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Functionalization of Silica Surface with UV-Active Molecules by Multivalent Organosilicon Spacer

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Abstract

Immobilization of active molecules by attachment onto solid surfaces is a well-established practice in many processes and applications. Silica micro- and nano-particles are attractive candidates as support for active molecules as a result of a combination of desirable properties. The present study deals with grafting of a functional UV active molecule onto silica surfaces via hydrosilylation reactions using multivalent organosilicon spacers. Different types of organosilicon precursors based on dimethylsiloxysilanes containing multiple SiH groups were used as spacers between vinyl-modified silica surface and the benzotriazole UV-absorber (UVA). Firstly, the surface of silica was modified with vinyltrimetoxsisilane coupling agent. The UVA molecules were attached to the silica-vinyl by a two-step procedure involving hydrosilylation reaction. The successful grafting was confirmed by FTIR, TGA and UV-Vis characterization. More than fivefold increase in UVA loading was found for the MH30 multifunctional spacer, which contains approximately 75 SiH groups per molecule, when compared to a four-functional spacer. Furthermore a branched, bulky six-functional spacer is preferred over a linear spacer of the same functionality. UV activity of functionalized silica was studied by UV-Vis spectroscopy, indicating that the immobilization of UVA onto silica surface has not altered its UV absorbance properties.

Keywords

Silica, Functionalized Silica, UV Absorbers, Hydrosilylation, Organosilicon

1. Introduction

Immobilization of active molecules by attachment onto solid surfaces in order to prevent their loss, facilitate

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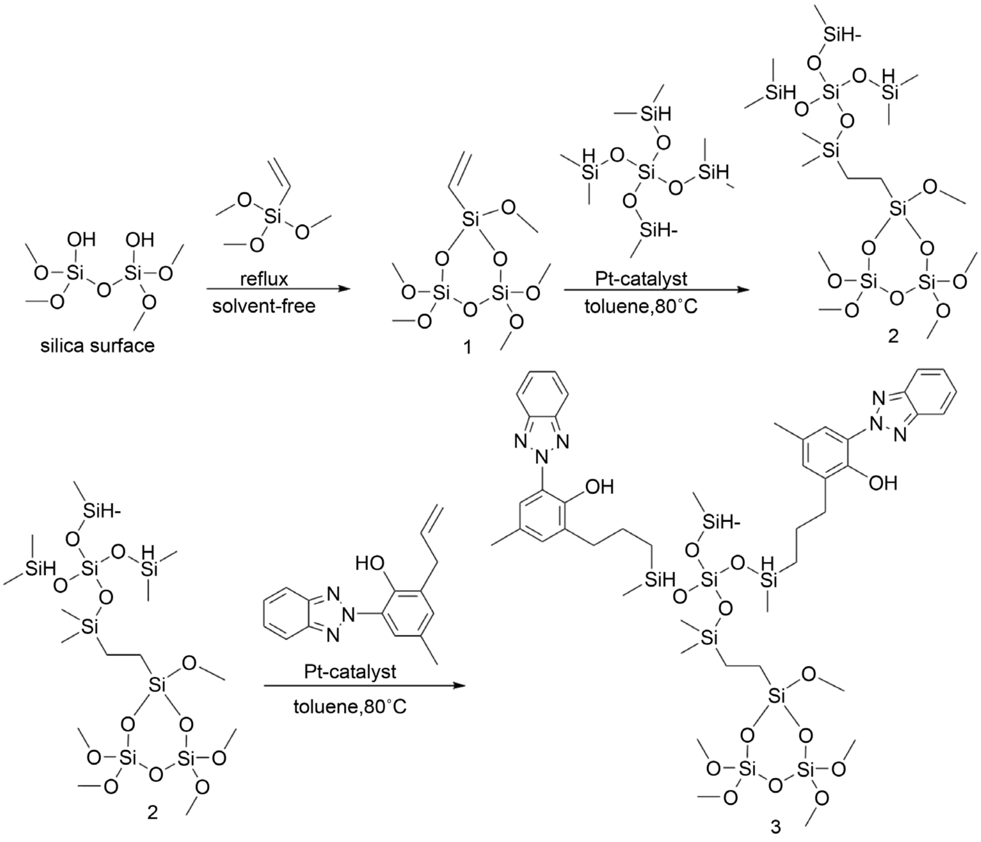
their extraction and recycling, or prevent migration and volatilization, is a well-established practice in many processes and applications. Silica micro- and nano-particles are attractive candidates as support for active molecules as a result of a combination of desirable properties: 1) a large number of surface silanol groups available for a myriad of coupling reactions, 2) particles readily available in a variety of sizes and aggregation states from a large number of commercial suppliers, 3) silica inertness, and 4) favorable economics. As a result, functionalized silica has found many applications in the fields of catalysis [1], chromatography [2] [3], carriers of bioactive molecules [4] [5], fillers in polymer based products [6] [7], and dispersants [8] to name a few. Still, a number of desirable organic molecules are devoid of a reactive group suitable for covalent grafting onto the silica surface as in the case of organic UV absorbing molecules commonly used as light-stabilizers in polyolefins. Because of their relatively low molecular weight and thermodynamic incompatibility with the substrate, they are easy to volatilize during polymer processing or usage and they tend to migrate and bleed-out onto the article surface after relatively short times.

