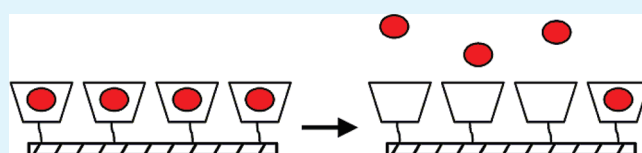


Controlled Fragrant Molecule Release from Surface-Tethered Cyclodextrin Host–Guest Inclusion Complexes

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ABSTRACT: β -cyclodextrin barrels can be tethered to solid surfaces using the Williamson ether synthesis reaction via an intermediate pulsed plasma deposited poly(4-vinylbenzyl chloride) linker layer. The loading and release of perfume molecules through host–guest inclusion complex formation with surface tethered β -cyclodextrin has been followed by infrared spectroscopy and quartz crystal microbalance measurements. Fragrance release lasts for several months and can be easily recharged.



KEYWORDS: host–guest inclusion complex, cyclodextrin, functional surface, molecule release, fragrance

1. INTRODUCTION

Human sensory awareness of volatile fragrant molecules (or perfumes) is commonly associated with cleanliness and freshness for consumer products.¹ Indeed, perfume delivery systems that maintain the sensation of fragrance over extended periods of time are of interest to the smart textiles sector.^{2,3} Among the many different alternatives available (e.g., microcapsules,⁴ microparticles,⁵ and polymer micelles⁶), the dynamic release by host–guest inclusion complexes is recognized as being highly promising.⁷ This stems from the lack of strong binding interactions between the guest and host molecules that underpin release (i.e., the hydrophobic effect and van der Waals interactions),⁸ whereas delivery from microcapsules or microparticles requires embedding within a matrix and physical or chemical triggers to instigate perfume release^{9,10} (e.g., external force, degradation over time, or pH change). In the case of host–guest inclusion complexes, perfume release is accomplished through natural replacement by other smaller molecules (usually water or small amines) from the surrounding environment.¹¹

Cyclodextrins are particularly well suited to host–guest inclusion complex interactions given their inherent cavity geometry. Their basic structure consists of cyclic oligosaccharides, with the most commonly available having six, seven, or eight glucopyranose units (α -, β -, γ -cyclodextrin, respectively). The oligosaccharide ring forms a torus, with the glucose unit primary hydroxyl groups located toward the narrow end, and the secondary hydroxyl groups positioned around the wider part.¹² A great variety of guests are able to form inclusion complexes leading to a range of surface related applications including drug delivery control,^{13,14} chromatography,^{15,16} immobilization of reactive chemicals,^{17,18} solubility enhancement,^{19,20} selective transport of compounds,^{21,22} and perfume release.^{23,24} These require immobilization of either the host or guest molecules onto a solid surface; where the important prerequisites are appropriate surface orientation of the β -cyclodextrin barrels, ease of accessibility for guest molecules into the cavity, and a high density of attachment to the underlying solid substrate. Previous attempts

aimed at forming oriented supported layers of cyclodextrins have included Langmuir–Blodgett films,^{25,26} self-assembled monolayers (SAMs) of thiolated cyclodextrin derivatives on gold surfaces,^{27–29} and chemisorption of cyclodextrin onto polymer supports.^{30,31} These approaches have experienced limited success due to their inherent complexities, such as the requirement for substrate-specific chemistries and inadequate functional retention capacity. Therefore, there exists a demand for selective release functional coatings that are applicable to a wide range of substrate materials and are easily recharged.

