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MICRO FIBRILLATED CELLULOSE (MFC) FILMS ON METAL SURFACES AS A SUBSTRATE FOR TEMPERATURE PROGRAMMED DESORPTION (TPD) EXPERIMENTS

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Key words: MFC, Micro fibrillated cellulose, TPD, Temperature programmed desorption, Adsorption, Desorption, n-Decane, Methanol

INTRODUCTION

In recent years the application of paper for packaging has been growing steadily. Food packaging underlies special scrutiny, as the package has to prevent the escape of aroma molecules at the one hand and prevent the contamination of the packaged good with unwanted substances on the other hand. For the transfer of organic molecules from the packaging to the food and vice versa one has to look at volatile organic molecules. For transport of such molecules through the porous structure of paper the interaction of the molecules with the surface of the paper fibers plays an important role.

When one follows an organic molecule flying from the packaged good through the porous structure of the paper the molecule will inevitable interact with the surface of one of the paper fibers, as there are hardly any straight paths through a

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piece of paper. When a molecule hits a surface there are three possible interactions. The first and simplest one is an elastic collision. In this case the molecule will continue its flight according to the incident angle. The second possible interaction is an inelastic collision. In this case the molecule will lose some of its kinetic energy and due to the short interaction with the surface it will not remember where it came from, so that it can continue its flight in any direction. The third possibility is that the molecule will adsorb on the paper surface and stay there until it gains enough energy to desorb again. These possible pathways have been studied in surface science for many decades (e.g. [1, 2]) with simple gases adsorbed on metal surfaces using temperature programmed desorption (TPD). This well-established method from surface science has the big advantage that it is very sensitive to different adsorption sites. It is even sensitive to the influence of the interactions between adsorbed species which has an influence on the adsorption energy and the adsorption kinetics.

TPD uses high vacuum in order to be able to investigate a clean surface and to exclude interaction between the molecules in the gas phase, as such collisions would influence the experimental result. As a consequence, TPD results are far from equilibrium. Nevertheless, the adsorption energies measured by TPD are very close to what has been found under atmospheric pressure conditions. For example, condensation energies measured using TPD usually perfectly fit to other measurements and to ab initio calculations.

More recently A. Winkler et al have shown that the TPD method can also be used to investigate the interaction of larger organic molecules with inorganic surfaces (e.g. [3]).

Even though the surface chemistry of paper is quite complex, we think that TPD investigations of the interaction of molecules with paper surfaces will bring new insights that are important if one attempts to model the transport of molecules through paper. It was shown recently that TPD measurements on thin cellulose films are possible and lead to similar results compared with other methods [4, 5, 6].

However, due to the experimental requirements only thin amorphous films of regenerated cellulose could be investigated by TPD previously [4, 5]. In this work we proof the concept that the TPD technique can be successfully extended to thin films of micro fibrillated cellulose (MFC). This step brings the analysis of the adsorption and desorption energies and the desorption kinetics of volatile organic molecules closer to actual paper as compared to the thin amorphous films of regenerated cellulose reported in [4].

The interaction of different gases and liquids with paper samples has of course been studied using many different methods like inverse gas chromatography [7], adsorption isotherms [8, 9], calorimetry [10] or surface plasmon resonance spectroscopy (RDS) [11], to mention just a view. In contrast to TPD all these methods measure under equilibrium conditions. Therefore, these methods are not very sensitive in terms of different adsorption energies on different adsorption sites on the surface investigated, as one always has co-adsorption phenomena. Here the TPD method is a lot more sensitive due to the absence of the influence of the atmospheric conditions. Therefore, we expect that the TPD method will be able to deliver adsorption energies as input parameters for modeling the transport of molecules through the pore structure of paper. In addition, the method might bring new insights in the adsorption of water on cellulosic surfaces due to its high sensitivity. In addition, TPD results contain information about the desorption kinetics. Delivering additional information that is not found in the equilibrium methods stated above. The information about the desorption kinetics can be found in the shape of the desorption peaks [1].

EXPERIMENTAL

The method of TPD has been described in some detail previously [4, 12, 13]. In short one uses a high vacuum system to establish a clean environment and a clean sample surface. Then the volatile organic molecules are adsorbed under controlled conditions on the freshly prepared MFC surface. After adsorption the sample is heated with a linear heating rate and the desorbing species are measured as a function of the surface temperature using a quadrupole mass spectrometer (Pfeiffer Prisma). As a linear heating rate on the surface is one of the requirements of the TPD method it cannot be done with paper samples, as both heating and temperature measurement are not possible with the necessary speed and accuracy with paper samples.

