Surface Modification Using Self-Assembled Layers of Amphiphilic Cyclodextrins

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ABSTRACT: In this study six amphiphilic cyclodextrin derivatives were prepared by esterification and used to coat five industrial products made from polypropylene, polyethylene, polyvinyl chloride, or polyurethane using a new, patented coating technology. This simple approach, which consists merely of dipping the material to be coated into a suspension of a given cyclodextrin derivative in an ethanol/water solution, was used to functionalize support materials with a coat that is stable in aqueous solutions and which renders the coated materials hydrophilic. The functionalization proved to be controllable in terms of amount of cyclodextrin on the surface and can be implemented in existing production lines without investment in advanced production equipment. It is hypothesized that the cyclodextrins order themselves in structured layers forming channel-like structures preserving the very large potential for uptake and release of active compounds that is known to cyclodextrins. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2014, 131, 41047.

INTRODUCTION

Modification of surfaces with cyclodextrins (CDs) in order to obtain new functionalities has been the subject of many studies the past years.[1–5] CDs are cyclic oligosaccharides most often consisting of 6, 7, or 8 α-1,4 linked glucose units, designated α-, β-, and γ-CD, respectively.[6] Because of the unique structure of the CDs with a hydrophilic exterior and a hydrophobic-like interior, the CDs have an inherent ability to form inclusion complexes with various hydrophobic molecules.[7] When the CDs are bound onto surfaces, this inclusion forming trait is transferred to the surface in question thus opening up a vast range of applications in which uptake, removal, and/or release of active compounds is a requirement: CDs or CD derivatives are known to be able to inhibit quorum sensing by forming inclusion complexes with the compounds involved in the signaling process.[8] They are also known to be able to take up compounds like endocrine disruptors and pesticides[2] as well as being able to release drugs, as antimicrobial agents or pain killers, from the cavity.[9,10] In other words, functionalization of surfaces with CDs had been proposed for a range of applications including mechanical filters, catheters, and band aids in which the CDs will enable the surfaces to remove small molecules, as endocrine disruptors, and/or release antibiotics, respectively.

However, the grafting of CDs onto relatively inert materials has traditionally required harsh organic solvents and/or advanced

equipment[2,11,12] as well as long reaction times: it is not unusual with production times of 2–3 days.[2,10] This means that the overall production process of the final product is very laborious and complicated resulting in high production costs. We have previously presented a new, simple method of coating polypropylene with CDs by dipping the material into suspensions consisting of amphiphilic CDs and appropriate ratios of water and ethanol. The applied amphiphilic CDs were produced by simple esterification of β-CD with alkyl chlorides and displayed the ability of self-assembling onto the surface of polypropylene nonwovens by the formation of multilayers. It was showed that the amount of amphiphilic CDs applicable to the surface can be controlled simply by varying ethanol/water ratios and that the coat proved stable even when exposed to 20 h of Soxhlet extraction with water. The entire process takes a few seconds and being based on simply dipping the support material to be coated into accessible household components as water and ethanol, the coating method is readily applicable for industrial scale in contrast to, for instance, functionalization methods requiring electron beams or plasma treatment.[11,13] It has the potential of being implemented in existing production plants thus substantially lowering the introduction costs compared to the traditional grafting methods.[14]

In the literature different techniques and set-ups are used to coat different support materials and a common feature in all

coat techniques seems to be the need for covalent grafting of the CDs to the surface.[10–13] Considering the fact that there is a significant difference in the chemical properties of materials such as polypropylene and polyurethane the apparent need for different approaches to the coat technique is understandable. However, for a company using several different materials in their production it would be a substantial price-raising issue if each material required specific equipment for the coating process.

In this article we demonstrate how our technology can be used to coat five different raw and processed synthetic materials using the same method and set-up. Using controlled syntheses of amphiphilic β-CDs with various degrees of substitution, characterized by NMR and MS, it is shown how a stable coat is formed by most likely a combination of hydrophobic forces and van der Waal forces. Various companies have kindly provided samples from their production line for the experiments thus enabling the demonstration of the versatility of the coating technology. The support materials for the coating process are polypropylene membrane sheets (PP), polyethylene carriers (PEC), polyethylene membrane sheets (PE), and catheters of polyurethane and polyvinylchloride (PU and PVC, respectively). Commercially available polytetrafluoroethylene tubes (PTFE) were used as a reference material. The extent of the coating is controlled using different ethanol/water ratios and the obtained coat is tested for aqueous stability, composition, and physically characterized by measuring the contact angle between water and the surface of the support material.