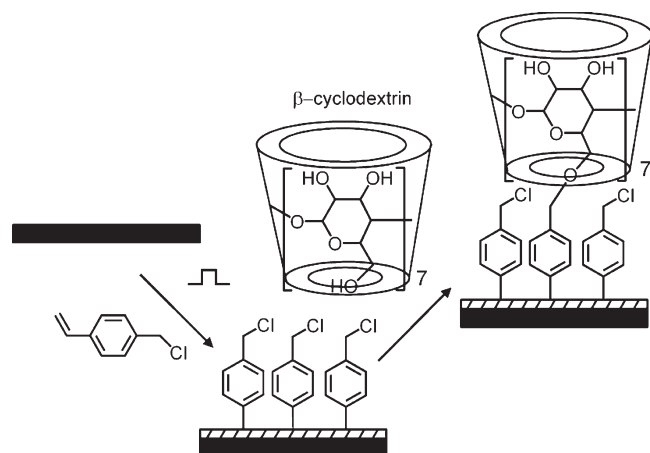
Earlier studies have shown that the amine-functionalized variant, 6-amino-6-deoxy- β -cyclodextrin barrels, can be successfully immobilized onto plasmachemical layers via reaction with the epoxide groups of pulsed plasma-deposited poly(glycidyl methacrylate), and these are capable of forming host–guest inclusion complexes with cholesterol (i.e., a bile acid) and *N,N*-dimethylformamide molecules.³² The major attribute of pulsed plasma deposition is that it is a straightforward and effective method for functionalizing solid surfaces (single step, solventless, and substrate independent). It constitutes the generation of active sites (predominantly radicals) at the surface as well as within the electrical discharge during the duty cycle on-period (microseconds), followed by conventional polymerization reaction pathways proceeding during each extinction period (milliseconds). The level of surface functionality can be tailored by simply preprogramming the pulsed plasma duty cycle. Well-defined functional films containing anhydride,³³ carboxylic acid,³⁴ cyano,³⁵ epoxide,³⁶ hydroxyl,³⁷ furfuryl,³⁸ thiol,³⁹ amine,⁴⁰ perfluoroalkyl,⁴¹ perfluoromethylene,⁴² and trifluoromethyl⁴³ groups have been successfully prepared in the past by this methodology. In the present article, we describe the in situ conversion of the primary hydroxyl groups contained within the β -cyclodextrin molecule to alkoxide groups, and their subsequent reaction with surface chloride centers contained in pulsed plasma deposited poly(4-vinylbenzyl chloride) thin layers using the

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Scheme 1. Attachment of β -Cyclodextrin via Primary Hydroxyl Groups to a Pulsed Plasma Deposited Poly(4-vinylbenzyl chloride) Surface Using the Williamson Ether Synthesis Reaction



Williamson ether synthesis,⁴⁴ Scheme 1. Compared to the earlier utilization of 6-amino-6-deoxy- β -cyclodextrin barrels for tethering to pulsed plasma deposited poly(glycidyl methacrylate), this approach allows unmodified cyclodextrins to be used. The guest–host interactions between perfume molecules and the immobilized β -cyclodextrin barrels have been characterized by infrared spectroscopy, quartz crystal microbalance (QCM), and human sensory testing.

2. EXPERIMENTAL SECTION

Pulsed plasma deposition of 4-vinylbenzyl chloride (+98%, Aldrich, purified using several freeze–pump–thaw cycles) was carried out in an electrodeless cylindrical glass reactor (5 cm diameter, 520 cm³ volume, base pressure of 1×10^{-3} mbar, and with a leak rate better than 1.8×10^{-9} kg s⁻¹) enclosed in a Faraday cage. The chamber was fitted with a gas inlet, a Pirani pressure gauge, a 30 L min⁻¹ two-stage rotary pump attached to a liquid cold trap, and an externally wound copper coil (4 mm diameter, 9 turns, spanning 8–15 cm from the precursor inlet). All joints were grease free. An L-C network was used to match the output impedance of a 13.56 MHz radio frequency (RF) power generator to the partially ionised gas load. The RF power supply was triggered by a signal generator and the pulse shape monitored with an oscilloscope. Prior to each experiment, the reactor chamber was cleaned by scrubbing with detergent, rinsing in water and propan-2-ol, followed by oven drying. The system was then reassembled and evacuated. Further cleaning consisted of running an air plasma at 0.2 mbar pressure and 50 W power for 30 min. Next a polished silicon (100) wafer (MEMC Electronics Materials, cleaned ultrasonically in a 50/50 propan-2-ol/cyclohexane solvent mixture), or nonwoven polypropylene cloth (Corovin GmbH) was inserted into the center of the reactor, and the chamber pumped back down to base pressure. At this stage, 4-vinylbenzyl chloride monomer vapor was introduced at a pressure of 0.2 mbar for 5 min prior to ignition of the electrical discharge. The optimum conditions for benzyl chloride functional group retention corresponded to a peak power of 40 W, in conjunction with a duty cycle on-time of 100 μ s and off-time equal to 4 ms.⁴⁵ Deposition was allowed to proceed for 10 min to yield 150 ± 5 nm thick layers. Upon plasma extinction, the precursor vapor continued to pass through the system for a further 3 min, and then the chamber was evacuated back down to base pressure.