For the TPD measurements shown here a high vacuum system was used as described in detail earlier [4, 12]. The system is pumped using a turbomolecular pump and a rotary vane pump. The background pressure without a sample is about 1×10^{-9} mbar without bake out. A one side polished stainless steel substrate was used that was resistively heated using tantalum wires spot welded to the back of the sample. The temperature measurement was obtained via a k-type thermocouple also spot welded to the backside of the stainless steel substrate.

The preparation of the thin films was discussed in detail in [12, 14]: the MFC (Exilva MFC Gel (1.8% dry MFC in H_2O) from Borregaard) was coated onto the stainless steel surface via drop casting of a suspension of the MFC in water. After drying at ambient conditions the films were mounted in the vacuum system and pumped until a base pressure of about 5×10^{-8} mbar was reached [12]. This background pressure is mainly due to water still associated to the MFC. The volatile organic molecules (n-decane or fully deuterated methanol (methanol-d4)) were brought into the vacuum system with a needle valve using the vapor pressure at room temperature of the volatile compounds. Adsorption was done for 6 minutes at a pressure of about 5 x 10^{-6} mbar at a sample temperature of – 80 °C [12]. Then the sample was heated up to 600 °C with a heating rate of 1 °C/s. During desorption the mass spectrometer detects the masses 34 (methanol-d4), 57 (n-decane), 44 (CO_2), and 18 (H_2O). Since the MFC film undergoes pyrolysis during the TPD experiment each experiment has to be done with a freshly prepared sample.

The pyrolysis can also be detected with the mass spectrometer with slightly different measurement parameters. The resulting 3-dimensional thermal desorption data of the thin MFC film is called fingerprint in [4, 12] and in this paper. For the acquisition of the fingerprint a full mass spectrum from mass 0 to 100 was measured repeatedly during heating with a heating rate of 0.5 °C/s. The lower heating rate is necessary, as the acquisition of a full mass spectrum takes up more time. With this setup we obtain a full mass spectrum about every 2 °C.

RESULTS AND DISCUSSION

In Figure 1 (a–d) one can see the polished stainless steel substrate (a) and films with increasing MFC film thickness (b to d) prepared by drop casting a suspension of MFC in water.

Contact angle measurements on the samples shown in Figure 1 (a - d) showed a contact angle of the pure stainless steel substrate of about 84° and an average contact angle of about 40° on the three MFC films [12]. For comparison a bleached unsized paper measured under the same conditions used here shows a contact angle of about 38° [12]. A regenerated thin cellulose film shows a contact angle of about 40° [15]. Figure 1 clearly shows that there are optically homogeneous dry films attached onto the stainless steel samples.

The properties of the used MFC are not given in detail by Borregaard, beside a patent [16]. To make sure we made reproducible films we characterized them using profilometry, optical microscopy, and atomic force microscopy (AFM). While these measurements showed us that we produced comparable films, it of course falls short on a complete description of all the MFC properties, like fiber

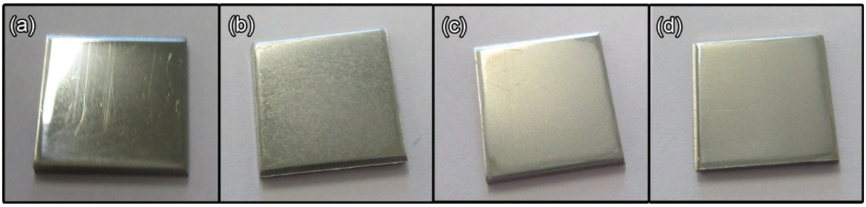

Figure 1. (a) Polished stainless steel sample, (b–d) MFC films with increasing thickness made by drop casting a suspension of MFC in water after drying at ambient conditions [12].

length distribution and fiber thickness distribution. For the purpose of this paper it was enough to make sure that our films are reproducible.

To get an idea of the MFC film thickness profilometry was measured (see Figure 2). For a film made with 100 µl of a 10% MFC paste suspension (0.18% dry MFC) in water an average film thickness of about 1.7 ± 0.5 µm was measured [12]. One can see in Figure 2 a quite high roughness of the film. This is due to the fibrils of the MFC thin films which will of course lead to rough surfaces.

In Figure 3 one can see an AFM image of the same sample as in Figure 1(d) which clearly shows the fibrils on the layer. The root mean square roughness obtained from the AFM measurements is about 221 nm [12].