EXPERIMENTAL

Materials

β-CD (pharmaceutical grade) was purchased from Wacker Chemie AG (Burghausen, Germany). 96% ethanol was obtained from Kemityl (Køge, Denmark). Boron trifluoride diethyl etherate (46.5%), tert-butyldimethylsilyl chloride (97%), caproyl chloride (98%), cesium carbonate (99%), diethyl ether (99%), 4-(dimethylamino)pyridine (99%), N,N-dimethylformamide (anhydrous 99.8%), hexanoic acid (99.5%), hydrochloric acid (37%), iodine (99.7%), pyridine (anhydrous, 99.8%), and triphenylphosphine (99%) (all from Sigma-Aldrich, Steinheim, Germany) were used as received. β-CD was dried in vacuo at 110°C overnight. Untreated, isotactic polypropylene was kindly provided by Fibertex A/S (Aalborg, Denmark). Polyethylene carriers and sheets were kindly provided by Anoxkaldnes AB (Lund, Sweden) and Hydrotech AB (Vellinge, Sweden), respectively. Polyurethane and polyvinylchloride catheters were kindly provided by Coloplast A/S (Humlebæk, Denmark). Polytetrafluoroethylene tubes were purchased at Buch & Holm A/S (Herlev, Denmark). Unless otherwise stated, purified water was used in the experiments and obtained as deionized water.

Synthesis of Amphiphilic Cyclodextrins

Primary side modified amphiphilic CD (ACD 2)[15] and secondary side modified amphiphilic CD (ACD 3)[16] were prepared according to literature. In brief, the primary side modification was synthesized via a heptakis-iodo-β-CD obtained by treatment of the β-CD with iodine/triphenylphosphine followed by

nucleophilic displacement of the iodo groups using a cesium carboxylate of hexanoic acid. Secondary side modification was made by esterification of heptakis-(tert-butyldimethylsilyl)-β-CD with caproyl chloride followed by deprotection of the silyl groups using boron trifluoride diethyl etherate. Randomly esterified amphiphilic CDs (ACD 1 and 4a-c) were prepared by the method of Gallois-Montbrun et al.[17] where native CD was esterified using different molar ratios of caproyl chloride in pyridine. One derivative, ACD 1, was prepared differently with respect to the purification: instead of precipitation in hydrochloric acid, as with ACDs 4a-c, the majority of pyridine was removed in vacuo and the amphiphilic CDs were allowed to crystallize during 24 h before being filtered off and washed successively with water and diethyl ether. Verification of the obtained products was conducted by NMR analyses in DMSO-d_6 at 310 K on a Bruker DRX600 spectrometer (5 mm TXI (H/C/N) xyz-gradient probe).

Characterization of the Amphiphilic Cyclodextrins

Determination of the Average Degree of Substitution. The average degree of substitution (DS) of the amphiphilic CDs was determined using MALDI-TOF MS. The double layer method was used consisting of a nitro-cellulose (NC) and α-cyano-4-hydroxycinnamic acid (CCA) matrix in a Reflex III (Bruker Daltonics, Bremen, Germany). A thin layer of freshly prepared 1:4 (v/v) mixture of NC and saturated CCA in acetone was deposited on a MALDI target plate and allowed to dry. The purified amphiphilic CDs was solubilized in ethanol and deposited directly onto the target plate by adding a 1 µL droplet of a 1:1 solution of ACD and saturated CCA in an aqueous solution of 2:1 (v/v) 0.1% trifluoroacetic acid and 80% acetonitrile. DS was calculated from the MALDI-TOF spectrum using the following equation:

$$DS = \frac{\sum_i I_i \cdot DS_i}{\sum_i I_i} \tag{1}$$

where "I_i" denotes the intensity of the i'th peak and "$_i$" denotes the degree of substitution corresponding to the i'th peak.

Coating of Materials with Amphiphilic Cyclodextrins

Prior to the coating procedure, each support material was washed several times alternately with warm ethanol and water to remove processing residues such as spinfinish and other surface treatments from the surfaces of the materials. The materials were left at room temperature overnight to dry before use. The catheters and the sheets were cut into suitable sizes while the plates and the carriers were coated without further treatment. Coat solutions with ethanol/water ratios of 100, 80/20, 60/40, 40/60, and 20/80 v/v, respectively, were prepared by dissolving 1 mg/mL of each amphiphilic CD in the suitable amount of ethanol before addition of water, using ~30 mL coat solution per g support material. Each material was then dipped into the solution for ~10 s before being left to dry horizontally on a steel mesh overnight at room temperature. The weight of the support material was noted before and after the coat procedure. All experiments were performed in triplicates.
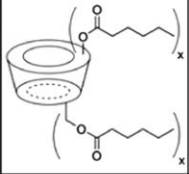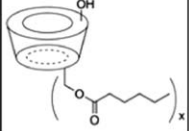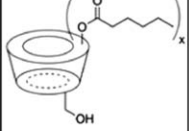
Name	Configu-ration	Average degree of substitution	Average molar mass (Da)
ACD 1	x = 3-8[i]	5.0	1627.9
ACD 2	x = 4-7	6.7	1798.2
ACD 3	x = 14-23[ii]	18.1	2949.0
ACD 4a	x = 2-5[i]	3.5	1481.2
ACD 4b	x = 5-11	8.4	1966.7
ACD 4c	x = 10-14	12.1	2333.4