Surface derivatization of the pulsed plasma deposited poly(4-vinylbenzyl chloride) layers with β -cyclodextrin (+99.9%, Fluka Chemicals)

entailed immersion of the coated substrate into various β -cyclodextrin solutions (1–40 μ M) combined with 25 μ M sodium hydroxide. This gave rise to a range of surface packing densities. After incubation for 72 h, the samples were thoroughly rinsed in high-purity water, ethanol, and propan-2-ol to remove any unbound β -cyclodextrin and reconvert any unused alkoxide groups back to primary alcohol groups. Inclusion complexes between guest vanillin (4-hydroxy-3-methoxybenzaldehyde, +99%, Aldrich) molecules with surface derivatized β -cyclodextrin were prepared by immersion into a 75 mM vanillin ethanolic solution for periods up to 72 h. Subsequent washing with ethanol and propan-2-ol, followed by drying in an oven at 35 $^{\circ}$ C for 60 min removed any unbound guest molecules.

Film thickness measurements were carried out using a spectrophotometer (nkd-6000, Aquila Instruments Ltd.). The acquired transmittance-reflectance curves (350–1000 nm wavelength range) were fitted to a Cauchy model for dielectric materials employing a modified Levenberg–Marquardt method.⁴⁶

X-ray photoelectron spectroscopy (XPS) analysis of the layers was undertaken on a VG ESCALAB instrument equipped with an unmonochromated Mg K α X-ray source (1253.6 eV) and a hemispherical analyzer operating in the constant analyzer energy mode (CAE, pass energy = 20 eV). XPS core level spectra were fitted using Marquardt minimization software assuming a linear background and equal full-width at half-maximum (fwhm) Gaussian component peaks.⁴⁷ Elemental concentrations were calculated using instrument sensitivity (multiplication) factors determined from chemical standards, C(1s):O(1s):Cl(2p) = 1.00:0.45:0.38. The absence of any Si(2p) signal from the underlying substrate was taken as being indicative of pinhole free layer coverage at a thickness exceeding the XPS sampling depth (2–5 nm).⁴⁸

Fourier transform infrared (FTIR) analysis of the layers at each stage of reaction was carried out using a Perkin-Elmer Spectrum One spectrometer equipped with a liquid nitrogen cooled MCT detector operating across the 700–4000 cm⁻¹ wavenumber range. Reflection–absorption (RAIRS) measurements were performed using a variable angle accessory (Specac Inc.) set at 66 $^{\circ}$ with a KRS-5 polarizer fitted to remove the s-polarized component. All spectra were averaged over 5000 scans at a resolution of 4 cm⁻¹.

Real-time guest–host interactions were followed by exposure of vanillin vapor at 0.2 mbar pressure for 345 s to a quartz crystal detector (Varian model 985–7013) using a 5 MHz AT-cut 13 mm diameter quartz crystal coated with pulsed plasma deposited poly(4-vinylbenzyl chloride) and either with or without 20 μ M β -cyclodextrin functionalization. Mass readings were taken every 5 s during exposure and for 60 s thereafter.