To overcome the inability to directly react the functional molecules with the surface silanol groups, the latter are reacted with organosilane coupling reagents that act as precursors for further immobilization [9] [10]. Nonetheless, typically due to steric hindrance during the reaction between the silane precursor and the functional molecule, this synthetic pathway leads to a relatively low loading of functional molecules. A possible way to improve the organic loading on the silica surface is by the utilization of multivalent precursors [11] [12].

The present study deals with grafting of a functional UV active molecule on silica particle surfaces via hydrosilylation reactions using multivalent organosilicon spacers. Different types of organosilicon precursors based on dimethylsiloxysilanes containing multiple SiH groups were used as spacers between vinyl-modified silica surface and the UV-absorber (UVA) molecules. 2-(2H-benzotriazol-2-yl)-4-methyl-6-(2-propenyl) phenol that belongs to the benzotriazole family, the most widely investigated and used group of UVA [13], was chosen as the UV active molecule due to its ability to undergo hydrosilylation reaction with SiH groups without the loss of UV-absorbing properties. Firstly, the surface of silica was modified with vinyltrimetoxysilane coupling agent (**Scheme 1**). The pre-activated silica-vinyl was fully characterized using complementary analytical methods.



Scheme 1. Functionalization of vinyl modified silica with UVA through A4 spacer.

The UVA molecules were attached to the silica-vinyl by a two-step procedure involving hydrosilylation reaction. The successful grafting was confirmed by FTIR, TGA and UV-Vis characterization.

2. Experimental

2.1. Materials and Methods

Fumed silica Cab-O-Sil® M5 with an average primary particle diameter of 14 nm and a specific surface area of 200 $m^2 \cdot g^{-1}$, was obtained from Cabot Corporation (USA). The surface silanol group concentration of the Cab-O-Sil® M5 material was determined by TGA analysis. The silica powder was pressed to pellets using a KBr pellet kit under pressure (2.5 ton) for 10 minutes. The pellets were pulverized and inserted into the TGA crucible. The weight loss of the silica powder sample over a temperature range of 298 K - 1373 K was used to extract the silanol concentration following the method of Ek *et al.* [14]. The measurements yielded a value of 1.36 mmol of silanol groups per gram of silica which corresponds in our case, to 4.1 OH groups nm^{-2} not different from 4.6 - 4.9 $OH \cdot nm^{-2}$ [15] and 3.7 - 5.2 $OH \cdot nm^{-2}$ [16], the values reported in the literature.

Polymethylhydrosiloxane Andisil® MH30 (**MH30**) was obtained from AB Specialty Silicones (IL, USA). The number average molecular weight of MH30 is $M_n = 4414$ $gr \cdot mol^{-1}$, determined by GPC calibrated with PDMS standards (PSS, Germany). The number of SiH units per MH30 chain is 75, as determined by ^{1}H-NMR with dioxane as an internal standard and in close agreement with the independently determined Mn value.

VTMS-vinyltrimethoxysilane (97%), **A6**-trimethylsilyl terminated poly (dimethylsiloxane-*co*-methylhydrosiloxane) (Mn ~ 950 $g \cdot mol^{-1}$, 6 hydrosiloxane groups per molecule), **Pt-catalyst**-cis-dichlorobis (diethyl sulfide) platinum (II), and **UVA**-2-(2H-benzotriazol-2-yl)-4-methyl-6-(2-propenyl) phenol (99%) were purchased from Sigma-Aldrich.

A4-Tetrakis(dimethylsiloxy)silane (97%) was supplied by ABCR GmbH (Germany), n-hexane (AR) was purchased from Bio-Lab (Israel), and toluene (AR) was purchased from Gadot (Israel). All solvents and reagents were used without further purification.

A6y-3,3'-(1,2-Ethanediyl)-bis(3-dimethylsilyloxy)-1,1,5,5-tetramethyl trisiloxane was prepared in our labs according to the procedure described in [17].

2.2. Instrumentation

Thermogravimetric analysis (TGA) was performed using a Mettler-Toledo model TGA/SDTA851. Typically, approximately 10 mg of the sample were heated in a standard 70 µL TGA alumina crucible, from 298 K to 1273 K, with a heating rate of 10 $K \cdot min^{-1}$ under nitrogen atmosphere. The FTIR spectra in KBr pellets were recorded on a Thermo Scientific, Nicolet™ iS™ 10 FTIR spectrometer. Nuclear Magnetic Resonance (NMR) spectra were acquired on a Bruker Avance II instrument, 500 MHz, CP-MAS 4 mm. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Analytical Ltd. (Kratos Axis Ultra) spectrometer. UV-Vis spectra were obtained using PerkinElmer, Lambda™ 35 spectrophotometer.

2.3. Synthesis

2.3.1. Modification of Silica Surface with Vinyl Groups

Modification of silica surface with vinyltrimethoxysilane (VTMS) was carried out following a modified literature procedure [18] as follows: 10 gr of the pure silica and 40 gr of VTMS were mixed in a 3-necked flask fitted with a reflux condenser and $CaCl_2$ trap. The mixture was heated to the boiling point of VTMS (b.p. 396 K) using an oil bath (383 K), and was continuously stirred with a mechanical stirrer at 225 rpm for 11 hours. After cooling to room temperature, the silica was washed three times with hexane (3 × 250 ml) in a filter funnel with sinter glass (P4) and was dried in a petri dish for half an hour in an oven at 438 K to obtain 9.56 gr of silica-vinyl (1, **Scheme 1**).