Figure 1. Overview of the six amphiphilic cyclodextrin derivatives synthesized for the purpose of coating the support materials. [i]Mainly primary substitutions; [ii]The high average degree of substitutions is caused by over-acylation as previously reported in the literature.[24]

Characterization of the Coat

Determination of Coat Amount. The quantity of amphiphilic CD on each sample of the support material was determined from the weight gain of the materials by weighing the samples prior and after coating. The amount of coat was then calculated as follows:

$$A = \frac{(W_2 - W_1)}{M\bar{w}} - W_1 \cdot 10^6 \qquad (2)$$

"W_1" and "W_2" are the weights (g) of the support material prior and after the coat procedure, respectively, "M_w" is the average molecular weight (g/mole) of the amphiphilic CD and "A" is the amount of coat as expressed in μmol/g. All experiments were performed in triplicates.

Stability in Water. The support materials were coated as described above. After drying overnight the coated support materials were placed in 20 mL glass vials filled with water and left at room temperature agitating at low rpm's overnight. Samples of 1 mL of the water were lyophilized and resuspended in 100 mL 96% ethanol and analyzed using MALDI-TOF MS, as described previously.

Contact Angle Measurements. The support materials were coated as described above. Totally, 10 μL water was placed carefully on the surface of the material and the contact angle between the surface and the droplet was measured after 10 s using a KSV Cam 200 contact angle meter (Espoo, Finland). The results were analysed with KSV Cam Optical Angle Software (vs. 3.95).

RESULTS AND DISCUSSION

Many different methods and set-ups can be found in the literature for the grafting of CDs onto surfaces. Most of these studies would require either a rather immense investment before being implemented in an existing production line and/or that the company rearrange their production line, for instance to implement the equipment for gamma irradiation or corona treatment. In this study we present how five different synthetic polymers can be functionalized with CDs, thus obtaining the complex formation abilities of the CDs, using a simple dip-and-coat process which can be performed on site. The selected support materials were samples used in a range of applications: catheters (PU and PVC), water purification (PE and PEC), cell cultivation (PS and PSC) and personal care products (PP). A stable coat is formed on the support materials based most likely on hydrophobic forces.

Synthesis and Characterization of Amphiphilic Cyclodextrins
Six different amphiphilic CD derivatives were synthesized with the purpose of investigating the versatility of the coat technology as well as the influence of the degree of substitution of the amphiphilic CDs on the coat efficacy and stability. The derivatives are sketched with the respective abbreviations in Figure 1 which also states the position of the substituents, the average degree of substitution as well as the average molar mass. Selective side modification was made with classical silyl protecting group strategies in order to avoid primary side modification in the case of ACD 3 whereas the heptakis-iodo-β-CD intermediate was applied in the synthesis of primary side modified ACD 2. The randomly modified derivatives were obtained by nonselective, direct esterification of native β-CD. All derivatives showed NMR-spectra in accordance with literature.

Characterization of the Coat
The amphiphilic CD derivatives were used to coat five different support materials, which are sketched in Figure 2. The materials differ not only in chemical composition but also in structure as the surface areas are very different. PP and PE are both fiber-based textiles whereas the other three are solid surfaces with a much lower surface area in comparison. The materials were provided as ready-to-use products straight from the respective production lines as opposed to crude, raw material which has not yet been modified for use. Each material was only washed in warm ethanol prior to the coating which was performed by dipping the material into a coat suspension consisting of 1 mg/mL of each amphiphilic CD and a solution of ethanol and water which varied from a content of ethanol of 100% v/v to a content of ethanol of 20% v/v. Earlier studies on the coat technology proved that the exact same coating technique but with native CDs instead of amphiphilic CDs did not yield any significant results on PP.[14] For this reason it was deemed futile to include native CDs in this study.

The experiments proved that all five support materials could be coated with every amphiphilic CD derivative using every ethanol/water ratio. The only exception to this observation, see Table I, was PVC which turned out to be uncoatable using coat solutions with a surplus of ethanol and the reference material PTFE which proved to be utterly uncoatable no matter which
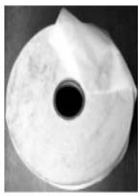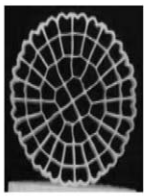
Figure 2. Overview of the five support materials used for the coating experiments with six different amphiphilic cyclodextrin derivatives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amphiphilic CD derivative were used at any given ethanol/water ratio. Attempts were made to coat PTFE using very high concentrations of ACD 1 and 3 (data not shown). When droplets of the coat solution succeeded to remain on the PTFE surface clusters of aggregated coat could be seen after evaporation of the ethanol/water solution. However, these coat clusters were very easily removed by simply shaking the material, using running water or other similar mechanical stress. Hence, a stable amphiphilic CD coat was not possible to obtain on PTFE using this coating method.