Inclusion complexes between guest essential oil molecules (lavender, sandalwood, jasmine, rosemary, lemon, and vanilla, The Body Shop Co. Ltd.) and 20 μ M β -cyclodextrin functionalized pulsed plasma deposited poly(4-vinylbenzyl chloride) onto nonwoven polypropylene cloth were prepared by exposure to a 75 mM essential oil ethanolic solution for 72 h. Subsequent washing with ethanol and propan-2-ol, followed by drying at 35 $^{\circ}$ C for 60 min removed any unbound guest molecules. Essential oil guest molecule loading concentrations were calculated by extraction with an ethanol/water (50:50 v/v) mixture for 12 h and then UV–vis absorption spectroscopy measurement at a wavelength of 276 nm (absorption maxima for all essential oils studied) over regular time intervals. Aroma activities of the freshly charged inclusion complex were evaluated by sensory tests that entailed placing the functionalized nonwoven polypropylene cloths in insulated booths stored at room temperature. They were nosed (i.e., smelt) at regular intervals in order to detect the scent. The fragrance release from the inclusion complexes were compared with control samples comprising the underivatized pulsed plasma poly(4-vinylbenzyl chloride) layer deposited onto nonwoven polypropylene cloth. Both sets of aroma nosing assessments were

Table 1. XPS atomic percentages

sample	elemental (%)		
	C	O	Cl
theoretical poly(4-vinylbenzyl chloride)	90.0		10.0
pulsed plasma poly(4-vinylbenzyl chloride)	90.6 ± 0.1		9.4 ± 0.1
theoretical β -cyclodextrin monolayer	54.5	45.5	
pulsed plasma poly(4-vinylbenzyl chloride)/ β -cyclodextrin (20 μ M)	65.4 ± 0.1	31.4 ± 0.1	3.2 ± 0.5

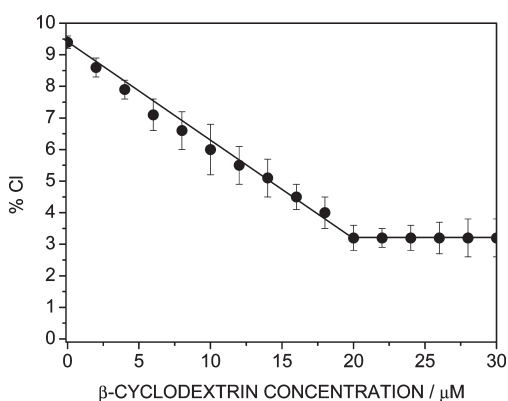


Figure 1. XPS chlorine concentration (% Cl) at the surface of pulsed plasma deposited poly(4-vinylbenzyl chloride) layers following reaction with β -cyclodextrin for 72 h as a function of solution concentration.

undertaken by several individuals according to single-blinded experimental conditions,⁴⁹ in which each insulated booth's scent was correctly identified before proceeding with scent intensity evaluation.

3. RESULTS

3.1. Surface Immobilization of β -Cyclodextrin. XPS analysis of the pulsed plasma deposited poly(4-vinylbenzyl chloride) layers confirmed the presence of carbon and chlorine at the surface, Table 1. Following reaction with β -cyclodextrin, there is the appearance of an O(1s) peak and accompanying attenuation of the Cl(2p) peak. The surface packing density of the tethered β -cyclodextrin barrels could be controlled by varying the reaction conditions, Figure 1. Concentrations exceeding 20 μ M of the β -cyclodextrin yielded a surface saturation level, whereas lower dilutions yielded submonolayer coverages.