2.3.2. Functionalization of Silica-Vinyl with UVA

1) General procedure: silica-spacer

The following procedure was used in all the reactions described below: the spacer molecule was added to a suspension of silica-vinyl in toluene, followed by the addition of the Pt catalyst solution (2% in toluene). The resultant mixture was vigorously stirred for 5 hours at 353 K. After cooling to room temperature, the product was washed three times with toluene and four times with hexane on a filter funnel equipped with sinter glass (P4). The product was placed in a petri dish and dried for one hour in an oven at 343 K.

The silica-spacer obtained above was subsequently suspended in toluene. UVA was added to the suspension, followed by the addition of the Pt catalyst solution (2% in toluene). The resultant mixture was stirred (225 rpm) for 8 hours at 353 K. After cooling to room temperature, the product was washed four times with toluene and three times with hexane on a filter funnel with sinter glass (P4). UV absorbance of the last portion of hexane was measured (250 - 450 nm) to ensure that all remaining UVA was washed away. The product was placed in a petri dish and dried for one hour in an oven at 343 K.

2) Preparation of silica-A4

The following reagents and conditions were used for the synthesis of silica-A4: 10.00 gr of silica-vinyl, 4.70 gr of A4, 54 gr of toluene, 425 µl Pt catalyst solution. After drying 9.95 gr of silica-A4 were obtained (2, **Scheme 1**).

Preparation of silica-A4-UVA

The following reagents and conditions were used for the synthesis of silica-A4-UVA: 9.45 gr of silica-A4, 5.33 gr of UVA, 60 gr of toluene, 445 µl Pt catalyst solution. The suspension was stirred (225 rpm) for 16 hours at 80˚C. After drying 9.29 gr of silica-A4-UVA were obtained (3, **Scheme 1**).

3) Preparation of silica-A6

The following reagents and conditions were used for the synthesis of silica-A6: 1.00 gr of silica-vinyl, 1.32 gr of A6, 5.22 gr of toluene, 50 µl Pt catalyst solution. After drying 0.982 gr of silica-A6 were obtained.

Preparation of silica-A6-UVA

The following reagents and conditions were used for the synthesis of silica-A6-UVA: 750.8 mg of silica-A6, 424.8 mg of UVA, 4.78 gr of toluene, 36 µl Pt catalyst solution. After drying 0.625 gr of silica-A6-UVA were obtained.

4) Preparation of silica-A6y

The following reagents and conditions were used for the synthesis of silica-A6y: 1.00 gr of silica-vinyl, 780 mg of A6y, 3.6 gr of toluene, 36 µl Pt catalyst solution. After drying 0.984 gr of silica-A6y were obtained.

Preparation of silica-A6y-UVA

The following reagents and conditions were used for the synthesis of silica-A6y-UVA: 627.8 mg of silica-A6y, 354.8 mg of UVA, 2.26 gr of toluene, 28 µl Pt catalyst solution. After drying 0.518 gr of silica-A6y-UVA were obtained.

5) Preparation of silica-MH30

The following reagents and conditions were used for the synthesis of silica-MH30: 1.00 gr of silica-vinyl (pre-dried for 1 h at 433 K), 3.29 gr of MH30, 2.6 gr of toluene, and 45 µl Pt catalyst solution. The resultant suspension was stirred for 8 hours at 323 K with a magnetic stirrer. The product was placed in a petri dish and dried in an oven at 318 K for one hour, to obtain 1.2 gr of silica-MH30.

Preparation of silica-MH30-UVA

The following reagents and conditions were used for the synthesis of silica-MH30-UVA: 0.5 gr of silica-MH30, 1.5 gr of UVA, 3 gr of toluene, 80 µl of Pt catalyst solution. After drying 0.45 gr of silica-MH30-UVA were obtained.

3. Results and Discussion

3.1. Characterization of Vinyl-Modified Silica

Solid-state ^{13}C NMR was used to characterize the chemistry of the silica surface. The NMR spectrum of vinyl-modified silica exhibits clearly the methoxy signal at ca. 48 ppm and two signals at ca. 134 - 128 ppm which correspond to the carbons of the vinyl groups on the silica surface as shown in **Figure 1**.

The FTIR spectra for the silica before and after reaction with VTMS are presented in **Figure 2**. The characteristic peaks of the unmodified silica are: a large band at about 3433 cm^{-1}, attributed to the O-H stretching frequency of silanol groups and to adsorbed water; a sharp band at 1631 cm^{-1} assigned to the bending vibrations of molecular water; a broad strong peak at 1254 - 1026 cm^{-1}, assigned to the Si-O-Si asymmetric bond stretching vibrations. This peak has a distinct "shoulder" at ~980 cm^{-1}, which corresponds to the asymmetric vibration of Si-OH. A band at 806 cm^{-1} is assigned to a network Si-O-Si symmetric bond stretching vibration; and the band at 460 cm^{-1} is associated with a network Si-O-Si bond bending vibration. New weak peaks at 3060 cm^{-1} and 3020 cm^{-1} are observed in the spectra for the vinyl-modified silica. These are attributed to C-H bands of the