Apart from PTFE, PVC was the material which in general was coated with the least amount even compared with similar solid surfaces like PU and PEC. PU was the only material which had no preference for any of the amphiphilic CD derivatives. Maximum coating was achieved using 100% ethanol no matter which derivative was used but the amount of coat differed only very little (mean: 2.1 μmole/g, $\sigma = 0.3$). As comparison, the ethanol/water ratio of the polyethylene materials varied greatly depending on which amphiphilic CD was used and covered all tested ratios. In opposition was PP which had a preference for a solution containing equal amounts of ethanol and water, however, PP had a clear preference for ACD3 and a great variation in the amount of coat (mean: 21.9 μmole/g, $\sigma = 12.1$). Never-

theless, PP was by far the polymer most susceptible to the coat which, of course, at least partly is explained by its large surface area in comparison with the other materials. Figure 3 gives an example of the difference between PP and the other support materials, here represented by PU, and the maximum achieved amount of CD coat for all support materials can be found in Table II. As seen in this table, the standard deviation is quite high which is a reflection of how depended the coat amount is on both the ethanol/water ratio and the actual CD derivative. It is a clear indication that it is possible to optimize the coat to numerous different surfaces by simply changing the ethanol/water ratio and/or choosing the right derivative for that specific surface. It is believed that the creation of the coat is the result of a phase transition from unstable suspended/solubilized amphiphilic CD aggregates/particles in the ethanol/water solution to solid form on the surface of the support materials. This hypothesis is supported by the fact that coat clusters were obtainable on the PTFE surface if droplets of the coat solution managed to remain on the surface. That is to say: the coat itself is formed upon evaporation of the ethanol/water solution subsequent to the dipping procedure. This means, that the reason for the high standard deviations may simply lie in the difference of the design of the materials: as mentioned before, PP and PE are both fibre sheets meaning that the coat solution is dispersed more easily on the entire surface leading to a more even distribution of the amphiphilic CDs. PEC, PU and PVC are hard, solid plastics which inevitably means that the coat solution will tend to form droplets on the surface and concentration gradients of the amphiphilic CDs across the surface is thus unavoidable.

Nielsen[14] performed a Soxleth extraction of PP coated with an equivalent of ACD 1, although the substituents were C4-chains rather than C6. It was shown that the amphiphilic CD coat generally remained on the PP even after 20 h of Soxleth extraction. A similar experiment was performed on every coated material although at room temperature. The samples were submerged in

Table I. Overview of the Coatability of the Various Support Materials

	PP	PEC	PE	PU	PVC	PTFE
100	x	x	x	x	–	–
80/20	x	x	x	x	–	–
60/40	x	x	x	x	–	–
40/60	x	x	x	x	x	–
20/80	x	x	x	x	x	–

X, coatable; –, uncoatable. The table is representative for every amphiphilic CD derivative.
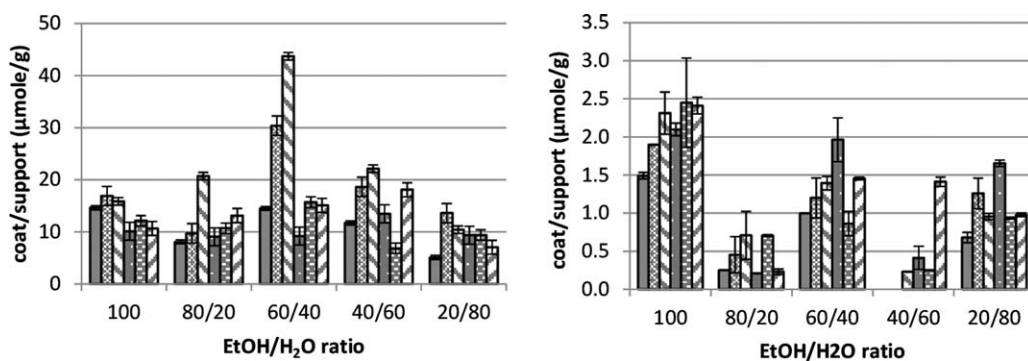
Figure 3. The amount of coat obtained at the various ethanol/water ratios on polypropylene fiber sheets (left) and polyurethane catheters (right). Error bars indicate standard deviation ($n = 3$). Note the different scaling of the ordinates. The amphiphilic CD derivatives are ordered from ACD 1 to ACD 4c in each cluster as seen from left to right.

