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UV induced cross-linking of starch modified with glycidyl methacrylate

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ABSTRACT

A new way to substitute cornstarch with glycidyl methacrylate (GMA) monomers is presented. This synthetic modification, carried out in DMSO, resulted in a DOS of 0.08. By exposing a water solution with modified starch and potassium persulfate (KPS), a radical initiator, to UV-light a free radical vinyl polymerization reaction is initiated making the starch solution chemically cross-link into a gel. The GMA modification increased the hydrophobicity of the polymer making it less water-soluble, increasing the adsorption tendency to a hydrophobic surface as seen in quartz crystal microbalance with dissipation monitoring (QCM-D) studies. The surface cross-linking process of the modified starch showed that after cross-linking the solubility of the polymer decreased resulting in a stronger adsorbed polymer to the surface compared to the non-modified starch. This proves that even though it is generally believed to be more difficult to cross-link polymers at surfaces this particular modification allowed for near complete cross-linking as suggested by the QCM-D data.

1. Introduction

In recent years there has been more and more work toward developing sustainable materials and one common approach has been to focus on those from green plants. One of these materials that have attracted special attention is starch. Starch is a polysaccharide with very high natural abundance, it is renewable and readily available at low cost. However, starch-based products such as wallpaper glues have some drawbacks compared to synthesized or petroleum-based products with respect to for instance poor mechanical properties and low water resistance. Some of these properties can however be strengthened by mixing the starch with other, most often petroleum-based, polymers into composites (Chiou et al., 2005; Ma, Chang, Yang, & Yu, 2009; Mohanty et al., 2005). Another way is by adding new chemical functionalities to the starch polymer which effectively also expands the application area for the material (Sherieva, Shustov, Mirzoev, Beshtoev, & Kanametova, 2006; Wurzburg, 2006). One example is by introducing chemical groups on the starch to allow for cross-linking of the polymer. A chemical cross-linking of starch is proven to increase both the mechanical strength and water resistance (Marques et al., 2006; Miyazaki, Yasunaga, Ishida, Ashizuka, & Ohtsuki, 2007).

In this study one of the aims was to find a new simple route for adding a vinyl functional group, a ligand, to the starch polymer enabling radical polymerization resulting in a cross-linked polymer material. We have used the grafting technique, which is a common and important technique to make active sites not only at the ends of a polymer chain but also along the polymer backbone (McNaught & Wilkinson, 1997). The ligand forming the active sites in this paper is the glycidyl methacrylate (GMA). The grafting of GMA to starch has previously been done in water with the presence of the strong oxidizing agent CAN (Ceric Ammonium Nitrate) (Athawale & Rathi, 1997; Han, Kumar, Rozman, & Noor, 2003; Willett, Kotnis, O'Brien, Fanta & Gordon, 1998). However, these reactions add the GMA in a way not preserving the vinyl group (Han et al., 2003). The addition of vinyl groups makes it possible for the polymer to react with radicals. One effective way to use this new functionality is to add a UV-sensitive initiator making it, by photopolymerization, possible to irreversibly switch the macroscopic and microscopic properties of the polymer solution. The photopolymerization method has in recent years been studied aiming for developing new drug delivery systems, such as hydrogels (Amsden, Sukarto, Knight, & Shapka, 2007). Hydrogels are polymeric material defined by a high water content, able to maintain its distinct three-dimensional structure (Kopecek & Yang, 2007). The advantages of photopolymerization in constructing, e.g. a drug delivery hydrogel are that the gelation can be performed at physiologic temperature and in situ with minimal heat generation. Bulk polymerization is the most commonly used, but the interfacial polymerization process is also very interesting and useful. For example, interfacial photopolymerization has been done in situ on cells to create a hydrogel coating resulting in greater cell viability and encapsulation efficiency compared to bulk photopolymerized gels (Nguyen & West, 2002).

In this paper the formation of a hydrogel of the starch polymer by photopolymerization in water solution as well as the interfacial

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photopolymerization process at a hydrophobic surface was studied. The adsorption process and cross-linking reaction at the surface was studied with a relatively new method, quartz crystal microbalance with dissipation monitoring (QCM-D). In addition to monitor the adsorbed amount and film thickness it is also possible to study the viscoelastic properties of the adsorbed layer. As seen in previous studies the ability to cross-link in solution does not directly imply a surface cross-linking ability (Hedin, Loefroth, & Nyden, 2007) since the polymer dynamics once adsorbed onto a solid surface is severely reduced.