Infrared spectra taken of the pulsed plasma deposited poly(4-vinylbenzyl chloride) layers were assigned as follows:⁵⁰ 1263 cm^{-1} halide functionality (CH_2 wag mode for $\text{CH}_2\text{-Cl}$), 1446 cm^{-1} polymer backbone CH_2 scissoring stretch, and para-substituted phenyl ring stretches at 1495 cm^{-1} and 1603 cm^{-1} , Figure 2. In addition, compared to the precursor, the absence of the vinyl double bond stretch at 1629 cm^{-1} is consistent with the monomer having undergone polymerization.⁴⁵ Derivatization of the pulsed plasma deposited poly(4-vinylbenzyl chloride) layer with β -cyclodextrin gave rise to the appearance of several new infrared bands⁵¹ at 754 cm^{-1} , 1045 cm^{-1} , 1085 cm^{-1} , and 1160 cm^{-1} which are all associated with β -cyclodextrin, Figure 2. The poly(4-vinylbenzyl chloride) $\text{CH}_2\text{-Cl}$ absorbance at 1263 cm^{-1} was noted to have significantly dropped in intensity with respect to the polymer backbone peak at 1446 cm^{-1} following the Williamson ether synthesis reaction, Scheme 1. Any remaining $\text{CH}_2\text{-Cl}$ groups detected following surface

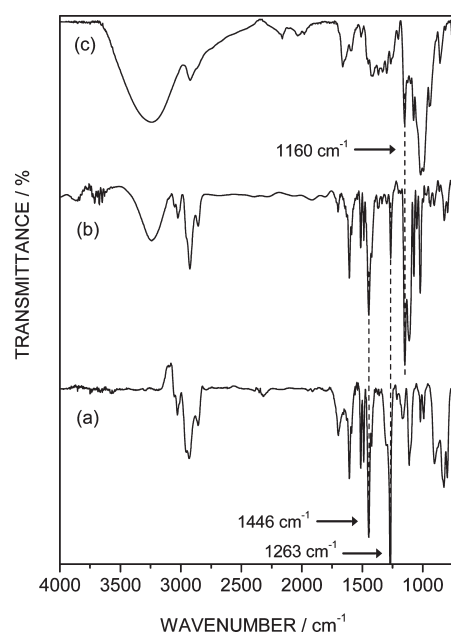


Figure 2. Infrared spectra of (a) pulsed plasma-deposited poly(4-vinylbenzyl chloride) layer ($P_p = 40$ W; $t_{\text{on}} = 100$ μ s; $t_{\text{off}} = 4$ ms; 10 min); (b) 20 μ M solution of β -cyclodextrin reacted with pulsed plasma-deposited poly(4-vinylbenzyl chloride) layer ($P_p = 40$ W; $t_{\text{on}} = 100$ μ s; $t_{\text{off}} = 4$ ms; 10 min); and (c) β -cyclodextrin.

tethering correspond to either unreacted $\text{CH}_2\text{-Cl}$ groups at the surface (not all primary hydroxyl centers on the β -cyclodextrin barrel need attach to the surface for successful binding) or they are located within the subsurface region of the pulsed plasma-deposited poly(4-vinylbenzyl chloride) layer. O–H stretching absorbance associated with the β -cyclodextrin barrels was also evident by the broad band centered around 3250 cm^{-1} , Figure 2.

3.2. Perfume Release. Vanillin host–guest inclusion complexes formed with the β -cyclodextrin derivatized pulsed plasma deposited poly(4-vinylbenzyl chloride) layers yielded two new prominent infrared absorbances appearing at 1665 cm^{-1} (aldehyde $\text{C}=\text{O}$ stretching) and 1587 cm^{-1} (benzene ring $\text{C}=\text{C}$ stretching),⁵² which are signature of the aldehyde and aromatic groups, respectively, contained in the vanillin molecule structure, Figure 3.