water and agitated overnight. The samples were then subtracted and 1 mL water samples were lyophilized and redissolved in ethanol before analysis on MS. The results showed that ACD 2, 3, 4b, and 4c provide a coat that is completely stable under the present conditions as no CD content could be detected by the MS analysis of the water samples. Concerning ACD 1 and 4a molecules of low DS could be detected. In the case of ACD 4a it meant that each of the derivatives, that is CDs with 2–5 substituents, were present in the water. However, weight controls on the dried materials did not show any significant change before and after the wash experiment, indicating that only a fraction of the coat was removed. It must seem likely, however, that the coat of ACD 4a would be removed over time with repeated wash cycles but the time frame is so far unknown. There did not seem to be any difference between the support materials—the above mentioned tendencies were the same no matter the support material. It is then possible to conclude that the stability of the coat is independent of the support material and to obtain a coat stable in aqueous environments one can used amphiphilic CDs with relatively high DS.

Previous unpublished studies showed that PP changed chemical properties going from hydrophobic to hydrophilic when coated with amphiphilic CDs equivalent to ACD 1. Consequently, it was expected that at least the more hydrophobic materials would be able to become more hydrophilic upon coating but

the extent to this change and the importance of the ethanol/water ratio was unclear. Hence, contact angle measurements were performed on all materials, coated with all amphiphilic CD derivatives using the before-mentioned ethanol/water ratios. With some exceptions all support materials became significantly more hydrophilic after the coating no matter which amphiphilic CD derivative was used, albeit the extent of the hydrophilicity varied, as seen on Figure 4. PVC showed the same tendency towards a more hydrophilic surface, however, with a very few exceptions, it was not statistically significant. In general, the ethanol/water ratio had no significant impact on the hydrophilicity except in PU coated with ACD 4a where the surface became significantly more hydrophilic when water was added to the coat solution. Overall, ACD 4a stood out as the amphiphilic CD with the best abilities to render the surface hydrophilic, most prominently seen with PP and PE: uncoated PP was the most hydrophobic with a contact angle of 141° ($\sigma = 0.3$) while PE was 116° ($\sigma = 4.7$). ACD 4a was capable of yielding a contact angle of 59° ($\sigma = 12.7$) (60/40 EtOH/H_2O) and 33° ($\sigma = 5.5$) (20/80 EtOH/H_2O) for PP and PE, respectively. With the definition of hydrophobic and hydrophilic being contact angles above or below 90°, respectively,[18] it seems as ACD 4a has changed the chemical properties of PP and PE from hydrophobic to hydrophilic. PU is a hydrophilic material with contact angle of 83° ($\sigma = 3.1$), while PEC was on boundary between the two stages with a contact angle of 95° ($\sigma = 3.6$). In both cases the most hydrophilic coat was obtained using ACD 4a with contact angles of 59° ($\sigma = 1.8$) (80/20 EtOH/H_2O) and 46° ($\sigma = 2.7$) (40/60 EtOH/H_2O) for PEC and PU, respectively.

It is a peculiar feature that a coat consisting of hydrophobic alkyl chains and a CD cavity which is relatively hydrophobic is capable of rendering a surface hydrophilic. We hypothesize that the explanation to this phenomenon is found in the arrangement of the CDs on the surface. It is a known fact that solid CDs can order themselves in crystal structures in which the cavities form long channels.[19] It is possible that a similar crystal structure is formed by the amphiphilic CDs as distinct layers of amphiphilic CDs have previously been reported.[20] The amount of coat found on the surfaces (Table II) suggests that the coat consists of multiple layers of amphiphilic CDs on top of each other. It is possible, that each CD layer will be stabilized by

Table II. Schematic Representation of the Maximum Coat Amount Achieved for Each Support Material

Support	CD	EtOH/H_2O ratio	µmole/g	Mean
PP	ACD 3	60/40	43.707	13.976 ($\sigma = 7.429$)
PEC	ACD 2	20/80	1.361	0.434 ($\sigma = 0.233$)
PE	ACD 2	40/60	3.679	1.454 ($\sigma = 0.873$)
PU	ACD 4b	100	2.449	1.065 ($\sigma = 0.777$)
PVC	ACD 1	20/80	0.246	0.061 ($\sigma = 0.089$)