2. Materials and methods

2.1. Materials

DMSO (ACS reagent ⩾99.9%, Sigma–Aldrich), starch (corn, 73% amylopectin and 27% amylose, the protein content is between 0.25% and 0.32%, Sigma), glycidyl methacrylate (GMA) (purum ⩾97%, Fluka), potassium *tert*-butoxide (purum ⩾97%, Fluka), potassium persulfate (KPS) (⩾99%, Sigma–Aldrich), H_2O_2 (25%, Merck), NH_3 (25%, Merck), hexadecanethiol ($HS(CH_2)_{15}CH_3$) (95%, Fluka), ethanol (99.5%, Kemetyl) and sodiumdodecylsulphate (SDS) (99%, Sigma–Aldrich) were all used without further purification. The non-modified and modified starch samples were prepared in exactly the same way for all experiments with the only difference that the GMA was not added during the last heating process for the non-modified samples. Water of Milli-Q quality was used for the QCM-D and bulk cross-linking experiments while the NMR experiments were carried out in D_2O (>99%, Glaser Lab). The concentrations given in % are in weight percent if not explicitly stated otherwise.

The UV-source used is a 6-W UVGL-58 (lamp: LW 34-0034-01, manufacturer: UVP) generating an UV-light at 365 nm with the intensity of 0.5 mV/cm^2. The glassware was made of borosilicate.

2.2. Synthesis of modified starch (see Fig. 1)

Cornstarch (2.5 g) was added under stirring to room tempered DMSO (200 ml) in a round-bottom flask (1000 ml). The mixture was then heated to 85 °C. After 1 h the starch was dissolved and the solution was then cooled to room temperature. Potassium *tert*-butoxide (^{t}BuOK, 1.6 g), dissolved in DMSO (50 ml) was then added under stirring and the final solution was kept at room temperature for 2 h. glycidyl methacrylate (3 ml) was added under stirring and let to react with starch during night (12 h) at 60 °C. The product was precipitated in ethanol and separated to the bottom of the flask. This precipitate was then dissolved in water and yet again precipitated in ethanol. The precipitation procedure was repeated three times in order to obtain a pure product (checked after the lyophilization with ^{1}H NMR). The final polymer mixture (water solution) was then lyophilized overnight.

2.3. QCM-D

The QCM-D technique simultaneously measures the frequency and amplitude of an oscillating quartz crystal covered with gold electrodes in contact with a solution (Hoeoek et al., 2001; Voinova, Rodahl, Jonson, & Kasemo, 1999). Measurements are carried out by applying an electric field over a piezoelectric quartz crystal. The crystal then starts to oscillate at a specific frequency directly dependent on the crystal mass. When the crystal surface adsorbs species the total mass of the crystal increases leading to a change in oscillation frequency, Δf. The mass uptake per unit area, $\Delta m_{QCM\text{-}D}$, can then be calculated by (Sauerbrey, 1959)

$$\Delta m_{QCM\text{-}D} = -\frac{\Delta f \times C}{n} = \rho_f \times \delta_f, \quad (1)$$

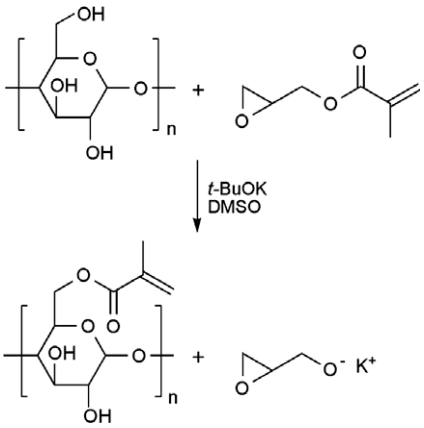

Fig. 1. The reaction of starch with GMA.

where C is the mass sensitivity constant (=17.7 ng/cm^2 Hz), n the overtone number (n = 1, 3, 5, ...), δ_f the thickness of the absorbed film and ρ_f is the effective density of the film. In the case of thin rigid films Eq. (1) is strictly valid. The film flexibility described by the dissipation factor (D) can be calculated by turning the electric field off and subsequently monitor the decay process of the oscillations. The D-factor depends on the dissipated and stored energies, both being higher for viscoelastic films, resulting in an erroneous underestimation of the adsorbed amount when using Eq. (1). However, due to the relatively small D-factors (the value of D is about 10% of the value of Δf) obtained in this work the Sauerbrey-based model (Eq. (1)) was used to calculate the adsorbed amounts.

For the QCM-D measurements AT-cut piezoelectric quartz crystals (Q-Sense AB), covered with gold, with a fundamental frequency of 5 MHz were used. The crystals were modified according to the following procedure. Crystals were initially cleaned for 10 min in a UV/ozone chamber. This was followed by immersion in a 1:1:6 mixture of H_2O_2, NH_3 and water for 10 min at 78 °C after which they then immersed overnight (>15 h) in 2 mM thiol solutions of hexadecanethiol in ethanol. This procedure results in SAM (self-assembled monolayers) with contact angles of 114° (MQ-water) (Oskarsson, 2006). Before use, the crystals were removed from the thiol solutions, ultrasonicated in ethanol for 5 × 5 min to remove excess thiols, and finally dried in a gentle flow of dry nitrogen.