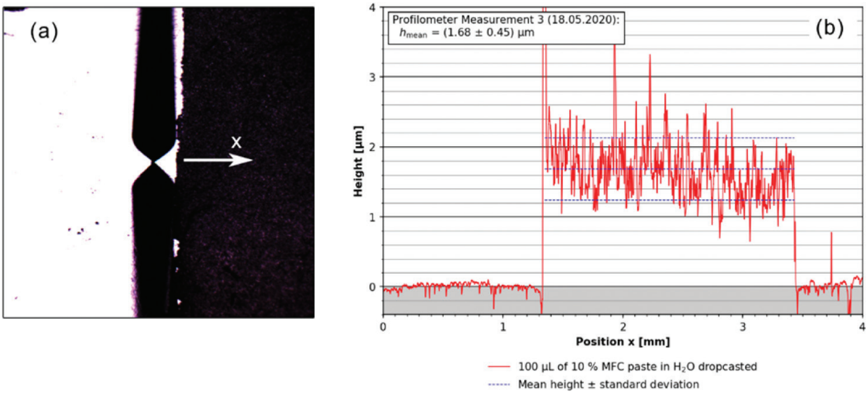

Figure 2. Profilometer analysis of a MFC film made by drop casting 100 µl of a 10% MFC paste suspension in water [12].

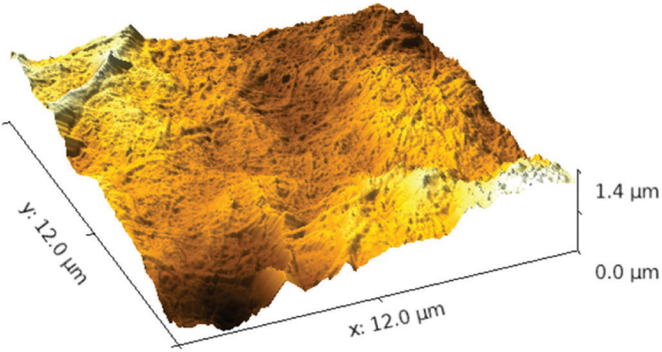

Figure 3. AFM image of a film prepared like seen in Figure 1(d) [12].

The fibril length distribution was investigated using optical microscopy by marking single fibrils and/or small fibril bundles with the help of the software ImageJ. From the marked fibrils a length distribution of the fibrils is obtained (see Figure 4(a, b)). The average length deducted from the Weibull distribution is about 20 µm [12]. From the optical microscopy image, it is also clear that fibril bundles with a diameter in the µm range can be found in the MFC suspension used for making the MFC thin films. A comparison of the optical microcopy (Figure 4(a)) and the AFM in Figure 3 and Figure 5 show that there also is a fiber length and width distribution in the nanometer scale. This distribution is not necessarily the same as in the optical region. However, for our proof of concept that TPD can be used with these MFC films, this distribution is of minor importance and will therefore be studied in detail in the future.

In order to further characterize the micro fibrils of the MFC used, very thin MFC films on silicon wafers were made by drop casting small volumes of highly diluted suspensions. The films were analyzed by AFM. An example of such an AFM image is shown in Figure 5.

In Figure 5 one can see both micro fibril bundles (top right in Figure 5) as well as individual micro fibrils (in the center of Figure 5). It is also quite clear that the fibril bundles stay in the nanometer diameter range. However, from the films studied by optical microscopy one can see also µm thick fibril bundles. The fibrils shown in Figure 5 were seen on several AFM images at different locations of one film and on different samples.

In order to be able to compare the TPD data from the MFC films used here to the regenerated cellulose films used in [4] we measured the fingerprint spectra of the films. For this purpose, we measured complete mass spectra from mass 0 to 100 as a function of temperature, as outlined in detail in [4, 12]. With a high scanning rate of the mass spectrometer and a heating rate of 0.5 °C/s one gets the fingerprint of the cellulose pyrolysis under high vacuum conditions shown in Figure 6. In Figure 6 one can see clearly that several masses are clustered together with regular distances. This is a well-known pattern from mass spectroscopy of organic molecules. This fingerprint is similar to the one obtained from regenerated cellulose films [4]. However, at close inspection one can see clear differences between the regenerated cellulose films and the MFC films. This is not surprising, as the MFC fibrils consist not only of cellulose, but also of hemicelluloses and probably some residual lignin. The fingerprint of the MFC thin film clearly shows that the films can be investigated using TPD. The pyrolysis seems to start around 200 °C according to the data in Figure 6.