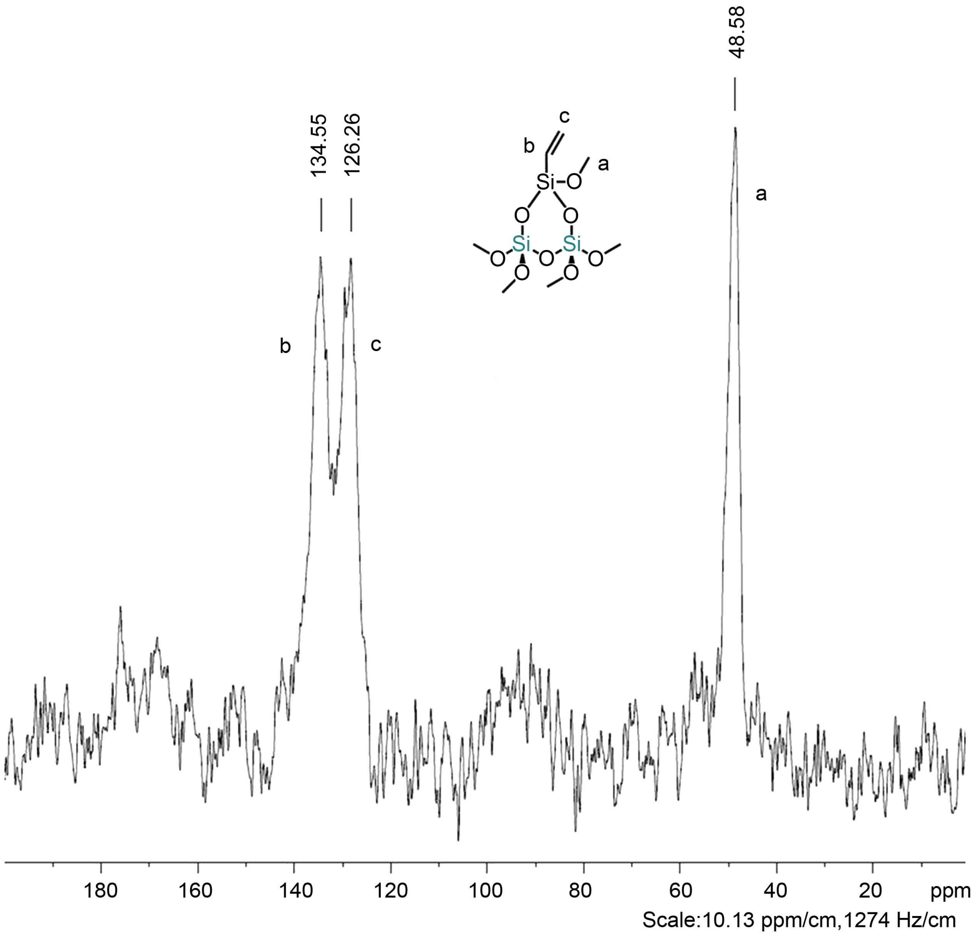


Figure 1. ^{13}C CPMAS NMR of vinyl-modified silica. Assignments are as follows: 48.58 ppm-methoxy group; 128.26 and 134.55-vinyl group (distal and proximal carbon atoms respectively).

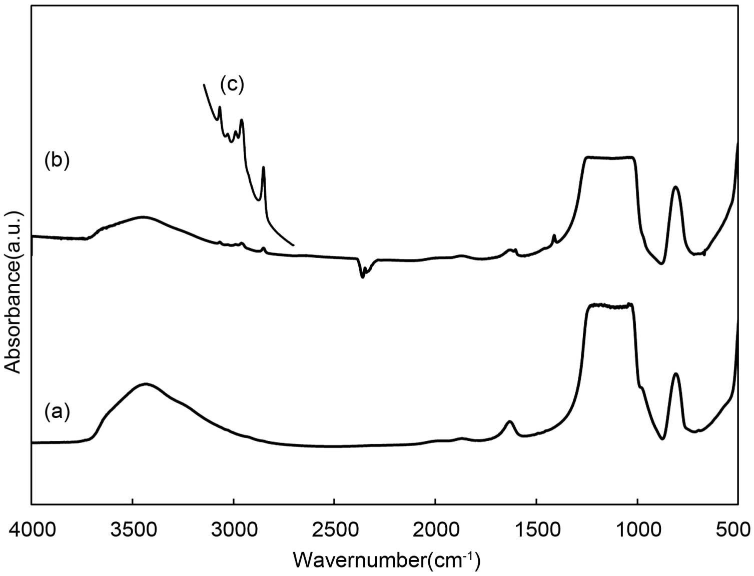


Figure 2. FTIR spectra for (a) pristine Cab-O-Sil M5, (b) silica-vinyl, vinyl modified silica. Magnification of spectrum (b) between 2700 cm^{-1} and 3150 cm^{-1} is shown as curve (c). Relevant assignments are discussed in the text.

Si-CH=CH$_2$ group. The peak at 1600 cm^{-1} is typical band of C=C vibrations and the peak appearing at 1410 cm^{-1} is assigned to C-H deformation vibrations of the =CH$_2$ group. The peaks at 2986 cm^{-1}, 2958 cm^{-1} and 2847 cm^{-1} are attributed to C-H bands of the unreacted methoxy groups of the VTMS (the characteristic Si-OCH$_3$ band, expected to be found around 1000 - 1100 cm^{-1}, is masked by the strong Si-O-Si absorption). Lastly, it should be pointed out that in the modified silica, the broad band at 3433 cm^{-1} is significantly decreased in comparison to that of the original sample. This decrease, along with the disappearance of the "shoulder" at ~980 cm^{-1}, clearly indicate that surface silanol groups have been consumed in the chemical reaction, *i.e.*, vinyltrimethoxysilane was covalently anchored to the silica surface by reaction with the surface silanol groups.