A static solution D300 machine (Q-Sense AB) with a window cell operating at 21 °C was used to carry out the QCM-D experiments. The window cell is equipped with a quartz glass enabling the UV-light to pass, see Fig. 2. The UV lamp was applied about 10 cm above the window chamber. To exclude the temperature effect on the change in measured frequency the UV lamp was always turned off 2 min before next action was taken in the experiment. The concentration of modified starch was 0.1% and KPS 2%. Only the third overtone (15 MHz) is shown in the figures as a result of the high representation of all frequencies.

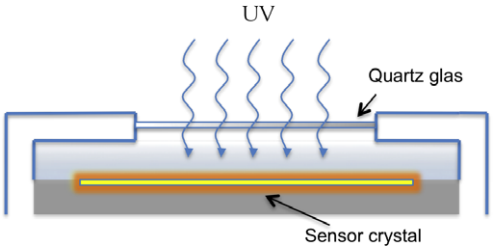

Fig. 2. Experimental setup of the window cell QCM-D experiment.

2.4. NMR and cross-linking in bulk

Cross-linking experiments in bulk were performed at room temperature by mixing the starch, KPS and water under stirring and let to dissolve during 2 h. The solutions were then degassed by bubbling the solution for 15 min with nitrogen gas. The cross-linking reactions were then carried out by exposing the solutions to UV-light (365 nm) for 5 min.

The ^{1}H NMR experiments were carried out on a JEOL spectrometer, model Oxford, 400 MHz, at 21 °C.

The chemical shift imaging (CSI) ^{1}H NMR experiments were carried out on a Varian Inova spectrometer operating at 500 MHz equipped with a conventional triple resonance probe with pulsed field gradient (PFG) working up to a maximum of 75 G/cm along the *z*-axes, i.e. along the length direction of the NMR tube. CSI NMR, a magnetic resonance imaging (MRI) method, is a well-known method which more recently has been used to study multiple nonlinear transport processes in colloidal systems including spatial resolution of the chemical shift as a function of time (Salvati, Lynch, Malmborg, & Topgaard, 2007). The NMR signals were encoded for position, so called phase encoded, by applying rectangular field gradient pulses of 0.1 ms, from −38 to 38 G/cm in 64 steps, generating an image with a spatial resolution of 0.3 mm. All experiments were done at 21 °C and during 5 min per image. In order to irradiate only the lower part of the sample most of the tube was covered with aluminum foil, see Fig. 3, leaving a thin slice of about 2 mm available for UV irradiation. After 3 min the UV-light was turned off and the sample was immediately inserted into the magnet and the experiment was started.

2.5. FT-IR

The FT-IR analysis was carried out on a Perkin Elmer FT-IR system 2000. The resolution was 4 cm^{-1}. Samples were powdered with KBr to make tablets.

3. Results and discussion

The ^{1}H NMR spectra of the non-modified and modified starch are shown in Fig. 4. The signals appearing at δ (δ = chemical shift) 6.2 ppm and δ 5.8 ppm in the modified starch spectrum are attributed to hydrogen atoms from the vinyl group (denoted as a). The signal at δ 1.9 ppm is from the methyl carbon hydrogens (denoted as b). As these are the only signals differing between the two spectra it is evident that it is indeed a transesterfication reaction and not an epoxide opening reaction that has occurred during the reaction of GMA with the primary alcohol group of the starch. This result is well in line with other reports from similar type of reactions when using aprotic solvents (Ferreira, Vidal, Geraldes, & Gil, 1999; van Dijk-Wolthuis, Kettenes-van den Bosch, van der Kerk-van Hoof, & Hennink, 1997). One possible explanation for this could be that in alkaline environment the by-product glycidol has a resonance structure stabilizing the molecule where the negative charge is delocalized over the two oxygen atoms.

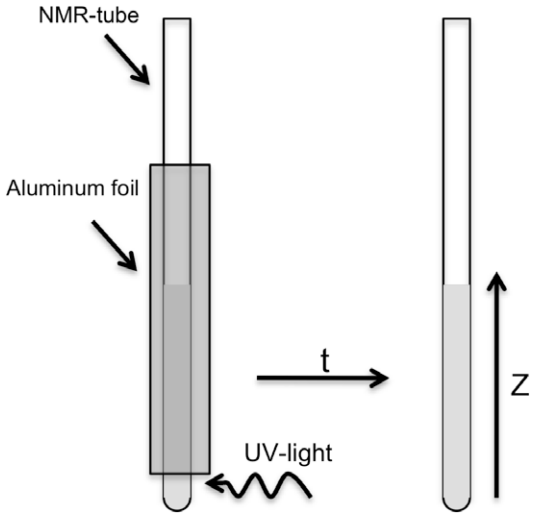

Fig. 3. During the UV-irradiation the NMR test tube was covered with aluminum foil.

