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Preparation of hydrophobic self-assembled monolayers on paper surface with silanes

Min-Jung Oh [a], Sun-Young Lee [b], Ki-Hyon Paik [a,*]

[a] Division of Environmental Science and Ecological Engineering, College of Life Sciences and Biotechnology, Korea University, Seoul 136-701, Republic of Korea
[b] Department of Forest Resources Utilization, Korea Forest Research Institute, Seoul 130-712, Republic of Korea

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ABSTRACT

This study was conducted to obtain hydrophobic self-assembled monolayers on paper surface with silanes by a simple and facile method in the vapor or solvent phase. Filter papers with water contact angle over 120° were successfully prepared under sufficient reaction time and silane concentration, and their hydrophobic properties were evaluated by the contact angle measurement and stöckigt size test. And the effect of SAM-formation on mechanical properties of paper like wet tensile strength and PPS roughness was also presented. Results from the study reveal the effective reaction time and silane concentration to form stable SAM depending on the coating method and the silane treatments. The fabrication of self-assembled monolayers on the surface of the papers with silanes proved to be a simple process for the preparation of the superhydrophobic papers.

1. Introduction

A sizing process is performed on most papers to provide resistance to liquid penetration. Internal sizing with a rosin acid sizing agent or Alkyl Ketene Dimer (AKD) and Alkenyl Succinic Anhydride (ASA) is performed at the wet end, but surface sizing uses mainly modified starches to form a water-repellent film on the paper surface [1]. It is a common practice to transform the hydrophilic papers into the water-repellent ones by the sizing process. On the other hand, there is a need to find a new and easy method to modify the surface properties of the papers in other industries, particularly nano-technology. This can be accomplished by using self-assembled monolayer (SAM) which is spontaneously formed monolayer and can produce needed surface properties on substrate. The SAM has high chemical and physical stabilities and a variety of the desired surface properties. For example, hydrophobic surfaces can be produced with the chemical treatment. Due to its advantageous properties, the SAM has potential applications in the surface modification, chemical and biosensor, and corrosion prevention [2–4]. The unique properties of the SAM can be utilized for the formation of the hydrophobic surface on papers.

The formation of the SAM can be accomplished by the reaction at an aqueous phase using various solvents or by the reaction at a vapor phase when absorbents have volatile molecules. Especially, alkylsiloxanes form the SAM on the surface with OH– such as SiO_2, Al_2O_3 and glass using alkylchlorosilanes and alkylalkoxysilanes. However, little information is available about formation of the SAM on soft materials such as cellulose, although there is some information in textile and packaging material fields. For instance, silicone nanofilament was formed on various substrates in aqueous TCMS (trichlorometylsilane) [5] and water vapor phase, and the SAM was formed on synthetic and natural textile materials in vapor phase of the TCMS [6]. The SAM was formed on cotton cellulose fiber by the chemical vapor deposition in a sealed chamber that maintained TCMS under a saturated atmosphere [7], and was formed on cotton fiber and paper by the method of solution-immersion method using potassium methyl siliconate (PAM) [8], resulting in the superhydrophobic surfaces on the cellulose based materials.

Meanwhile, the formation of the SAM is generally dependent on the reaction condition, and chemical and physical characteristics of silanes. It was reported that the formation of SAM can be affected by the end groups of matrix surface [9,9a], length of elements and chains connected to silanes [10,11], type of functional groups, [12,13], type of solvents [11], concentration of chemical solution and reaction time [14–17], moisture content [16,18–20], and temperature [17,21,22].

This study was conducted to modify the surface properties of papers by the formation of hydrophobic self-assembled monolayer (SAM) on paper surface with silanes, and to decide effective reaction time and silane concentration for preparation of the SAM. In addition, the surface wettability of the SAM-treated papers was

* Corresponding author. Tel.: +82 2 3290 3012.
E-mail address: khpaik@korea.ac.kr (K.-H. Paik).

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characterized by contact angle measurement and stöckigt size test. We also evaluate the influence of the surface modification by the SAM-formation on the mechanical properties of the papers such as wet tensile strength and print-surface roughness.

2. Experimental

2.1. Materials

Filter papers (Whatman No. 1) and three different silane reagents, 1H, 1H, 2H,2H-perfluorodecyltriethoxysilane (PFDTES, $C_{16}H_{19}F_{17}O_3Si$); methyloctadecyldichlorosilane (MODDCS, $C_{19}H_{40}Cl_2Si$); Fluka, dimethyl-dichlorosilane (DMDCS, $(CH_3)_2SiCl_2$), with different functional groups were purchased from Sigma–Aldrich (Fig. 1). All these reagents were used as received without further purification. Anhydrous toluene was purchased from Sigma–Aldrich and used as received.

