P7 – Determination of Functional States of Molecularly Imprinted Polymer (MIP) Thin Films Used in Biosensors

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Molecular imprinting of polymers (MIP) is a chemical technique for the production of molecule-specific cavities that mimic the behavior of natural receptor binding sites, but may be created for any target molecule. The MIP is generated by dissolving the polymer in the presence of the template, allowing the new network to form in solution and then precipitating the MIP or casting it as a film. When dissolved, the crystalline polymer is separated into elongated chains and the template molecules form bridges between the polymer chains via weak interactions such as hydrogen bonds. Thin, selectively imprinted films of nylon-6 and other polymers such as polyvinylphenol and PMMA are produced with amino acids, aromatic molecules, carbohydrates or pesticides as template molecules. The film recognition activity is coordinated with the appearance of nanometer-sized pores both on the surface and within the film. Depth sensing indentation has become an important technique used to measure the mechanical properties of polymers. In nanoindentation, load and penetration depth are simultaneously recorded during loading and unloading. If the polymer unloading curve is not purely elastic, hysteresis loops appear and reflect the visco-elastic energy loss in multi-indentation cycles.

Changes in the polymer network or the inclusion of different template molecules are directly causative to variations in the nanomechanical properties. Three specific functional states of the imprinted polymer were observed: as produced films with template still incorporated in the network, extracted films in which the template has been chemically removed and reinserted films in which the template has been reintroduced into empty recognition sites. Changes in indentation modulus, hardness and visco-elastic energy loss may be used to distinguish quickly among these different functionalized states.

References:

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Introduction

This selectively imprinted films of nylon-6 are produced by spin coating with glutaric acid and alanine as amino acids used as template molecules. The film thickness ranges from a few micrometers down to less than one micron, depending on nylon and on template concentration in the casting solution. The template molecules could be removed by formic acid from the films and relaxed with the same molecule. Thus, these films can be used as biosensors for specific amino acids. The effectiveness of this method could be proved by infra-red spectroscopy.

Method

SFM investigation gives a characterization of the surface of the films. Pores are visible in the MIP films.

Depth sensing nanoindentation is applied to determine mechanical properties of molecularly imprinted polymer films. A multicycling test function with a sequence of several loading and unloading procedures shows typical hysteresis loops and allows the quantitative measurement of the visco-elasticity of the samples and a comparison relative to the total elastic contribution during the deformation. The characteristic depth dependent contact pressure and the elastic indentation modulus are also obtained from the nanomechanical tests.

Results & Conclusions

Changes in the polymer network or the inclusion of different template molecules are directly observable in variations in the nanomechanical properties. Functional states of MIP thin films such as:

- produced films with template still incorporated in the network,
- extracted films in which the template has been chemically removed and
- reinserted films in which the template has been reinserted into empty recognition sites

can be distinguished by nanoindentation.

- The loading of glutaric acid based MIP films increases the hardness and the indentation modulus, and decreases the visco-elastic energy in comparison to pure nylon films.

- The removal of the glutaric acid shifts the nanoindentation which is visible with a decrease in hardness and indentation modulus. This process leads to a higher visco-elastic energy loss.

- Reinserting of glutaric acid results in an increase of the hardness and the indentation modulus to allow the same values as in original state in the case of original glutaric acid loading. Again, the visco-elastic energy loss relative to the original states could not be achieved.

- Amine or template molecules in the amine matrix contain the nanomechanical properties of the MIP network with a slightly lower hardness and indentation modulus in comparison to pure films. The visco-elastic energy loss is even higher in comparison to pure nylon films and glutarimide based MIP films.

Acknowledgement: The project was supported by the DAAD PP99SE-USA grant No. 1298706.

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