By comparing the total area of the two vinyl peaks in the spectrum from the modified starch (Fig. 4) with the starch peak at δ 5.4 ppm, which is attributed to the hydrogen at the α-carbon (carbon c in Fig. 4) the degree of substitution (DOS) can be calculated as;

$$\mathrm{DOS} = \frac{I_{5.8} + I_{6.2}/2}{I_{5.4}} \Big/ 3, \qquad (2)$$

where I is the area of the peaks for the respective chemical shifts. The expression is divided by 3 since there are 3 hydroxyl groups per glucose monomer. From the data shown in Fig. 4 the integration procedure after a careful base line correction gives DOS = 0.08 ($I_{5.8} \approx 1$, $I_{6.2} \approx 1$, $I_{5.4} \approx 4$). This rather high yield makes the polymer suitable for a material with a high cross-linking density. In passing we note that the synthesis route for the GMA modification as suggested by Reis et al. failed, most likely due to ring opening of the epoxide by water used as a solvent (Reis et al., 2008). Referring to the literature our conclusion is that the degree of substitution is higher for the amylose compared to the amylopectin part of the starch polymer (Aggarwal & Dollimore, 1999; Huang, Schols, Klaver, Jin, & Voragen, 2007).

As seen in the NMR spectra the line widths of the peaks arising from the glucose monomer are substantially affected by the acrylate modification, where the line width is larger for the modified starch. The width of the water peak is however exactly the same in the two spectra showing that this is not an effect of magnetic inhomogeneities. There are two plausible explanations for this result. The first is that as the starch polymer is modified it reacts with other polymers and thereby increases the total molecular weight leading to a decrease in motion of the polymer as such (internal polymer chain dynamics as well as rotational diffusion of the polymer complex). The other explanation, just as shown by Bravo-Osuna et al., is that the modification increases the hydrophobicity of the polymer (Bravo-Osuna, Ferrero, & Jimenez-Castellanos, 2005). These hydrophobic sites decrease the water solubility of the polymer and similar to the first explanation effectively increases the molecular weight (although not in a covalent manner) by self-aggregation. The subsequent slowing down in polymer motions leads to broader signals in the NMR spectrum due to the faster transverse relaxation rate. We believe strongly that it is the second explanation that is the origin of the increase of the line width of the NMR-signal.

The IR-spectra, shown in Fig. 5, validate the observations and conclusions drawn from the ^{1}H NMR spectra. The figure shows the results for both starch and modified starch. The main difference between the two spectra is the shoulder arising at about 1700 cm^{-1}, after the vinyl modification, which is attributed to the C=O stretching in a conjugated system. This together with the NMR data clearly shows that the acrylate is bound to the starch polymer. Also the small change around 1630 cm^{-1} indicate that the reaction has occurred since this wavelength corresponds to the C=C stretching of a conjugated system. The large shoulder at 1000–1200 cm^{-1} is from the C—O stretching of the starch.

3.1. Cross-linking in solution

The change in bulk properties as a result of cross-linking the polymer in water solution is shown in Fig. 6. The vials contain

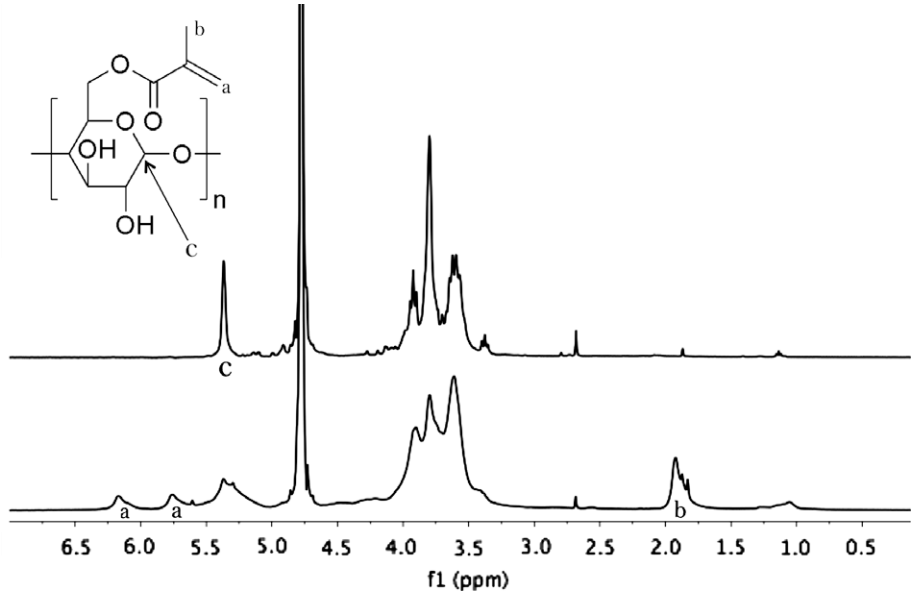

Fig. 4. ^{1}H NMR spectra of unmodified (top spectra) and modified (lower spectra) starch. The concentration of starch was 2%. Note the spectral changes at the a, b and c positions.