In Figure 7 one can see the result of a TPD experiment after adsorption of n-decane. One can clearly see that the n-decane (m/z = 57) has a marked desorption feature at about –55 °C. At the same temperature also (m/z = 44) desorption is seen. This can stem from both a fragment of n-decane and CO_2. At –55 °C the

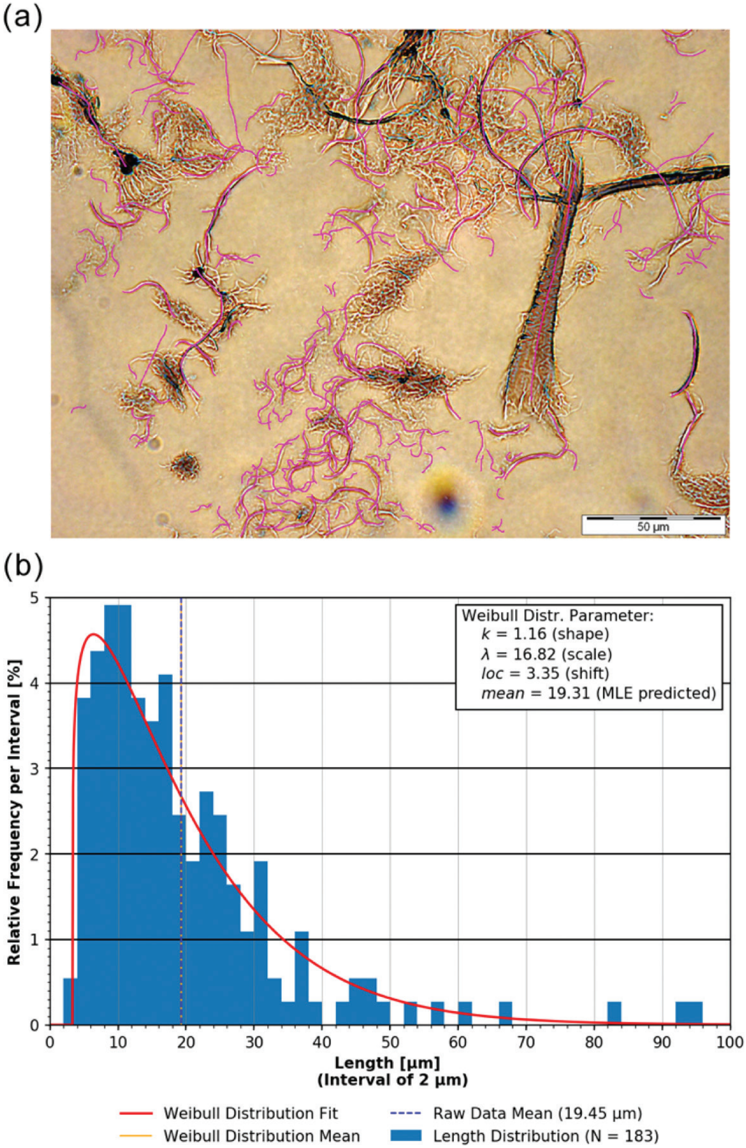

Figure 4. (a) Optical microscopy image of a dried MFC film on a glass substrate, and (b) Fibril length distribution obtained from the pink marked fibrils in (a). The Weibull distribution parameters are given in the legend [12].

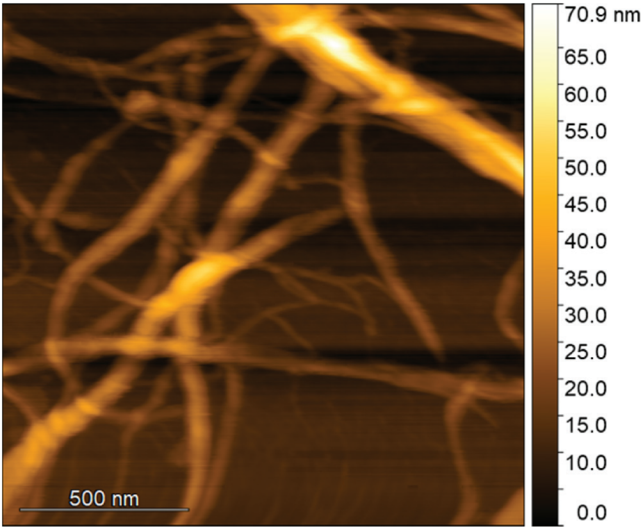

Figure 5. AFM image of highly diluted MFC film on a silicon wafer substrate. Individual micro fibrils can be seen near the center of the image [12].

m/z = 44 desorption most likely stems from CO_2 adsorption from the residual gas in the vacuum chamber during cooling of the sample.