Quartz crystal microbalance measurements were used to track the capture of vapor phase vanillin molecules by the surface bound β -cyclodextrin barrels in real time, Figure 4. The mass detected by the quartz crystal microbalance increased rapidly upon exposure of the surface tethered β -cyclodextrin barrels to vanillin, reaching saturation after approximately 55 s. Termination of the vanillin feed followed by evacuation, produced a

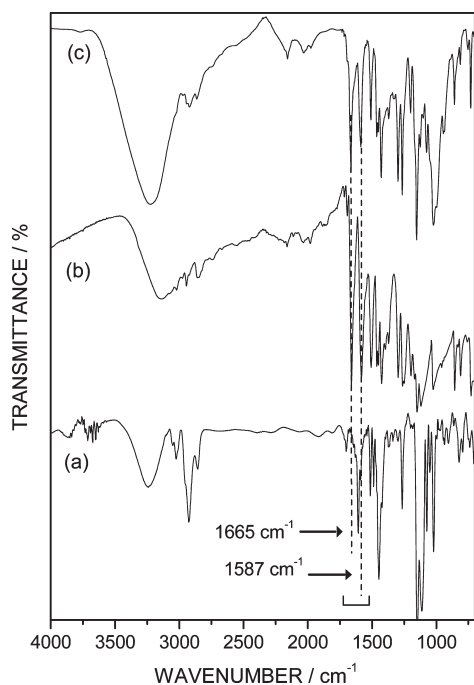


Figure 3. Infrared spectra of (a) 20 μM β -cyclodextrin-derivatized pulsed plasma-deposited poly(4-vinylbenzyl chloride) layer; (b) vanillin; and (c) following exposure of layer a to 75 mM solution of vanillin.

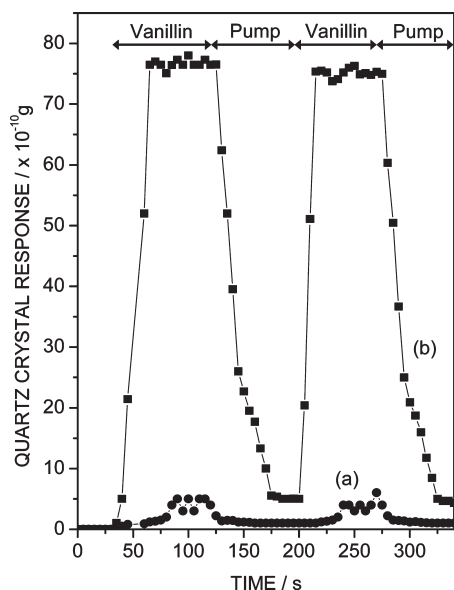


Figure 4. Quartz crystal microbalance measurements during vanillin vapor exposure to: (a) pulsed plasma-deposited poly(4-vinylbenzyl chloride) layer ($P_p = 40$ W; $t_{\text{on}} = 100$ μs ; $t_{\text{off}} = 4$ ms; 10 min); and (b) 20 μM β -cyclodextrin derivatized pulsed plasma poly(4-vinylbenzyl chloride) layer ($P_p = 40$ W; $t_{\text{on}} = 100$ μs ; $t_{\text{off}} = 4$ ms; 10 min).

drop in mass reading correlating to a loss of vanillin molecules from the β -cyclodextrin barrels under vacuum. A theoretical monolayer coverage level of 5.65×10^{13} molecules cm^{-2} can be calculated using a β -cyclodextrin surface area footprint of 1.77 nm^2 ,⁵³ (with the barrel aligned vertical to the surface so as to facilitate host–guest molecule interactions), Scheme 1. The quartz crystal microbalance measurements yield approximately

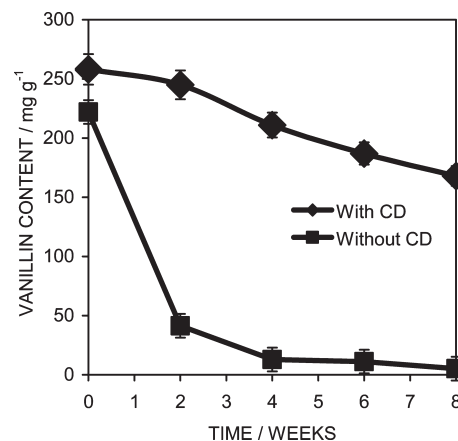


Figure 5. Rate of vanillin release from pulsed plasma poly(4-vinylbenzyl chloride) layer ($P_p = 40$ W; $t_{\text{on}} = 100$ μs ; $t_{\text{off}} = 4$ ms; 10 min) deposited onto nonwoven polypropylene cloth with and without β -cyclodextrin (CD) functionalization measured using UV–vis spectroscopy of solvent extracts.