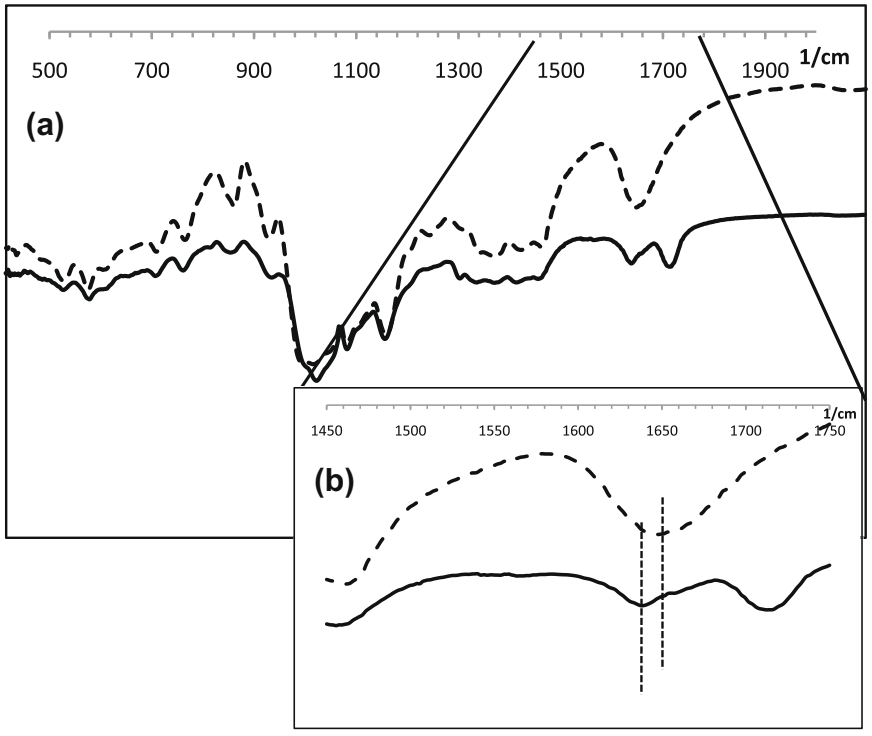

Fig. 5. Infrared adsorption spectra of non-modified (dashed line) and modified (solid line) starch. Notice the difference at wavelength 1700 cm^{-1} rising from the modification.

different concentrations of the modified and non-modified polymer and are tilted backwards causing, in sample (b) and (c), the non-cross-linked solutions to flow, whereas the cross-linked materials do not. The cross-linking of the polymer also changes the turbidity of the samples. The reason for the turbidity increase is the strong heterogeneity introduced during the cross-linking reaction. Locally the material has a high cross-linking density and thereby also a high polymer concentration while other parts of the material have much lower polymer densities. When these spatial fluctuations occur on length scales corresponding roughly to the wavelength of visible light and upward the sample scatters the light and appears turbid. The same experimental setup was performed for the non-modified starch but this experiment did not result in any noticeable change in either viscosity or transparency/turbidity of the materials.

As the initiation of the radical polymerization reaction is ended (by removing the UV-light) the reaction proceeded for several hours and was considered finalized after 24 h (as judged by visual inspection).

The cross-linking reaction was studied in more detail by NMR chemical shift imaging (CSI). The result from this experiment is shown in Fig. 7. The spectral window (the observed length in the

Fig. 6. Tilted samples showing cross-linked (the left of the two samples containing modified starch and KPS 2%) and not cross-linked (the right of the two samples containing native starch and KPS 2%) starch solution with concentrations 1% (a), 5% (b) and 10% (c). The small rods are magnetic bars used for creating a homogeneous mixture during the photopolymerization. However, as the viscosity increased the rods were out of use.

z-direction of the NMR tube) was about 1.9 cm and the small change in chemical shift in the lower part of the sample (corresponding to the CSI results at the bottom of the graphs) is due to magnetic field inhomogeneities at the bottom of the NMR tube. The set of spectra obtained immediately after the UV-irradiation, (a), showed that the sample volume was macroscopically homogeneous as noted by the independence in signal intensity with regard to *z*-direction. Thus, very little had happened during the first minutes after UV irradiation. As seen in image (b), after 5 h, the cross-linking process had resulted in a decrease of the NMR signal from the starch but still all the peaks were clearly visible in the spectrum. This indicates that all polymers had not cross-linked since a complete cross-linking reaction should make the effective molecular weight very large resulting in a decrease in polymer mobility and thereby also a loss in signal intensity. After 24 h (image not shown) the polymer signals are broadened to the extent that only the water signal is present and no further changes are noted after this time, i.e. all images received hereafter are identical (see image (c)). One interesting and surprising result from the CSI experiments was that the solution appears to cross-link homogeneously along the *z*-direction of the NMR tube (on the studied length-scale). The expectation was that the signal intensities from the starch would depend strongly on the distance in the *z*-direction, with lower intensities close to or in the region of the irradiation due to a rapid local cross-linking reaction. Instead the CSI results show that the signals are broadened equally along the *z*-direction as time goes by, i.e. the reaction depends on time as expected but is independent on *z*-position. As noted above the spectral window is 2 cm and we note that it would take roughly 2 days for the initiator to move by self-diffusion from the bottom of the tube (where the UV-radiation was applied) to the top of the sampling volume (calculated from the diffusion rate that is approximately 10^{-9} m^2/s). The temperature induced convection effect was excluded by doing a control experiment, were the temperature was measured inside the NMR test tub showing that the temperature was constant during the experiment. Thus, the rate-limiting step of gelation in the experimental setup shown in Fig. 7 is the radical polymerization reaction and not the diffusion rate of the initiator. If the gelation process was diffusion controlled the lower part of the tube would cross-link long before the upper part that would have been seen as a *z*-dependence in the signal intensities. The radical polymerization reaction is normally considered fast but in this experiment it is the reaction between two different polymers that is resulting in a cross-linking reaction. Since there is a limited numbers of vinyl groups on each polymer and because it is a limited motion of the polymers the cross-linking reaction caused by the radical reaction is relatively slow.