The desorption feature between about 250 °C and 420 °C stems from the pyrolysis of the MFC under vacuum conditions. This peak can also be found without prior gas adsorption as well as after methanol adsorption and is also reflected in the fingerprint shown in Figure 6. Therefore, it is most likely due to the decomposition of the MFC film, similar to what has been found for thin regenerated cellulose films before [4].

Figure 8 shows the thermal desorption of methanol-d4 from the MFC film. In this case neither a low temperature nor a high temperature peak (except for the MFC pyrolysis) can be found. On regenerated cellulose films we have found a strong influence of the adsorbed methanol-d4 on the pyrolysis of the thin films [4]. The desorption of mass 34 (methanol-d4) in the pyrolysis range is most likely due to the pyrolysis as a small feature at mass 34 which cannot be seen in the fingerprint in Figure 6. However, if one looks at the individual spectra from Figure 6 (not shown here) one can see this small feature.

The adsorbed methanol-d4 might show in the onset of the pyrolysis which is at about 230 °C with methanol. In comparison with n-decane pyrolysis starts at about 250 °C. Considering the lower heating rate in the fingerprint a direct comparison of the start of the pyrolysis between the fingerprint and the TPD measurements cannot be made.

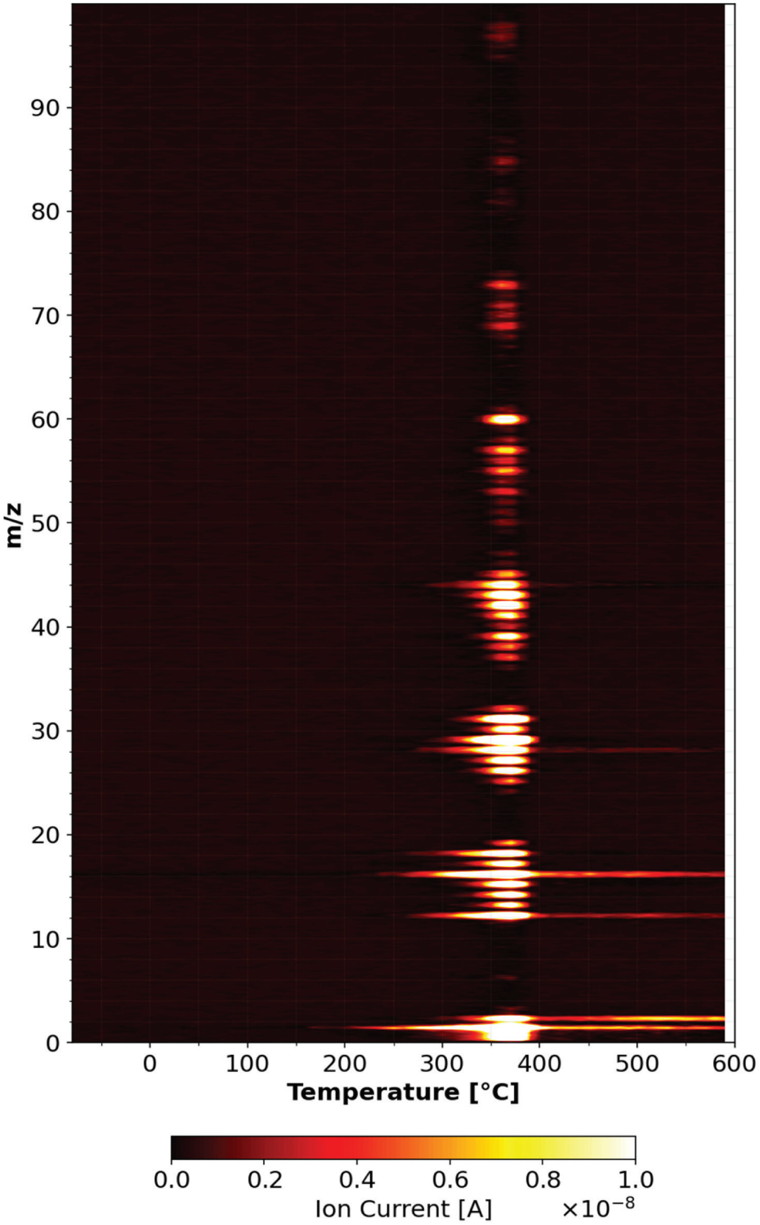

Figure 6. Pyrolysis fingerprint of a thin MFC film on a stainless steel substrate with a heating rate of 0.5 °C/s.

