity, the structures shown in Fig. 1 will be used to represent this mixture. Solutions of SilRes were prepared at 7 wt% in n-heptane (Sigma) unless otherwise stated. DI water used as a pre-coat to emulate a partially dried paper was deionized with a Direct-Q # UV purification system.

Whatman qualitative filter paper (90 mm, grade 1) was used as pure

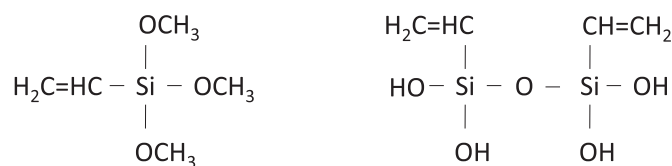


Fig. 1. Chemical structure of vinyltrimethoxysilane (left) and its hydrolyzed form siloxane (right), both of which are present in SilRes BS290. Siloxane is prepared via hydrolysis and condensation of silane. Polysiloxane (not shown) will occur via the –OH groups in the siloxane molecule [20].

cellulose substrates.

2.2. Methods

2.2.1. Preparing the paper substrates

A ChemInstruments Laboratory Coater was used to coat the Whatman filter paper with silane solution. The filter paper was attached to the pull-through substrate provided, and coated initially with 1.1 mL water delivered with a syringe. The height of the two rolls was set at 100 μm to evenly spread the coating across the substrate sample. The water-coated samples were loosely wrapped in paper toweling, covered and stored at room temperature for an average of 48 h. Coating with 7 wt% silane solutions in n-heptane (Sigma) proceeded in a similar fashion, using 1.2 mL of solution on the ChemInstruments coater to ensure an even coverage.

2.2.2. Curing times

Room temperature studies required prepared coatings to be stored overnight for full curing. Those done at 40 °C were typically placed in the oven for at least 5.5 h, and those at 110 °C for at least 3 h following coating application, when fully cured samples were required. These times were determined from preliminary silane trials. Any testing performed ‘during curing’ was done within these maximum time limits.

2.2.3. Contact angle (CA) analysis

CA analyses were performed using a Biolin Scientific OneAttention|Theta, to accurately track the hydrophobic development of the surface with time. Coated samples were maintained in the Precision Oven at either 40 or 110 °C, and removed at various times to undergo CA testing. Using the OneAttention software and a calibration ball, the USB3 video camera was focused and calibrated before every experiment. The water droplet was then dispensed from an overhead syringe onto a small section cut from the original coated cellulose substrate. Images were recorded at 14 frames per second (fps) until such time as the droplet had penetrated the substrate, and the results were analyzed using the OneAttention software.

2.2.4. FTIR analysis

ATR-FTIR studies on the surfaces were conducted using an Agilent Cary 630 instrument to determine the degree of polymerization of the silane coatings and identify any covalent bonds forming between the coating and substrate. The samples were typically tested one hour after being placed in the oven set to either 40 or 110 °C, and then subsequent times when doing kinetic monitoring of peak development. Methodology followed instructions provided in the Cary software.

2.2.5. SEM imaging

A JSM-5600 unit (JEOL USA Inc., Peabody, MS) with in-built software (JSM-5000) was used to take images of partially and fully-cured samples, prepared at 40 and 110 °C. The samples were partially cured for approximately 1 h and imaged no more than 2 h later, while the fully cured samples were prepared and then imaged up to 3 days later. Each sample was coated for 120 s with gold particles using a sputter coater Hummer 6.2 (Anatech USA, Union City, CA) at near vacuum

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