Several concentrations of the modified starch have been examined to find the critical gelation concentration (CGC), which is defined as the concentration at which the cross-linked material creates a homogenous non-flowing gel. The CGC was found to be about 2% for the type of starch used here. At lower concentrations the cross-linking process resulted in an inhomogeneous, non-transparent solution where large polymer particles precipitated and phase separated to the bottom of the tube.

3.2. Cross-linking at surface

Fig. 8 shows the QCM-D response during the adsorption process of modified starch to a hydrophobic surface. The surface was made hydrophobic by the well-known SAM (self-assembled monolayers) technique, which creates a well-defined surface with a contact angle that assures a large amount of polymer adsorbed to the surface. The adsorbed amount after the water rinsing was about 2500 ng/cm^2, which corresponds to a layer thickness of about 25 nm. The amount of polymer leaving the surface upon rinsing was very small which means that the adsorbed layer is strongly attached to the surface. As seen on the *y*-axis in Fig. 8 the dissipation factor, *D*, was about 18 after adsorption indicating that the adsorbed layer is rather flexible, most likely as a result from large amounts of water swelling the polymer film. It has previously been shown that SDS unimers adsorb to starch polymer causing the polymer to swell in water (Saito, 1957). This implies that a starch–SDS complex is more water-soluble than the corresponding starch without adsorbed SDS. After cross-linking, the molecular weight of the polymer increased significantly, an effect that results in a dramatic lowering of the water solubility. This leads to the conclusion that the cross-linked adsorbed polymer is less prone to desorption following SDS addition compared to the non-cross-linked adsorbed polymer. In the latter case SDS will adsorb into the polymer layer making it much more water-soluble and finally the layer will completely desorb into the solution. In Fig. 8 a large difference between the UV- and the non-UV-treated surface is noted after rinsing with SDS. For the non-UV-treated surface the rinsing with water and SDS caused a significant desorption. From the values before and after rinsing it appears as if the entire polymer layer was desorbed leaving the surface with a monolayer of SDS. In order to validate this interpretation a control experiment entailing adsorption of SDS to the same hydrophobic SAM surface was performed and showed a decrease in frequency of 10 Hz, which is about the same as the shift obtained after rinsing with SDS in Fig. 8. For the UV-treated surface however the SDS rinsing still caused desorption but much less than for the non-UV-treated surface. As SDS adsorb to the polymer the polymer layer swells significantly as noted both as an decrease in frequency and an increase in the dissipation factor. Due to the increase in flexibility of the polymer layer and thus increase in the dissipation factor the use of the Sauerbrey equation (Eq. (1)) leads to a systematical underestimation of the adsorbed amount. This effect makes us interpret the small desorption noted in Fig. 8 for the UV-treated surface as an effect of the invalidity of the equation and not due to actual desorption of material. Thus, we suggest that the UV-treatment results in a more or less complete chemical reaction of the polymer layer, leaving very few polymers non-cross-linked.

As seen in Fig. 9 the behavior of the non-modified starch differs significantly from the modified starch. The adsorbed amount is much smaller. The frequency shift is about 15 Hz, which is very small compared to the modified polymer (roughly 10%). As the GMA modification makes the polymer more hydrophobic it is no surprise that this polymer adsorbed less to the hydrophobic sur-

