Macromol. Symp. **145**, *103–111 (1999)*

Thin Layers of Cellulose Derivatives - Selected Analytical Aspects

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SUMMARY: New hairy-rod like cellulose polymer layers were developed as a model system for corrosion protection and adhesion promotion in medical technology. Using the Langmuir-Blodgett technique a mixture of a cinnemate containing and a phosphate containing cellulose were transferred on titanium and steel surfaces. The cinnemate can be crosslinked by ultraviolet light (UV). Differences in the formation of multilayers were found and analyzed by atomic force microscopy, scanning auger microscopy and ellipsometric measurements.
Phosphate cellulose forms homogenous layers at all substrate surfaces. With increasing layer thickness a mixture with low phosphate content becomes homogenous, too. Only mixtures with high content of phosphate keep imperfections with increasing layer thickness. For the pure component cinnemate cellulose the imperfections arise only in the case of titanium surfaces.

Introduction

The research project deals with investigations of cellulose polymers and their further application as surface coatings. Cellulose polymers as the most common biopolymer in nature are very often used for medical products, e.g. for dialysis membranes where its biocompatibility was proven several times[1)]. Coating metals with such polymers could help to prevent corrosion. This is sometimes a problem for implants consisting of steel where toxic ions (like nickel or chromium) are released in the presence of chloride-containing blood. These ions can cause inflammations. Another potential application of cellulose polymers is the field of adhesion promotion. It is often a problem that implants lose the mechanical support to the natural bone after a couple of years and have to be replaced by the surgeon. To avoid these problems new cellulose layers seem to be very promising materials.

As a special cellulose polymer type we used the so called hairy-rod like cellulose polymers well known by the extensive studies of Wegner[2-3)] and his coworkers. They can form very homogenous cellulose layers even for less layer thicknesses[4)]. They are best described by a

CCC 1022-1360/99/$ 17.50+.50/0

rigid backbone with flexible alkylside chains which can have functional groups at the end of the alkyl-chain.

Experimental

The strategy to obtain cellulose polymers which give strong interaction at different substrate surfaces like titanium or steel was to introduce alkyl-phosphate groups well known to adsorb strongly at reactive metals[5]. The synthesis was carried out by the work group of Prof Adler at the TU Dresden[6].

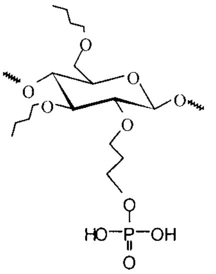

Fig. 1: Diagram of one monomer of the new cellulose phosphate, showing alkyl-spacer-groups, which are necessary for LB-capability, and the alkyl-phosphate-group responsible for a strong interaction with the oxide surface.

Because the polymers were transferred on the substrates using the Langmuir-Blodgett (LB) technique the polymers must have alkyl groups, namely butyl goups, to obtain Langmuir-Blodgett capability. The sophisticated LB-technique was necessary to form layers with defined and reproducable layer thickness.

As solid substrates we used titanium and steel DIN 1.4441 - both typical implant metals. To obtain smooth surfaces for the Langmuir-Blodgett technique we evaporated the titanium on silicon wafers. The steel was sputtered on silicon wafers with the crystal orientation (111).

The degree of substitution (DS) for the phosphate group in the phosphate cellulose is 0.2. This is rather low but it is the maximum content to keep the polymer Langmuir-Blodgett capable. The degree of substitution for the butyl groups is 2.3 according to a molecular weight of 47800 g/mol for this polymer. In the case of the cinnemate cellulose the DS for the cinnemate functional groups is 0.27 and 2.26 for the alkyl spacers, namely isopentyl groups. The molecular weight for this polymer is 53300 g/mol. The cinnemate groups are necessary to form stable layers by UV cross-linking[7)].

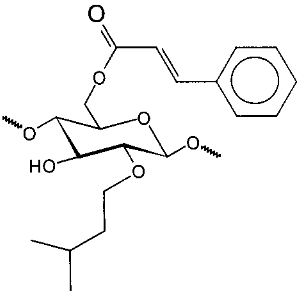

Fig. 2: Diagram for the used cinnemate-cellulose. The monomer with isopentyl and cinnemate substituents.