The successful attachment of vinyltrimethoxysilane to the surface of the silica particles is also demonstrated by the XPS analysis. The modification of the silica surface is expected to lead to a significant decreased oxygen/carbon and silicon/carbon ratios measured on the silica surface. This is indeed shown by the results set forth in **Table 1**.

The chemical composition of the vinyl-modified silica was further studied using high resolution C1s spectrum. Two main bands corresponding to the following bonds: C-H (285 eV) and O-CH$_3$ (287 eV) were obtained (**Table 2**). Based on the deconvoluted band areas, the ratio between the C=C and C-O was found to be approximately 2:1. The ratio of the two carbon bands reflects the proportion of the vinyl to methoxy groups. Therefore, we can estimate that on average there is one vinyl group to one methoxy group per each grafted VTMS molecule on the silica surface. Hence we conclude that on the average two out of the three methoxy groups in a VTMS molecule have reacted and one is left unreacted (as also indicated by the FTIR spectra above).

The quantitative determination of the extent of VTMS incorporation onto the silica surface was achieved by thermogravimetric analysis. The dehydroxylation [15] [16] which may occur in this temperature range, is neglected since most of the silanol groups are assumed to have reacted during the functionalization reaction. NMR and FTIR results clearly indicate that not all the alkoxy groups are hydrolyzed, therefore it should be taken into account in the TGA analysis employed for the determination of the amount of surface vinyl groups. In combination with the XPS results discussed above a reliable account for the organic content decomposed during TGA analysis may be obtained. The value of M = 58 g·mol^{-1} is used for the molecular weight of the decomposed organic molecule based on one vinyl group and one methoxy group per VTMS molecule. The following equation was used to derive the concentration of vinyl groups on the silica surface in terms of C_{Vi}, mmol vinyl groups/g-sample (silica + VTMS):

$$C_{Vi}\left(\text{mmol}/\text{g}_{\text{sample}}\right) = 10^3\, f_{Vi}/M \tag{1}$$

where, f_{vi} is the weight fraction of sample decomposed in the temperature range from 423 - 1273 K. The TGA thermogram for the vinyl modified silica is presented in **Figure 3**. A vinyl surface concentration of 0.68 mmol·g^{-1} was obtained from Equation (1). This value should be compared to the concentration of surface silanols determined above (1.36 mmol·g^{-1}). It indicates that approximately two silanol groups have been consumed for every VTMS molecule attached to the surface, in agreement with previous discussion.

3.2. Characterization of Silica-Spacer-UVA

TGA analysis was used to calculate the amount of UVA molecules attached to the silica surface at the end of

Table 1. Atomic concentrations, O/C and Si/C ratios obtained by XPS.

Sample	O1s (%)	N1s (%)	C1s (%)	Si2p (%)	O/C	Si/C
Pristine silica	70.0	0	1.5	28.6	47.9	19.6
Silica-vinyl	63.2	0	9.6	27.2	6.6	2.8

Table 2. Deconvoluted band areas of the vinyl-modified silica obtained from high resolution C1s XPS.

Atom	Position (eV)	Area (%)
C1s (C-H)	285	66
C1s (C-O)	287	34

sequence of reactions described above. The difference in weight loss between the silica-spacer particles and UVA functionalized silica particles was taken as the content of UVA that has been incorporated into the silica. Thus, the concentration of UVA molecules per gram of the functionalized silica, C_{UVA} (mmol·g^{-1}), was calculated by the following equation.

$$C_{\text{UVA}}\left(\text{mmol}-\text{UVA}/\text{g}_{\text{sample}}\right)=10^{3}\left(f_{\text{UVA}}-f_{\text{spacer}}\right)/\left[\left(1-f_{\text{spacer}}\right)M_{\text{UVA}}\right] \quad (2)$$

where f_{spacer} and f_{UVA} are the weight fractions of decomposed material in the temperature range 373 - 1273 K for a sample of silica-spacer, and a sample of silica-spacer-UVA respectively, and M_{UVA} is the molecular weight of UVA (265.31 g·mol^{-1}). Results are summarized in **Table 3**.

The results presented in **Table 3** indicate that relative to A4 there is more than fivefold increase in UVA loading for the MH30 spacer, which contains a considerably larger number of SiH groups. A6 and A6y also showed increase in the UVA concentration relative to A4. The "bulky" A6y spacer are preferred over the "linear" A6 spacer. The increase in UVA loading from A4 to A6y is roughly proportional to the increase in available SiH groups for UVA attachment (3 in the former, 5 in the latter).

It should be noted that UVA grafting improves the thermal stability of MH30 modified silica. **Figure 4** represents TGA curves silica-MH30 and silica-MH-30-UVA. These curves indicate that the onset of decomposition of the organic components in silica-MH30 is at about 398 K, while the decomposition in UVA functionalized silica occurs at a considerably higher temperature of about 598 K. Thermograms for additional spacers are provided in the **Appendix** (cf. **Figures A1-A3**).