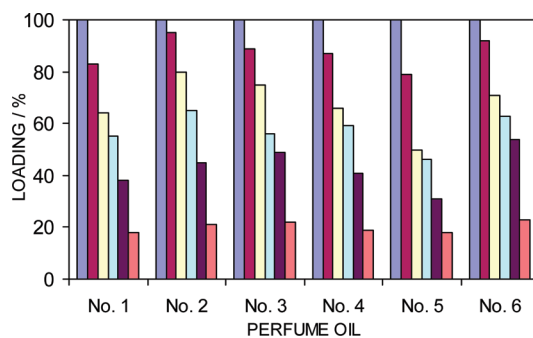


Figure 6. Relative loading of essential oils on 20 μM β -cyclodextrin derivatized pulsed plasma poly(4-vinylbenzyl chloride) layer ($P_p = 40$ W; $t_{\text{on}} = 100$ μs ; $t_{\text{off}} = 4$ ms; 10 min) deposited onto nonwoven polypropylene. Essential oils: (1) lavender; (2) sandalwood; (3) jasmine; (4) rosemary; (5) lemon; and (6) vanilla. For each oil, sequential vertical bars correspond to 0, 2, 4, 6, 8, and 10 months storage in open laboratory (20 $^{\circ}\text{C}$) averaged over 5 readings.

4.54×10^{13} vanillin molecules cm^{-2} which equates to around 80% surface coverage by cyclodextrin barrels. A second exposure to a vanillin feed recorded less than a 2% drop in the overall inclusion complex forming capability, thereby exemplifying the surface anchored β -cyclodextrins' recharging behavior. A control experiment using the underivatized pulsed plasma poly(4-vinylbenzyl chloride) layer displayed minimal interaction with the vanillin probe molecule, where a small rise in detected mass was lost upon evacuation, Figure 4.

Further exemplification using an everyday substrate (nonwoven polypropylene cloth) showed retention of high loading levels of vanillin over time (as measured by solvent extraction) when compared to a control pulsed plasma poly(4-vinylbenzyl chloride) layer coated onto nonwoven polypropylene cloth sample, Figure 5. Indeed by employing comparable initial loadings, release rates for the control samples (82% after 2 weeks and 99% after 8 weeks) were much faster in comparison to the β -cyclodextrin functionalized surfaces (5% after 2 weeks and 35% after 8 weeks).

The robustness and general applicability of these β -cyclodextrin functionalized nonwoven polypropylene cloths was further

Table 2. Sensorial Evaluation of Essential Oil Scent Intensity Emanating from Tethered Cyclodextrin Host–Guest Inclusion Complexes

perfume	scent intensity at given no. of days ^a							
	10	40	80	120	160	200	240	280
lavender	+++++	+++++	++++	+++	++	++	+	–
sandalwood	+++++	+++++	+++++	++++	+++	+++	+	–
jasmine	+++++	+++++	+++++	++++	+++	++	++	–
rosemary	+++++	+++++	+++++	++++	+++	+++	++	–
lemon	+++++	+++++	++++	+++	++	+	+	–
vanilla	+++++	+++++	+++++	++++	+++	+++	++	–

^a +++++, very strong; +++++, strong; +++, common; ++, weak; +, very weak; –, none.

demonstrated by monitoring release rates (over a period of 10 months) for several well-known essential oils (lavender, sandalwood, jasmine, rosemary, lemon, and vanilla), Figure 6. The essential oil loadings diminish in a controlled manner reaching approximately 81% ± 4% release after 10 months, whereas control experiments for these essential oils loaded onto pulsed plasma poly(4-vinylbenzyl chloride) layers deposited onto nonwoven polypropylene cloth indicated approximately 82% ± 6% release after 2 weeks and 99% ± 1% after 2 months.