Strategy

As a complete new strategy a two component system was developed to meet the stress attacks the layers are exposed to as implant coatings. Instead of using only one polymer, a mixture of a phosphate containing and a cinnemate containing cellulose was used. The cinnemate polymers can be crosslinked by UV-radiation to form a mechanical stable matrix. The phosphate polymers are embedded in this matrix. This polymer does not take part at the cross-linking reaction. Beside the advantage to build up a mechanical stable polymer layer, the selected strategy avoids complicated synthesis routes. It seems nearly impossible to introduce either the phosphate group and the cinnemate group in one polymer at the same time[6)]. This advantage is most essential for a potential technical application.

For the first part of the project basic studies were carried out with the model system. Mixtures of alkyl-phosphate cellulose and cinnemate-cellulose were transferred using the Langmuir-Blodgett technique. We decided to make studies with a mixture having a low content of phosphate cellulose, respectively 10%, and with a high content of phosphate cellulose, respectively 30%. The selections are reasonable because the model phosphate cellulose has a low content of phosphate functional groups and a lower portion of this polymer would not give a strong interaction with the metal surfaces. In contrast, a high portion of phosphate in the mixture lowers the degree of crosslinking in the cinnemate matrix as the phosphate containing polymer does not take part at the cross-linking reaction.

Layer formation-model systems

The coated metal surfaces were analysed using scanning auger microscopy (SAM) and atomic force microscopy (AFM). Selected results are presented below. The thickness of each layer was measured using ellipsometry.

We found that phosphate cellulose forms homogenous layers at all substrate surfaces. As can be seen by scanning auger microscopy maps (two dimensional images – 2D) in figure 3 a uniform distribution for the carbon signal can be detected for a phosphate cellulose layer, 15nm thick, indicating that this polymer forms homogenous layers. We obtained the same results when we used steel substrates. In contrast to this is a layer consisting of a mixture with high phosphate cellulose content (ratio two cinnemate to one phosphate molecule): figure 4 shows that the carbon signal and respectively the polymer carbon is inhomogenously distributed. These imperfections have a size of 50 - 200nm.

The thickness of this layer is 17nm. The cinnemate cellulose forms imperfections, too (see below). The mixture with low content of phosphate forms imperfections in the layer which are very similar to them shown in figure 4.

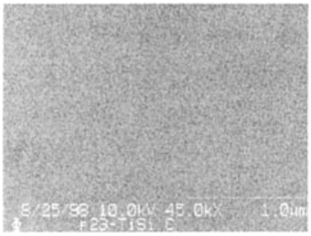

Figure 3: 2D Auger-signal distribution for the polymer-carbon in a LB-multilayer of cellulose phosphate. A unique grey tone reveals a homogenous layer composition The layer is about 15nm thick.

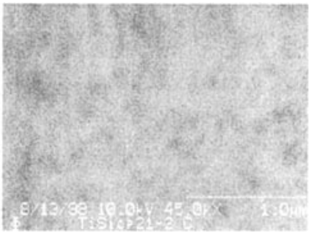

Figure 4: 2D Auger-signal distribution for the polymer-carbon in a LB-multilayer of the mixture cinnemate-phospate, ratio 2:1. 17 nm thick. Regions of less density are proven by dark regions due to imperfections in the layer.

Figure 5 shows that with doubling the layer thickness from at about 20nm to nearly 40 nm the imperfections in the layers of the composite system with low phosphate content disappear.