2.2. Methods

2.2.1. Solution-immersion method

The papers were cut into 22 mm × 40 mm pieces for contact angle and ATR-IR measurements, 65 mm × 65 mm for PPS roughness and stöckigt sizing degree, 25 mm × 180 mm for wet tensile strength test and dried in an oven at 103 °C for 2 h to keep papers free of water. The three silane reagents of varying concentrations (10, 50, 200, 1000 μl) were added by a syringe in 40 ml of anhydrous toluene. The papers were submerged in the solutions at room temperature for 15, 30, 120, 300 and 1440 min, respectively. The papers were then removed from the solution, then washed carefully with 2 × 40 ml of toluene, 4 × 40 ml of ethanol to remove excess reagents, and dried in a clean oven at 130 °C for 90 min to generate stable silane monolayers on the paper surface.

2.2.2. Chemical vapor deposition method

Typically, the DMDCS with boiling point of 68–70 °C was chosen for vapor deposition method, as it is easier to evaporate than PFDTES and MODDCS. The schematic diagram of the apparatus used for the chemical vapor deposition is shown in Fig. 2. The reaction chamber was flushed with a stream of high purity nitrogen gas (above 99.999%) and calcium chloride was used as a desiccant agent to keep to a minimum of residual water in the reaction system. The temperature outside the reaction chamber was kept at 80 °C by a heating pad and temperature controller to evaporate the DMDCS. After pre-conditioning, the papers were immediately placed inside a closed reaction chamber containing a vial with liquid DMDCS (10, 50 and 1000 μl) in 40 ml of anhydrous toluene. Reactions between DMDCS vapor and the papers were carried out at 80 °C for 30, 60 and 240 min, respectively. The papers were then isolated, washed and dried in the manner as described above for the solution-immersion method.

2.2.3. Measurements

The surface wettability of the silane-treated filter papers was characterized by the water contact angle (WCA) measurements and stöckigt size test. The WCA were measured using Surface Electro Optics (Phoenix300) at an ambient temperature in the style of TAPPI standard method T458 [23], and the reported values are averages of 5–8 measurements made on different areas of the paper surface.

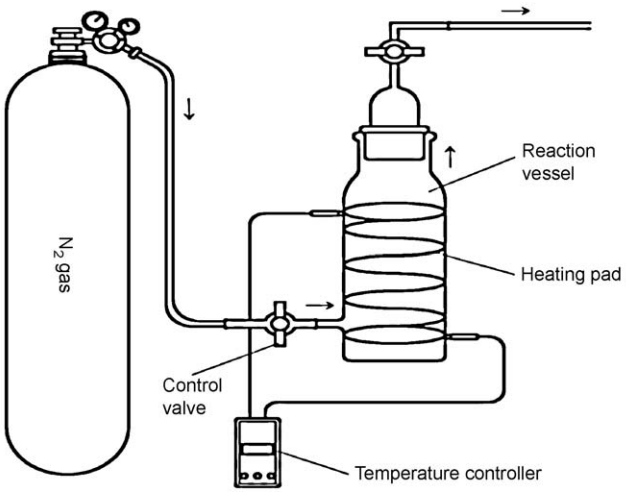

Fig. 2. Schematic diagram of the apparatus used for chemical vapor deposition method.

The stöckigt size test was performed to evaluate the sizing degree of the silane-treated filter papers according to KS M 7025 [24]. The paper samples of 50 μl silane-treated for 60 min by immersion method were used for stöckigt size test, ATR-IR, wet tensile strength, and Print-surface roughness measurement. The silane-treated filter papers were floated on a 2% solution of ammonium thiocyanate and a 1% ferric chloride was dropped on the upper surface of the filter papers. The sizing degree is the time of when the reddish brown of ferric thiocyanate appears on the surface of the filter papers.

The Si–O–C, and Si–C bonds between silanes and cellulose were confirmed by ATR-IR. ATR-IR spectra were recorded on a Spectrum RXI (Perkinelmer) instrument operating at 4.0 cm^{-1} resolution with 24 scans per sample.

The wet tensile strength of silane-treated filter papers were evaluated on a Instron 3366 universal testing machine according to KS M 3781 [24] using the following parameters: sample width: 25 mm; initial length of the sample: 180 mm. The measurements were repeated at least 5 times.

The print-surf roughness of paper (PPS) is a significant factor in determining the printability of papers. The paper was tested using L&W PPS tester (Clamping pressure: 1 MPa, Back plate: rubber) following TAPPI standard method T555 [23].

3. Results and discussion

3.1. Solution-immersion process

The water contact angle (WCA) of the native filter paper were 0° as it absorbed water immediately due to the hydrophilic hydroxyl group of the cellulose. The reaction between PFDTES and filterpaper results in the transformation of hydrophilic to hydrophobic paper surfaces, with a WCA above 120° because of

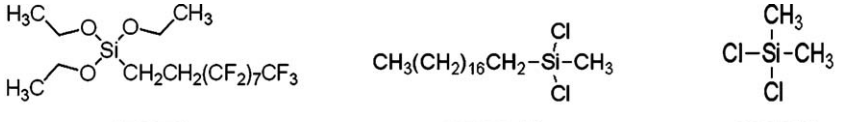

Fig. 1. The structure of silanes.