UVA functionalized silica was also examined by FTIR spectroscopy. **Figure 5** shows spectra of UVA, silica-MH30 and silica-MH30-UVA. When comparing the spectra of silica-MH30 (**Figure 5(b)**) and silica-MH30-UVA (**Figure 5(c)**) new peaks are observed for the latter at 745 cm^{-1} and in the region from 1500 to

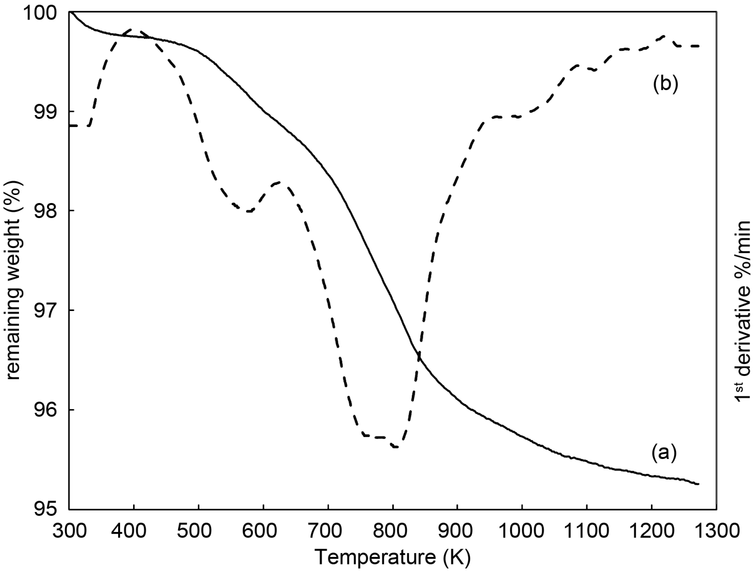


Figure 3. TGA diagram of vinyl-modified silica. (a) Percent of remaining sample weight, (b) 1st derivative.

Table 3. Measured amount of UVA molecules attached to the silica for the different spacers used in this work[†].

Sample	f_{spacer}	f_{UVA}	C_{UVA}
sillica-A4-UVA	0.05	0.11	0.26
silica-A6-UVA	0.06	0.14	0.31
silica-A6y-UVA	0.06	0.19	0.51
silica-MH30-UVA	0.09	0.41	1.36

[†] f_{spacer}—weight fraction of decomposed silica-spacer in the temperature range 373 - 1273 K; f_{UVA}—weight fraction of decomposed silica-spacer-UVA in the same temperature range; C_{UVA} (mmol·g^{-1}) concentration of UVA molecules per gram of functionalized silica.

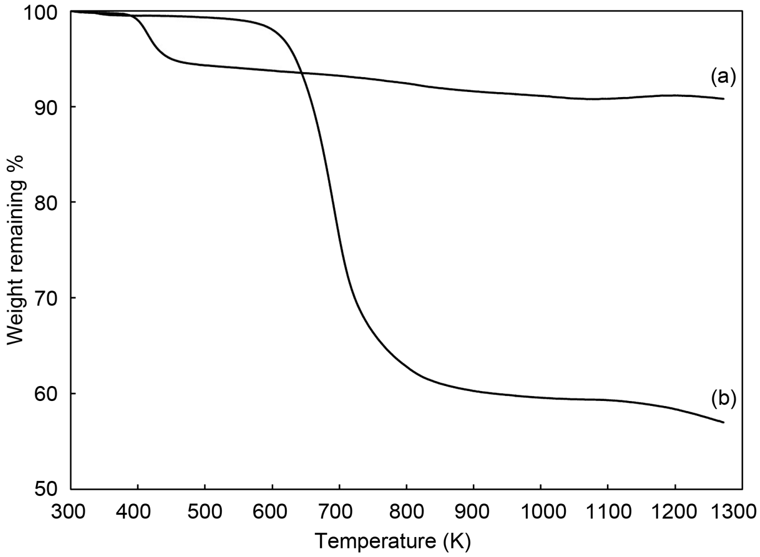


Figure 4. TGA thermograms for silica-MH30 (a), silica-MH30-UVA (b).

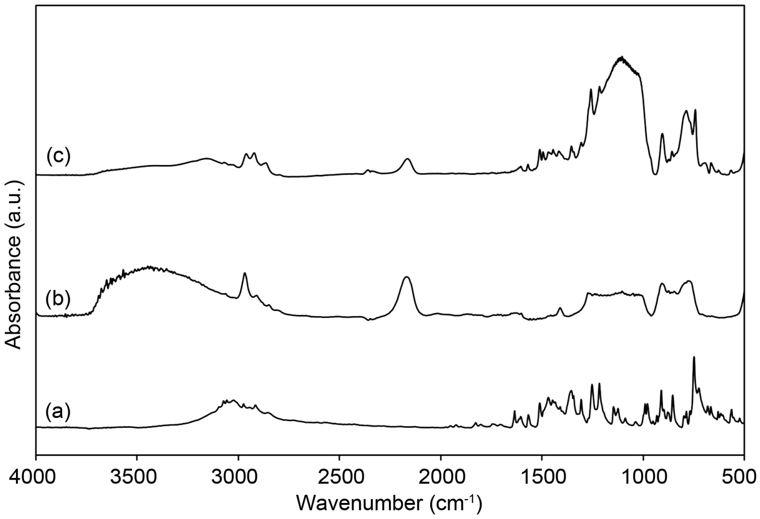


Figure 5. FTIR spectra of UVA (a), silica-MH30 (b) and silica-MH30-UVA (c).