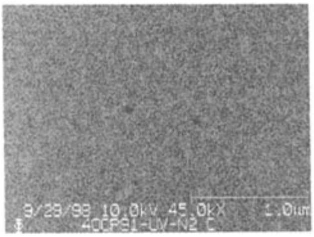

Figure 5: 2D Auger-signal distribution for the polymer-carbon in a LB-multilayer of the mixture cinnemate-phospate, ratio 9:1, 35 nm thick. A unique grey scale proves a homogenous distribution of carbon

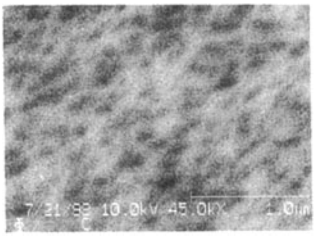

Figure 6: 2D Auger-signal distribution for the polymer-carbon in a LB-multilayer of the mixture cinnemate-phospate, ratio 2:1, 33nm thick. Regions of less density are proven by dark regions due to imperfections in the layer

In contrast to this thick layers with high phosphate content keep imperfections as can be seen in figure.6.

This means areas of lower material density start from the oxide layer of the substrate and in the case of a high phosphate content seem to continue even for thicker layers.

The situation becomes much more complicated as the imperfections in the case of the one component cinnemate cellulose are typical only for coatings on titanium substrates whereas at steel surfaces homogenous layers are formed. This situation is described in figure 7 below.

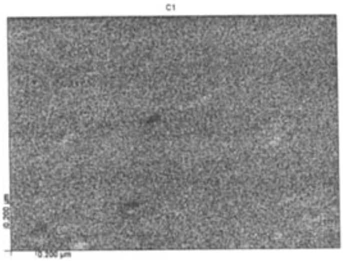

Figure 7: 2D Auger-signal distribution for the polymer-carbon in a LB-multilayer of cinnemate-cellulose. Regions of less density are proven by dark regions due to defects in the layer. Substrate is steel. The layer thickness is 21 nm.

The mechanical state of the surface does not influence the appearance of defects: Comparing the roughness from AFM measurements it can be seen that titanium surfaces are smoother than steel surfaces and that differences in the layer homogenity at the interface metaloxide/polymer have to be refered to the different chemical nature of each substrate.

For steel the roughness is 3.1nm over 20 µm and for titanium it is 2.2 nm over 20 µm, both values are root-mean-square (RMS) values measured by AFM.

To find out if theses defects are holes - essential for a further application demanding a completely covered metal surface - several AFM studies were carried out to find out how the polymer covered surfaces look like. All measurements, see figure 8 and 9 below, reveal homogenous surface structures either for the pure polymers and for the mixtures.

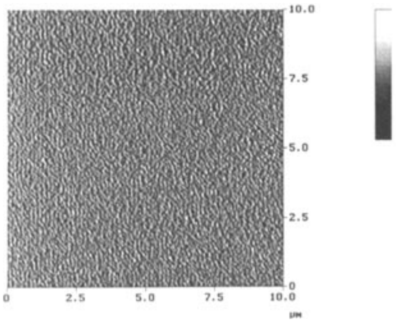

Figure 8: AFM Topography (contact mode) showing a very smooth surface structure in the case of the phosphate polymer.

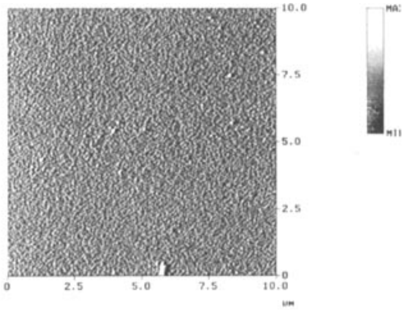

Figure 9: AFM Topography (contact mode) showing a very smooth surface structure in the case of the polymer mixture CP 21.

As the morphologies of all layers look very similar only pictures from phosphate cellulose (Fig. 8) and from the mixture with high phosphate content (Fig. 9) are shown. The roughness values for the four layers are all similar. These values are shown in table 1. Maximum height differences are 5 to12 nm.

Table 1: Roughness at each layer. AFM RMS values.