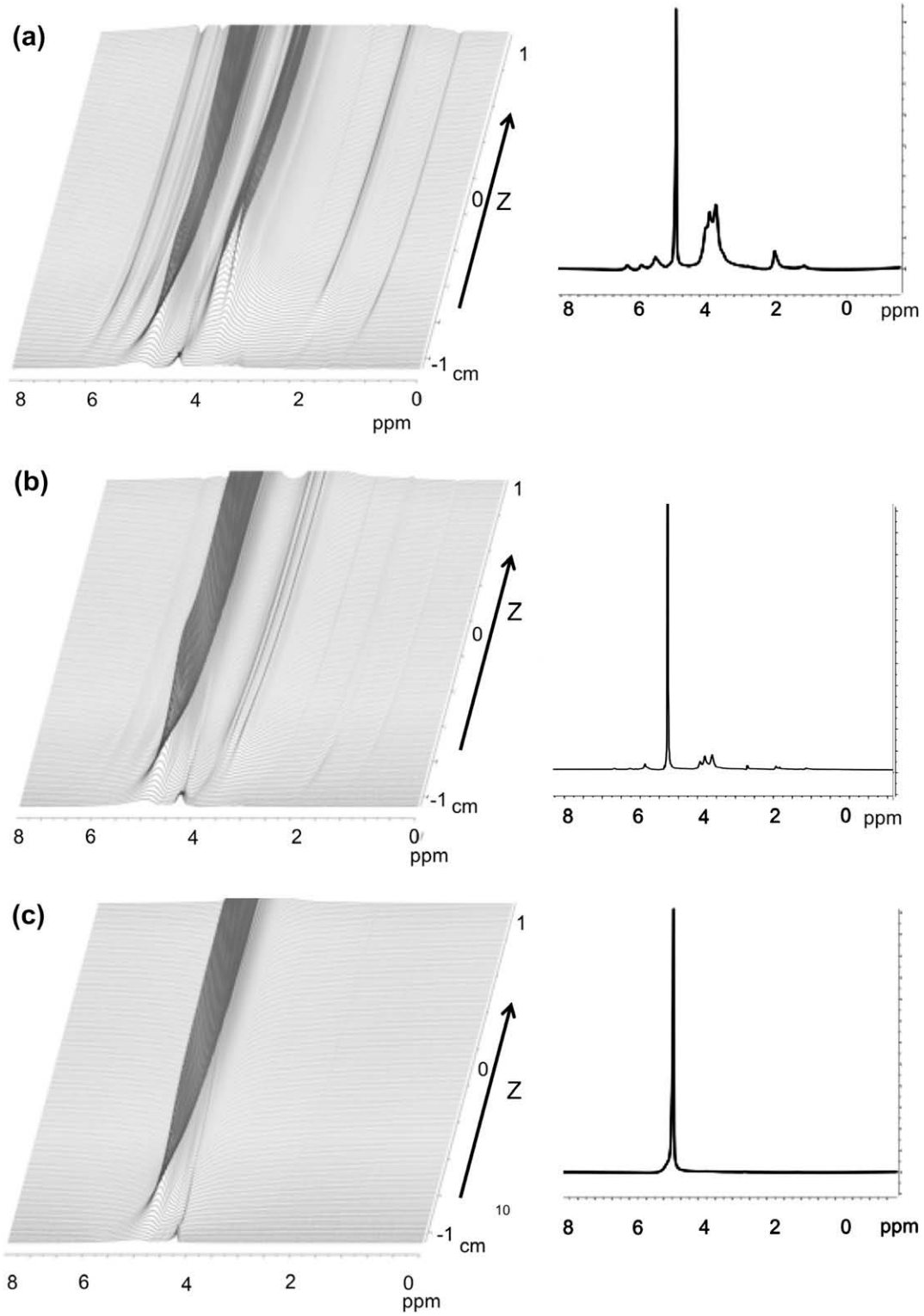

Fig. 7. Chemical shift imaging spectra obtained after 0 h (a), 5 h (b) and 48 h (c). The one-dimensional spectra in the right part of the figure are chosen from arbitrary positions along the *z*-directions since there is no difference in this direction.

face. After rinsing with SDS the polymer desorbed from the surface and a monolayer of SDS is formed.

Returning to the result for the modified starch we noted previously that the increase in dissipation was a result of the increase in viscoelasticity of the adsorbed layer following the swelling of SDS and water. The dissipation increased very fast indicating that the adsorption process entails small molecules making the process fast. Since the *D*-factor can be dependent on the adsorbed amount, it is sometimes informative to plot the *D*-factor as a function of the adsorbed amount. This will allow further understanding of the adsorption and cross-linking process in general. This plot is shown in Fig. 10. During the initial adsorption of polymer to the surface,

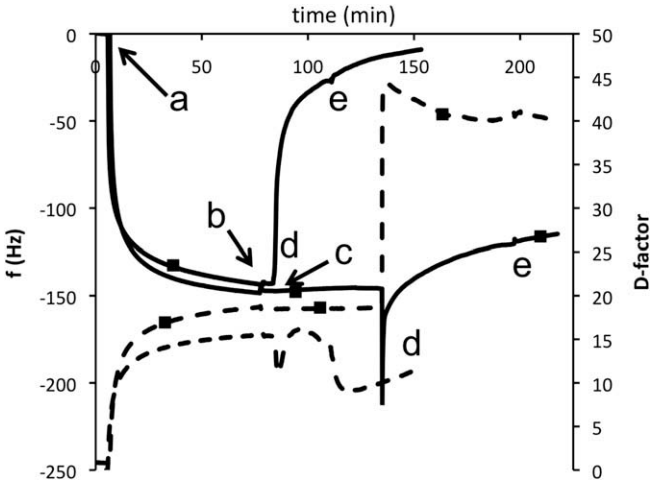

Fig. 8. QCM-D results of the adsorption behavior of modified starch characterized by the change in frequency (solid lines) and the *D*-factor (dashed lines) for the UV- (squared) and non-UV-treated surfaces. The surface was exposed to the modified starch (0.1%)/KPS solution (2%) (a) and rinsed with water (b) thereafter the surface was irradiated with UV-light (c). The polymer surface was then exposed to a SDS solution (50 mM, d) and clean water (e).