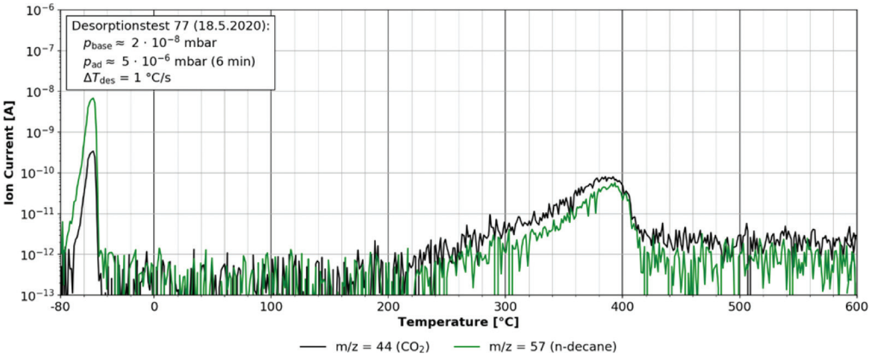

Figure 7. TPD spectrum of n-decane desorption from a similar MFC film shown in Figure 1(d) and Figure 2 [12].

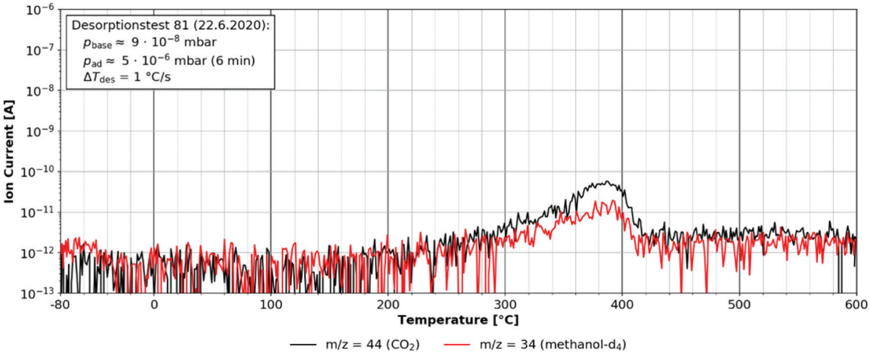

Figure 8. TPD spectrum of d-methanol desorption from a similar MFC film shown in Figure 1(d) [12].

The desorption of water from the MFC sample during pumping down to the base pressure may lead to different amounts of water in the sample before the experiment starts. Therefore, we also studied the adsorption and desorption of water on/from the MFC films. The result from such an experiment can be seen in Figure 9. Please note that in this case the Ion Current axes is linear, in contrast to Figure 7 and Figure 8.

In this case the adsorption of water was done at about -130 °C in order to also record the physisorbed water that desorbs at around -75 °C. From a Redhead analysis [13] one gets about 52 kJ/mol as the desorption energy. A leading edge evaluation [17] leads to a desorption energy of about 48 kJ/mol [18]. Both values fit to the heat of condensation of water of about 45 kJ/mol stated in the literature

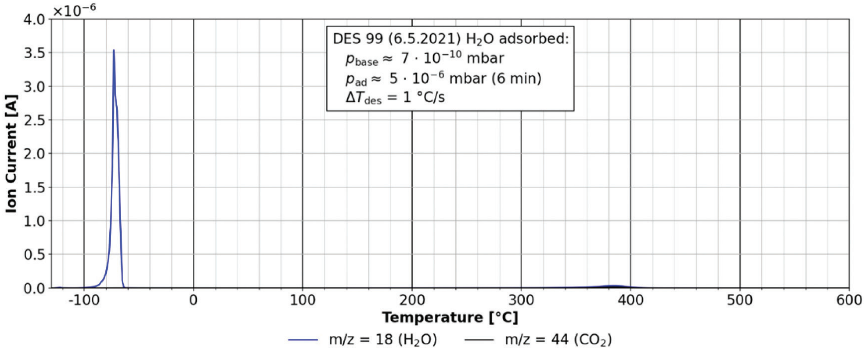

Figure 9. Desorption of water adsorbed on the thin MFC film.