The amount is calculated as µmoles amphiphilic CD per gram support material, as described previously. The mean value (standard deviation stated in parentheses) is calculated on the basis of all experiments with all derivatives at every ethanol/water ratio.
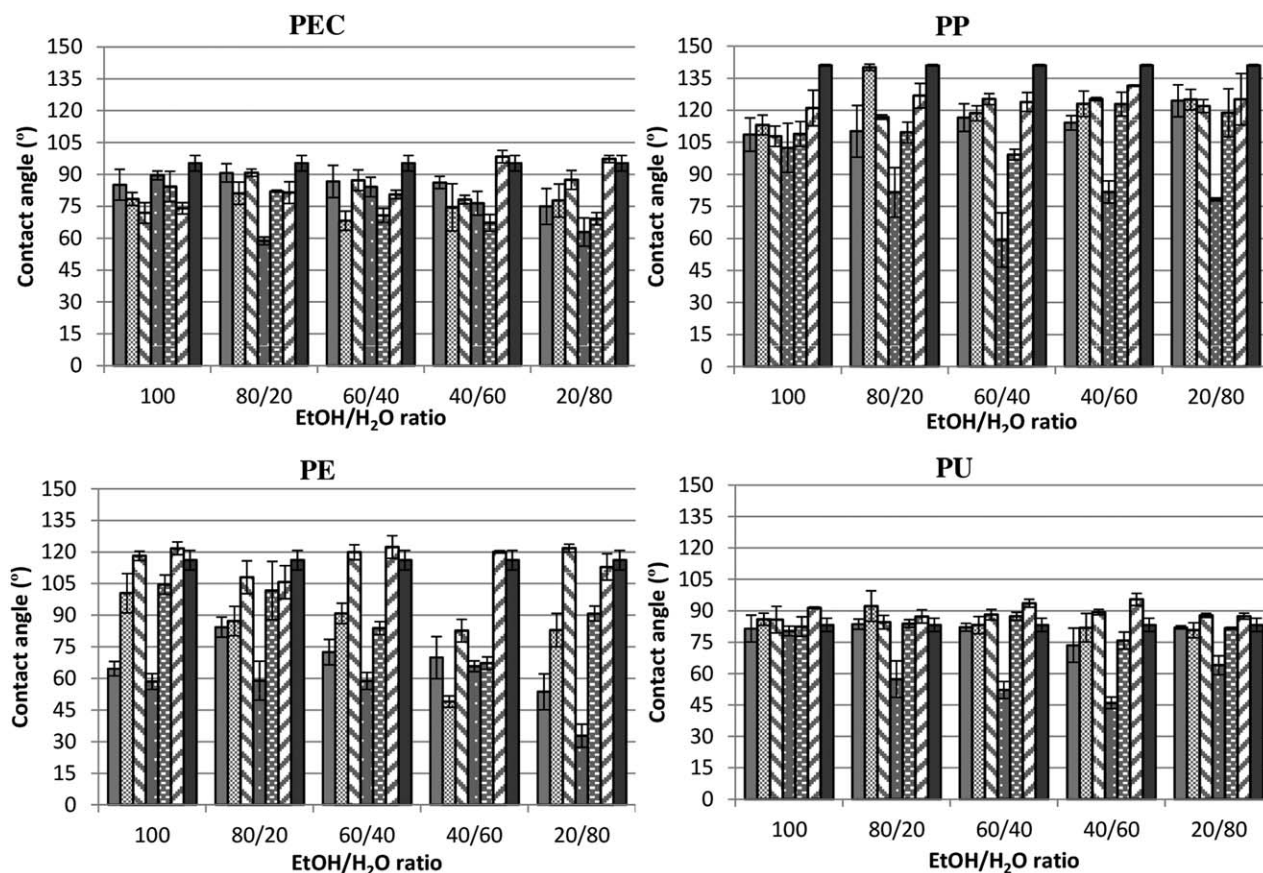
Figure 4. Contact angle measurements of the support materials before and after treatment with the amphiphilic CD derivatives. PVC showed only very few statistical significant changes in the contact angle and is not shown. Error bars indicate standard deviation ($n = 3$). The amphiphilic CD derivatives are ordered from ACD 1 to ACD 4c in each cluster as seen from left to right. The final column of each cluster represents the results of the noncoated support material.

either hydrogen bonds between the unsubstituted hydroxyl groups or hydrophobic interactions and van der Waals forces between adjacent alkyl chains, as sketched in Figure 5, depending on the location and number of substituents. The alkyl chains can either intertwine away from the cavity or be positioned vertically as an elongation of the cavity. It is probable that the coat is assembled in a manner where the amphiphilic CDs of lower DS, and thereby the most hydrophilic, are on top and close to the bulk water while the amphiphilic CDs of higher DS, and thus most hydrophobic, are at the bottom, near the surface of the support material. With the cavities arranged on top of each other, as opposed to a more random orientation, for instance similar to the cage formation of solid native CDs,[19] and with the most hydrophilic derivatives closest to the bulk water it can thus be speculated that a long channel is formed through which water can form a column stabilized from the bulk water by hydrogen bonds. A similar water passageway is seen in nature: the xylem tissue of trees is used to transport water up through the stem by forming a column of water molecules. The water column is stabilized due to hydrogen bonding between the water molecules and adhesion of these molecules to the cell wall. A plant cell wall is comprised partly of cellulose, an organic polymer consisting of β-1,4-linked glucose, that is, the same building blocks as CDs, the only difference, apart

from the geometrical structure, being the orientation of the glycosidic bond.[21]