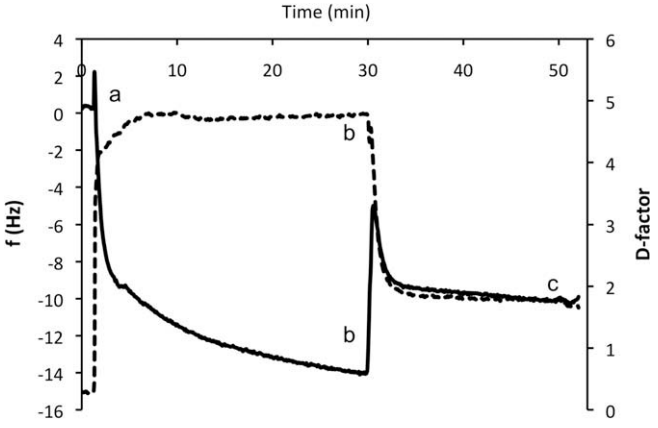

Fig. 9. QCM-D results of the adsorption behavior of non-modified starch characterized by the change in frequency (solid lines) and the *D*-factor (dashed lines). The surface was exposed to a starch solution (0.1%) (a) followed by SDS (50 mM) (b) and water (c).

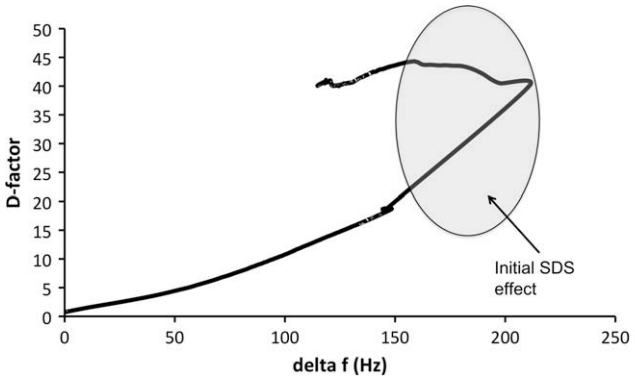

Fig. 10. The *D*-factor as a function of Δf showing the structural changes of the adsorbed layer. The marked area is mainly an effect of the initial changes in bulk properties of the SDS solution.

up to 150 Hz, there is nearly a linear slope of the curve. This indicates that the polymer surface continuously increased the viscoelasticity as more polymer adsorbed. At this stage it should be realized that the adsorption process of polydisperse polymers to a surface involves early adsorption of small polymers and a subsequent slow continuous shift towards larger polymers (from entropic reasons, see references Liu, Mu, Liu, & Ying, 2004; Roefs, Scheutjens, & Leermakers, 1994). As larger polymers adsorbed the viscoelasticity increased due to the more flexible nature of these polymers. During the time that the surface was UV-irradiated (which in Fig. 10 started at 150 Hz) there was a very small change in the slope of the $D/\Delta f$-ratio indicating that the cross-linking did not change the structure of the adsorbed layer significantly. After rinsing with SDS the slope of the curve again increased significantly (the marked area), but as seen in Fig. 8 this is just an effect of the initial addition of SDS, which is mainly a bulk effect. When this initial effect has declined the $D/\Delta f$-ratio increased significantly showing that the adsorbed layer has swelled and thereby became more flexible.

4. Conclusions

In this study we have modified the natural polymer cornstarch and thereby enabled a cross-linking both in solution and at a hydrophobic surface. As the polymer at the surface is cross-linked the solubility is severely decreased, the adsorption strength is increased and the rinsing with SDS is negligible. The data suggest that the cross-linking reaction in solution and at the surface are more or less complete with very few polymers not participating in covalent bonds with the rest of the polymer matrix.

Photopolymerization is an effective and easy method to cross-link vinyl functionalized polymers in solution. Since the reaction is simple to control and no heating is needed the method is suitable in biological applications such as tissue immunoisolation and drug delivery materials such as polymer hydrogels. Cross-linking polymers in solution is a rather straightforward procedure but as the polymer dynamics is severely reduced when polymers adsorb to a surface a successful cross-linking in bulk does not directly mean that cross-linking the same polymer at a surface is possible.

This study has shown that a simple chemical modification of starch can result in a material highly suitable for cross-linking bulk solutions into hydrogels, e.g. drug release purposes, and for preventing polymer desorption from surfaces. Applications for the latter purpose may be new glue applications where the material needs to be made from natural raw materials.

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