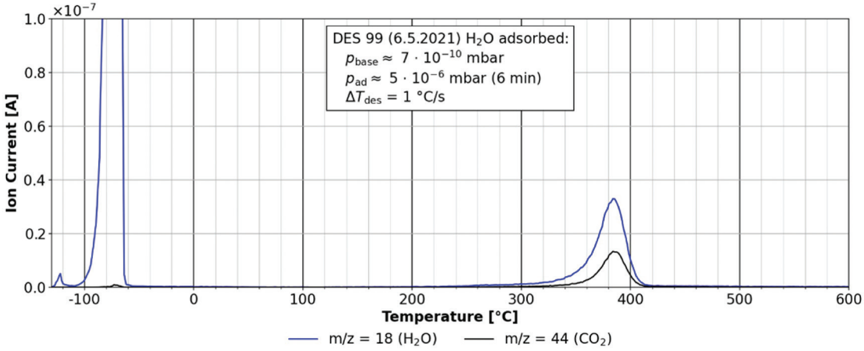

Figure 10. Zoom into the TPD experiment from Figure 9.

[19]. As multilayers of physisorbed water desorb in the TPD experiment one can hardly see the pyrolysis peak around 380 °C. To get a more detailed idea about the water desorption and its influence on the MFC pyrolysis, two zooms into the data shown in Figure 9 are depicted in Figure 10 and Figure 11.

In the zoom in Figure 10 the pyrolysis peak is obvious, however, it is hard at this zoom to really tell when the pyrolysis (strongly bound water desorption) starts. In addition, one can see a small water desorption peak at around – 120 °C. This peak most likely stems from the water desorption from the tantalum wires that are resistively heated in the TPD experiment and therefore reach much higher temperatures much faster than the sample.

In order to better visualize the end and the onset of water desorption a further zoom into the data from Figure 9 was done. This zoom is shown in Figure 11. Here one can see that after the desorption of physisorbed water there is still water

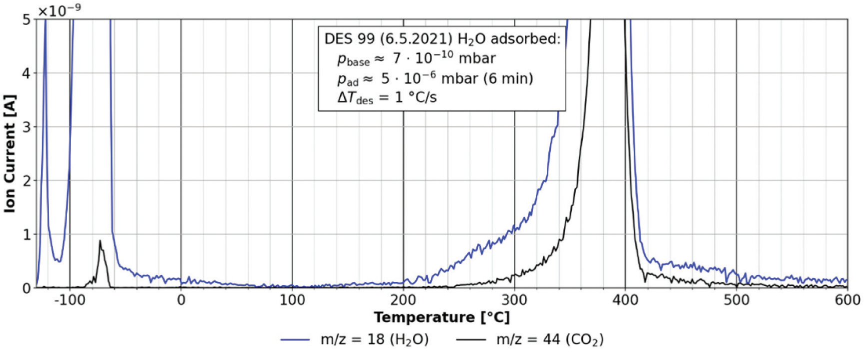

Figure 11. Further zoom into the TPD experiment from Figure 9.

desorption up to about 40 °C. This is most likely connected to the different chemisorption sites available for water on the MFC film. This will be investigated in more detail in the future by making experiments with different amounts of adsorbed water.

At about 140 °C the desorption of mass 18 (most likely still water as other fragments from the pyrolysis can only be seen at higher temperatures) sets in again. This can either be more strongly chemisorbed water, that maybe was not desorbed during the pump down of the vacuum chamber. To differentiate between water stemming from pyrolysis and adsorbed water we are planning experiments with heavy water (D_2O) in the future. With increasing temperature, the mass 18 signal further increases and at around 240 °C also the mass 44 signal which most likely stems from CO_2 from the pyrolysis increases significantly.

The CO_2 desorption feature (mass 44) at around -70 °C most likely stems from adsorbed carbon dioxide during the cooling of the sample to the starting temperature of the experiment. This feature is always seen at the same temperature in all measurements we made. Therefore, one can be quite sure that it stems from CO_2 co-adsorption during cooling. The mass 18 and 44 residual desorption seen at temperatures above about 420 °C is probably associated with pyrolysis of some residual MFC. When the sample is inspected at atmospheric conditions after the TPD experiment the surface of the sample is completely black and glassy which most likely is due to residual carbon from the pyrolysis.

CONCLUSIONS

We have shown that it is possible to use MFC films on a stainless steel support to make temperature programmed desorption experiments under high vacuum conditions. From such TPD measurements it is possible to deduce the adsorption energy of volatile molecules on a MFC surface. As adsorption energies govern the interactions of molecules with surfaces, one can use the TPD results as an experimental input to modeling the transport of molecules through paper. The results are very good comparable to experiments made with regenerated thin cellulose films [4]. We also have shown that the adsorption and desorption of water can also be studied using TPD. This might help in the future to gain further insight into the interaction of water with cellulosic materials. In this context measurements with heavy water will be performed in the future. With co-adsorption experiments one can in the future also test the interactions of the adsorbed species with e.g. water or other species, in order to get a deeper insight into adsorption mechanisms on the surface of cellulose based materials.