ACD 4a showed a distinctively better ability to render a surface hydrophilic compared with the other derivatives. ACD 4a is the most hydrophilic of the derivatives with a DS of 3.5. Hence, the density of the substituents is low especially compared with derivatives like ACD 3 and ACD 4c. It is easily imaginable that the higher the density of the substituents the higher the likelihood of the alkyl chains to interfere with the column of water, by covering parts of the cavities simply due to lack of space and/or interrupting the adhesion to the glucose units by forming a too hydrophobic environment. This tendency is particular obvious when looking at PE (Figure 4) where ACD 1 and ACD 4a with low DS render the surface more hydrophilic than ACD 3 and ACD 4c.

Two materials stood out in the contact angle measurements: PVC and PU. As mentioned briefly above, no statistical significant difference in the hydrophilicity of PVC was observed, with only a few exceptions, albeit the tendency could be seen. The mentioned exceptions were all found using ACD 4a. With a contact angle of 92° ($\sigma = 3.7$) PVC was not the most hydrophilic starting material but similar to that of PEC (95°). The two materials are quite similar in structure and the differences
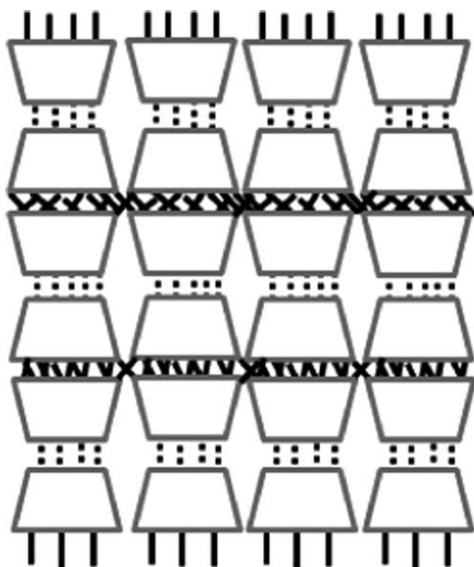
Figure 5. A schematic representation of one of the hypothesized structure of the amphiphilic CD coat. The black lines represent the alkyl side chains while the dotted lines represent hydrogen bonds between hydroxyl groups on the CD. The alkyl chains are thought to either align with or spread out from the cavity, either way allowing the formation of a channel structure for water passage.

in the effect of the amphiphilic CD coat can at first seem peculiar. However, the difference between polyethylene and PVC is that one hydrogen atom in the ethylene monomer is substituted by chlorine in PVC as compared with polyethylene (Figure 2). Chlorine is a rather large atom and quite electronegative. As mentioned earlier, PVC was not coated to the same extent as the other materials and it can be speculated that the electronegative chlorine on an alkane backbone cannot form van der Waals forces in the manner required for this coat. Another possibility is that the sheer size of chlorine is enough to disrupt the strict alignment of the cavities on top of each other that is needed to form the channels and thus the water columns. This could be the reason why there seems to be only very little effect on the hydrophilicity of PVC even though an effect can be observed on PU, a more hydrophilic material than PVC.

As mentioned, also PU stood out in the contact angle measurements on two occasions. First, there seemed to be an apparent dependency on the ethanol/water ratio of ACD 4a, as mentioned previously, second, there was the fact that when coating PU with ACD 4c, a significantly less hydrophilic surface was obtained. This tendency was also observed with the other materials, apart from PP, at a majority of the ethanol/water ratios, albeit not statistically significant, see Figure 4. The obtained contact angles using ACD 4c on PU was in the range of 87–95° ($\sigma = 0.4$–3.2) which means that PU actually change from having a hydrophilic surface to having a somewhat hydrophobic surface. This can also be explained by the channel structure theory: ACD 4c stands out from the other CD derivative by having multiple substituents on both rims of the CD. ACD 1 and ACD 4b also have substituents on both rims, however, not nearly as many and not to the same extent, as the synthesis clearly favors

substitutions of the primary hydroxyl groups. The location as well as the number of the substituents is likely to affect the structure of the CD layers of the coat and it is likely that a denser layer of alkyl chains is capable of blocking the cavities. The significance of the fact that the substituents are located on both rims is more unclear but it can be speculated that this placement can cause a disturbance of the ordered CD layers and thus disrupt the cavity channels. Disruption of the water channels caused by an uneven distribution of the cavities can also be the reason to why the tendency of a more hydrophobic surface with ACD 4c is more pronounced with PU than the other materials, given that the structure of PU rather different compared with the others.