Cellulose Polymer	**Phosphate**	**Cinnemate**	**Mixture CP 91**	**Mixture CP 21**
RFM- AFM Roughness in nm over 20μm	**2.38**	**1.84**	**1.78**	**3.1**

The morphology studies are supplied by a depth profile analysis which reveals for every layer no significant height differences at the surface which could be referred to pore-like structures. Figure 10 below represents one of the examples which was performed with a layer with high phosphate content (CP 21)

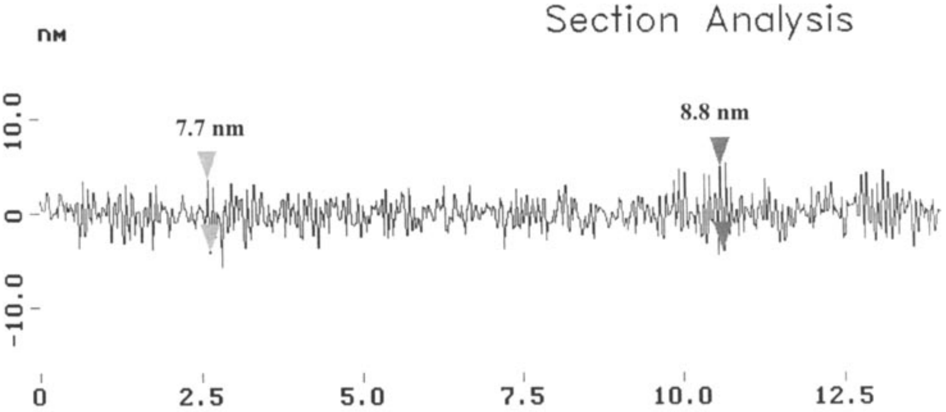

Fig.10: AFM depth profile. A layer of the polymer mixture with high phosphate content (CP 21)

As can be seen in figure 10 the maximum height differences are 8nm and very close to each other providing that pores can be excluded.

All results for the mixtures and the cinnemate are presented for layers which were not crosslinked by UV.

Measurements with crosslinked systems gave no differences to the uncrosslinked system due to AFM and SAM studies. Only the layer thickness is decreasing by 5 % according to ellipsometric measurements.

Summarized results and discussion

Phosphate cellulose forms homogenous layers at all substrate surfaces. With increasing layer thickness (up to 30nm) a mixture with low phosphate content becomes homogeneous, too. Only mixtures with high content of phosphate have areas of lower materials density compared to the surrounding, this applies even to layer thicknesses up to 60nm. In the case of the matrix forming component cinnemate cellulose the defects seem to be specific for each substrate. At steel 1.4441 homogenous layers with no defects can be obtained, whereas titanium surfaces always contain a significant part of imperfections.

To explain these imperfections two aspects have to be taken into consideration: On the one side the imperfections could be due to prepolymerisation. This problem was discussed extensively for the cinnemate cellulose by Schaub7) and Tebbe8). On the other hand there could be the phenomenon of demixing of both polymers. We made several attempts to find out more information on this question e.g. by using fluorescence microscopy or Scanning Auger Microscopy but we did not succeed because none of the markers we used was bound by the polymer. This could be explained by the low degree of substitution of the phosphate group necessary for Langmuir-Blodgett capability (an alkyl-phosphate group at every fith repeating unit) and the lower content of the phosphate polymer compared to the cinnemate polymer on the other hand (mixture ratio is nine cinnemate to one phosphate part on the one hand and two cinnemate parts to one phosphate part on the other hand).

It seems probable that the effect of prepolymerisation is a phenomenon which takes places at the interface of metaloxide/polymer because with increasing layer thickness in the case of the polymer system with low phosphate content these defects seem to fade. Hence, demixing could be excluded in this case.

Conclusively, the investigated polymer mixtures cover the implant metals, titanium and steel 1.4441 completely, which is most essential for a potential application of this polymer type for corrosion protection. To be used as a layer which has to stand mechanical stress the imperfections could arise problems because the composite could be peeled off from the surface.

Acknowledgement

We appreciate the support with cinnemate cellulose by the work group of Prof. Wegner from the Max-Planck-Institute for Polymer Research in Mainz.

The project is sponsered by the DFG in the programm "Cellulose and Cellulose derivatives – molecular and supramolecular structure design". We thank the DFG for financial support.

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