Finally, human sensorial evaluation performed with these (guest) essential oil loaded β -cyclodextrin (host) derivatized pulsed plasma poly(4-vinylbenzyl chloride) layers deposited onto nonwoven polypropylene cloth indicated a lasting nose for 240 days (approximately 8 months), Table 2. In comparison, perfume release from the control pulsed plasma poly(4-vinylbenzyl chloride) layer deposited onto nonwoven polypropylene cloth displayed no scent after 14 days. Recharging of the β -cyclodextrin functionalized samples yielded no deterioration in human response over each subsequent 280 day trial period.

4. DISCUSSION

Tethering of the β -cyclodextrin barrels to pulsed plasma deposited poly(4-vinylbenzyl chloride) surfaces is accomplished by ether linkage formation using the Williamson ether synthesis reaction.⁵⁴ When in the presence of sodium hydroxide, the primary hydroxyl groups on β -cyclodextrin readily undergo an in situ conversion to alkoxide groups, which are then able to form an ether linkage via nucleophilic substitution of chlorine centers contained in the pulsed plasma-deposited poly(4-vinylbenzyl chloride) film, Scheme 1 and Figure 2. The high surface packing density of β -cyclodextrin barrels inferred by quartz crystal microbalance measurements (80% monolayer coverage) is indicative of the β -cyclodextrin barrels being suitably oriented as a consequence of the overall inherent steric flexibility of the underlying polymeric linker layer so as to allow for a greater range of surface orientations helping to maximize host–guest inclusion complex formation.

Previous attempts aimed at utilizing chemisorbed β -cyclodextrin barrels (e.g., β -cyclodextrin chemically “fixed” to naturally occurring fabrics using linking agents such as triazinyl chloride, epichlorohydrin, or polycarboxylic acids)⁶⁰ are reported to display erratic perfume persistence for periods between 1 to 6 months.^{1,5,55} In comparison, the performance of the present surface tethered β -cyclodextrin barrels toward controlling volatile perfume molecule release has been exemplified as being superior over a 10 month period, Figures 5 and 6. All of the

essential oils contain lipophilic (fatty-type) alkane segments,⁵⁶ which, like cholesterol³² (a lipid binding molecule), are capable of forming inclusion complexes inside the β -cyclodextrin cavities.^{57,58} The driving force toward complex formation is the displacement of high enthalpy polar–apolar interactions (e.g., between the apolar cyclodextrin cavity and polar water molecules initially solvated within the cyclodextrin) for apolar–apolar interactions (between the guest and the cyclodextrin cavity)¹ caused by the disruption and loss of water molecules. Subsequent slow release of guest molecules occurs as water molecules interpose the apolar–apolar interactions between guest and host over time,⁵⁹ and thereby lead to volatility of the guest molecule. Given that β -cyclodextrin can be incorporated into shoe insoles to allow the easy removal of sweat so as to inhibit microbial growth and malodors,^{1,5,60} perfume release fabrics could function in this context via a smart dual mechanism, where large guest perfume molecules are displaced by malodorous small molecules to assist in masking the offensive smell. Furthermore by combining the inherent advantages of plasmachemical functionalization (substrate independence, solventless, and low material wastage) with the ability to easily recharge tethered cyclodextrin barrels, there exists the potential for many more applications in the future involving controlled molecule release.

5. CONCLUSIONS

β -cyclodextrin host molecules can be tethered to pulsed plasma deposited poly(4-vinylbenzyl chloride) layers using the Williamson ether synthesis to form host–guest inclusion complexes for a wide range of perfume molecules. Enduring fragrance release is achieved together with the capability for recharging of the β -cyclodextrin barrels.

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