1200 cm^{-1}. These peaks are characteristic to the UVA molecule (**Figure 5(a)**), indicating successful functionalization of the silica surface. The presence of the characteristic Si-H band at 2160 cm^{-1} is also detected in the spectrum of silica-MH30-UVA (**Figure 5(c)**) indicating that not all the SiH groups have been consumed by the hydrosilylation reaction. Spectra for all other materials prepared here are presented in **Figures A4-A6** in the **Appendix** section.

Upon successful covalent functionalization of silica with UVA, its UV transmission properties were examined to ascertain its UV absorbing properties in typical applications. For this propose, silica-MH30-UVA was compounded into a polyethylene matrix to prepare 50 µm thick, three-layered film with the additive incorporated into the 7 µm thick core layer. The composition of the core layer consists of 93% LLDPE and 7% additive (by weight). The UV-VIS spectrum of the film is similar to that of the UVA molecule, with the characteristic absorption bands at λ ~ 345 nm and 304 nm, although some broadening of the bands is observed for the film (**Figure 6**).

4. Conclusion

UV active molecule has been successfully attached onto vinyl-modified silica surface using different types of

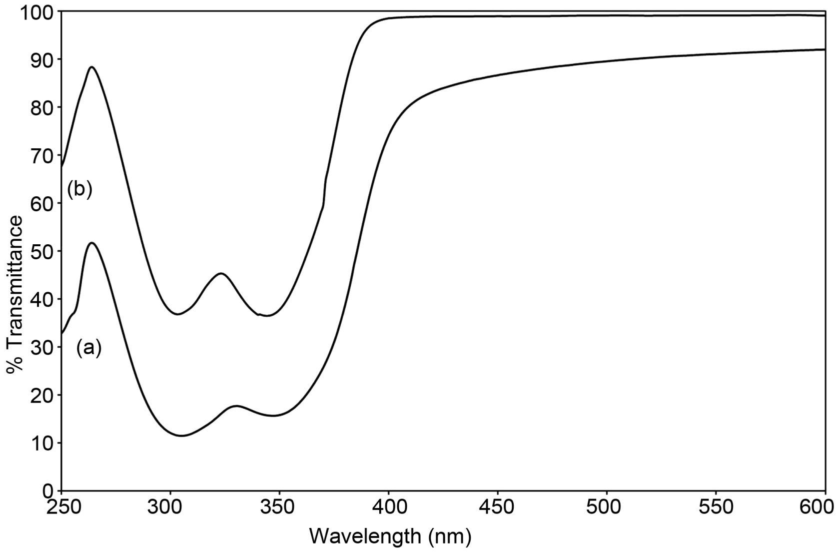


Figure 6. (a) UV-VIS spectra of 50 μm multilayered LLDPE film with Sil-MH30-UVA additive in the core layer; (b) 11.5 ppm hexane solution of UVA.

multivalent organosilicon precursors, which were used as a spacer between vinyl-modified silica surface and the UV-absorber. The new materials were characterized by TGA and FTIR. More than fivefold increase in UVA loading was found for the MH30 spacer, which contains a large number of SiH groups, when compared to a four-functional spacer. Six-functional spacers also showed increase in the UVA concentration compared to the four-functional spacer. Furthermore a branched, bulky six-functional spacer is preferred over a linear spacer of the same functionality. UV activity of functionalized silica was studied by UV-VIS spectroscopy, indicating that the immobilization of UVA onto silica surface has not altered its UV absorbance properties.

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Appendix

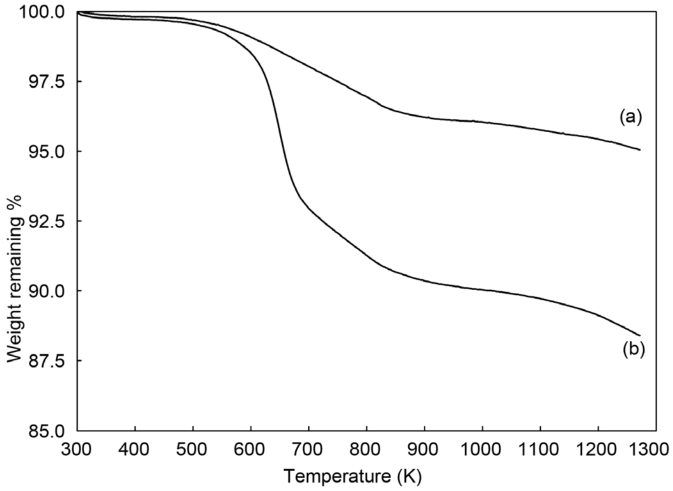

Figure A1. TGA thermograms for silica-A4 (a), silica-A4-UVA (b).

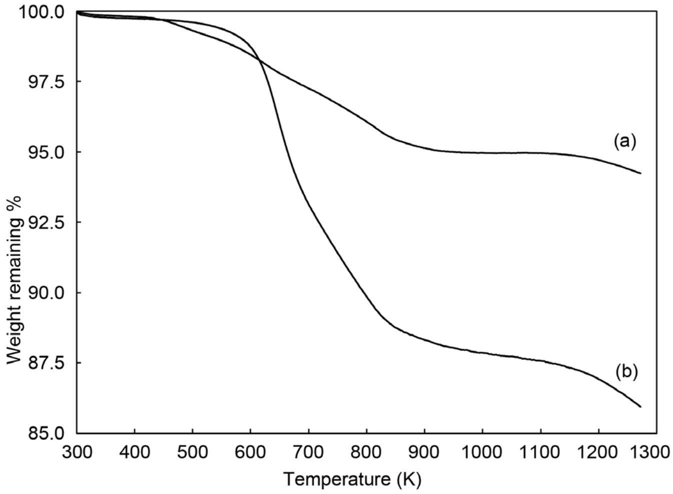

Figure A2. TGA thermograms for silica-A6 (a), silica-A6-UVA (b).