ACKNOWLEDGEMENTS

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Warren Batchelor Monash University

What are the characteristics of the film that you require? What grammage do you need? Does it need to be very thin?

Robert Schennach

Well, the only thing that I need to have is that the film should have the same temperature as my substrate. So, if the film gets too thick and temperature conduction is bad, we will start running into problems, but otherwise there are no restrictions whatsoever.

Alexander Bismarck University of Vienna

I found your method very interesting, particularly that your desorption peaks are non-symmetric, does it tell you anything about the heterogeneity of your surface or the energy distribution of desorption?

Discussion

Robert Schennach

Yes, it does. So, it is easy to interpret with simple molecules. So, if it is a molecular absorption, the maximum of the desorption peak is always at the same temperature and if it is associative desorption, so from hydrogen atoms to hydrogen molecules, they are less symmetric, so there is a change of the maximum temperature with coverage, so yes, the form of the peak has information about what is going on in the desorption process.

Alexander Bismarck

How would you interpret the desorption data for n-hexane from cellulose, because that peak has a massive desorption peak or massive distribution?

Robert Schennach

Yes, this looks like what surface scientists would call a zero-order desorption process, so that is multilayer desorption. So, there the shape comes mainly from the multilayer desorption; however, it is not a perfect multilayer desorption; in a perfect multilayer desorption, all the adsorption energies of all layers are the same. Now, if it is spread out like you have seen here, that means that some of the layers are more strongly bound. That is why the peak has a tail towards the higher temperature side.

Alexander Bismarck

You said cellulose does not like these n-hexane but if you believe Staudinger, who postulated inclusion compounds of very hydrophobic materials within cellulose, could that be because the molecules are somewhat intercalated in the amorphous region, or strongly adsorbed within the pores based on pore condensation?

Robert Schennach

Well, the N-hexane does adsorb on the cellulose surface, both on the MFC as well as on the regenerated cellulose films and we see the adsorption also under the equilibrium method with the GCMS. So, it does adsorb; however, the adsorption energy is not very high, which means it will desorb already at room temperature under normal conditions, but that does not mean that it cannot adsorb and stay there for a while.

Peter de Clerck PaperTec Solutions Pte Ltd

Water has many different conformations. Bound water may be adsorbed in many different conformations, involving very different energy levels. For example, Ice VII is 1.5 times as dense as normal ice (ice I). You may find the different conformations of the adsorbed water molecule account for the different energy levels that you are seeing during desorption.

Robert Schennach

Yes, of course, that may be as well the reason as different adsorption sites, or a surface scientist would say these different densities are different adsorption sites. Well yes, I absolutely agree.

Lars Wågberg KTH Fiber and Polymer Technology

First, a small comment to the statement that "to like or not like cellulose" We have to be "hygienic" when discussing interactions between cellulose and other materials! Cellulose has a very high dispersive energy so it interacts strongly with a lot of other molecules and materials regardless if they are hydrophilic or not!! Then to my question; when you show these desorption peaks from cellulose, I interpret it as the water is desorbing, it is desorbing at a same time as the carbon dioxide is starting to develop. Can you get any mass information about how much water that is coming off at these temperatures since I think it is really interesting?

Robert Schennach

In principal, the answer is yes, we can do that. We do not do it because it is extremely difficult to quantify the area under the desorption peak: This area is proportional to the amount of species adsorbed; however, we do not know the proportionality factor. It can be found but that's half a years' worth of work to be able to do that so I am not sure I am going to do that, but yes, you could.

Lars Wågberg

But is my interpretation correct that the water is desorbing at the same time as the cellulose is decomposing?

Robert Schennach

Yes!

Discussion

Antti Paajanen VTT Technical Research Centre of Finland Ltd

You mentioned that the water desorption peak goes up to 80 degrees Celsius and is interpreted as water bound in different ways. Does that mean that the shape of the desorption peak is independent of the heating rate, or is it possible that there are some transport limited effects?

Robert Schennach

Of course, the desorption depends on the heating rate; that is why a very linear heating rate is so important in this experiment because if the heating rate changes in my experiment, I will get a peak but it has nothing to do with adsorption energies in that case, so you can only compare measurements made at the same heating rate. If you have the same heating rate there, you can compare them without any problems.