The experiments presented in this article attributes to a better understanding of the forces behind the formation and stability of the coat. At first it would seem plausible that the link between the coat and the support material is due to hydrophobic interactions between the surface of the support material and the alkyl chains of the amphiphilic CDs—both of which are hydrophobic. However, why then was it not possible to coat PTFE? The fact that it seems impossible to coat PTFE could indicate that the link between the very first layer of amphiphilic CDs and the surface of the support materials is caused, at least not only by hydrophobic interactions, but also by van der Waal attraction forces, in this case London dispersion forces, as fluorine is incapable of forming these bonds. As mentioned previously, the other layers are probably stabilized by a combination of hydrogen bonds, van der Waals forces and hydrophobic forces between adjacent alkyl chains. Albeit being rather weak forces it seems that the vast amount is enough to keep the coat stable.

There is a large difference between the affinities of the amphiphilic CD derivatives towards the various support materials with PP as the most preferred material by far. It is remarkable that the addition of a methyl group to the monomer unit can be that significant as it seemingly is when comparing PE and PP, e.g., see Table II, which are both fiber-based materials and should have a comparable surface area. It indicates that the geometrical structure is crucial to the amount of coat obtained. However, substitution of the methyl group of the monomer with chlorine as in PVC creates a surface that is only very little prone to the various amphiphilic CD derivatives so clearly structure is not everything. This said it has been shown that the amount of coat obtained on PP is proportional with the initial concentration of amphiphilic CD in the coat solution.[14] There is so far nothing that indicates that this observation should not be valid for any material coatable with the amphiphilic CDs. This means that it should be possible to optimize the coat amount, and thus improve the uptake ability of the material in question markedly, simply by increasing the concentration of the coat solution.

In the literature technologies like electron beams, gamma irradiation, corona treatment etc. are used in order to functionalize surfaces with CDs. A common feature of these methods is the very long production time, ranging from a couple hours[9,11,12,22] to several days,[2,10,13] depending on the amount of coat desired on the surface,

excluding drying time. Dip-coat technologies have been reported which result in a layer-by-layer build-up, somewhat similar to the technology of this work. However, the layer-by-layer technology requires pretreatment of the support material for it to be susceptible to the functionalization and furthermore the process of building up each layer is reported to take at least 2 h.[23] In comparison, the technology presented in this article, requires seconds of dipping in order for the material to be coated. Previous, so far unpublished, experiments have been carried out where PP successfully is coated with an equivalent of ACD 1 using the industrial kiss-roll technique—a method in which the polymer is transferred to large rolls directly in the production line and coated from these rolls by letting the polymers roll through large containers of coat substrate. This shows that the technology can easily be implemented in existing production lines, for instance as the final step, without reducing the speed of the production line significantly. As it is based only simply dipping the support material into a coat solution of rather harmless solvents this also implies that a private customer would be able to modify an already purchased product at home. Furthermore, the coat technology presented in this work is not limited to geometrical structures as it only requires a contact between the surface and the coat solution. Hence, it enables coating of porous materials, such as membranes, as well as catheters (like PVC and PU) which were also coated on the inside of the tubes. Coating on the inside of a tube would usually not be possible with any other technologies in the literature. When looking at coat efficiency the literature reports varying results: some comparable to the present study[12] and some showing considerably larger amounts of coat with support material weight gains of up to 15%.[2] However, as mentioned above, it has previously been shown that the amount of coat obtained by dip coating with amphiphilic CDs is proportional to the initial concentration of amphiphilic CD in the coat solution.[14] Hence, similar weight gain results can easily be obtained using the method presented in this article, if so desired.

CONCLUSIONS

This study presents a new and easy method to functionalize materials made from various synthetic polymers with CDs using an approach easily implementable in an existing production line as it based on a simple dip and dry procedure. It is highly comparable with existing coat methods as it is both faster and equally, if not more, efficient, regarding coat amount. The coat obtained renders the surface more hydrophilic, a feature that is of importance in for instance water purification where hydrophobic filter materials requires high pressure with increasing costs as a result. It is stable in water and can be optimized to specific surfaces by altering either the amphiphilic CD used, the ethanol/water ratio of the coat solution and/or the concentration of the amphiphilic CD. Experiments indicate that long channels of CD cavities are formed on the surface which provides a great potential for uptake and/or release of various guest compounds. In this study β-CD has been used as it is widely available. There are no indications that the ability of the coat is depended on the cavity size. This means that it is also possible to use α- or γ-CD—or a mixture of some or all three CDs—thus increasing the range of potential guests in the cavities.

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