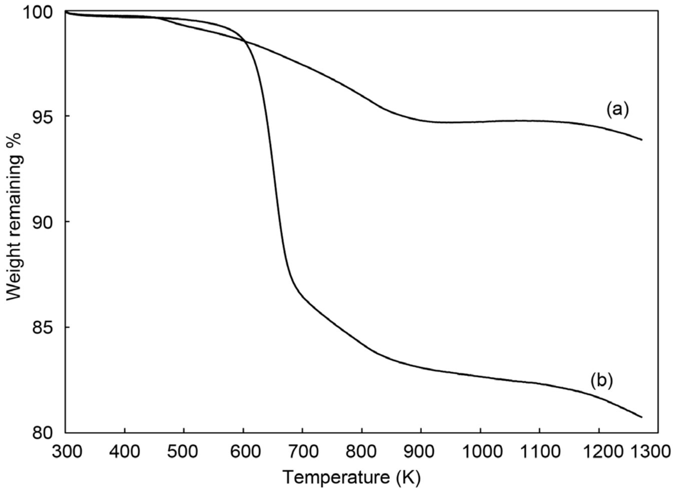

Figure A3. TGA thermograms for silica-A6y (a), silica-A6y-UVA (b).

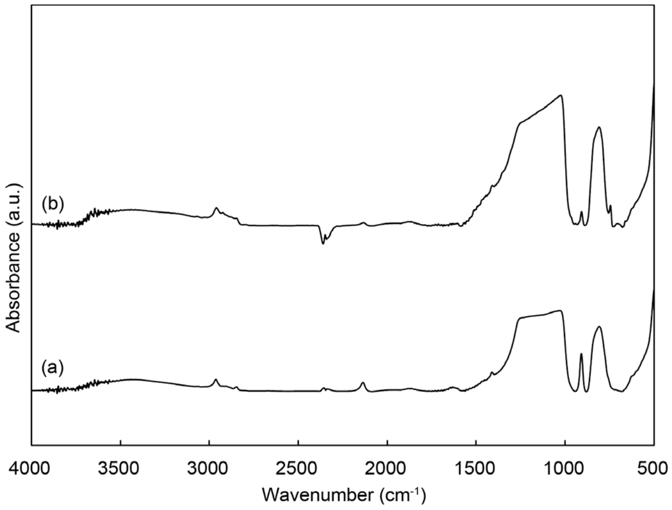

Figure A4. FTIR spectra for silica-A4 (a), silica-A4-UVA (b).

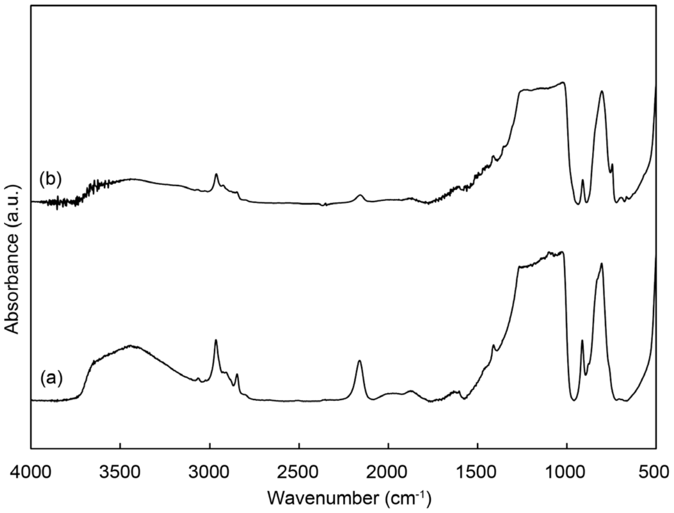

Figure A5. FTIR spectra for silica-A6 (a), silica-A6-UVA (b).

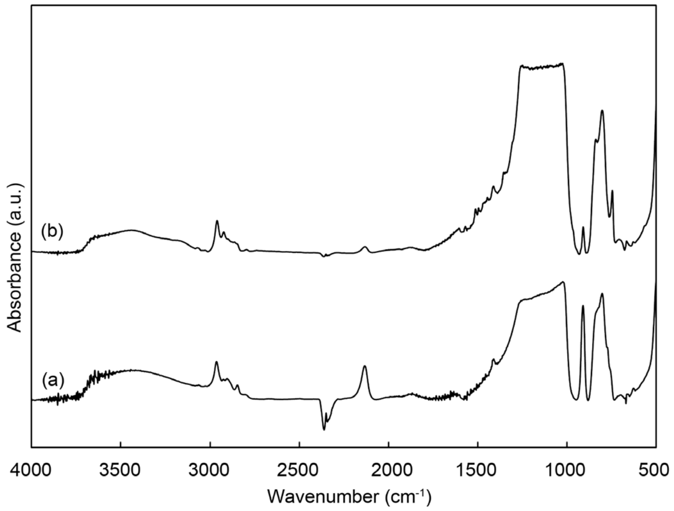

Figure A6. FTIR spectra for silica-A6y (a), silica-A6y-UVA (b).