FAKULTA MECHATRONIKY,
INFORMATIKY A MEZIOBOROVÝCH
STUDIÍ TUL

SKFM 2023
STUDENTSKÁ KONFERENCE FM

OPTIMIZATION OF CATECHOL-BASED SURFACE MODIFICATION

Izabela J. Gallus <izabela.gallus@tul.cz>, Daniel Karthik <daniel.karthik@tul.cz>

The previously optimized coating of catechol with Tris(2-aminoethyl)amine (TAEA) for various textiles was tested. Various combinations of catechol with different chemical substrates were tested and optimization of catechol - cysteamine coating was performed.

Key words: surface funcionalization, optimization, coatings, catechol, textile materials

INTRODUCTION

Functionalization of materials is a very common procedure because it allows materials to acquire new properties. The inspiration for developing a coating based on catechol comes from a protein derived from mussels that remain on rocks under conditions of constant exposure to water. This leads to the conclusion that catechol-based coatings are characterized by high adhesion and stability [1]. By adding suitable agents to the coatings, it is possible to control the properties of the surfaces by giving them new properties. For example, adding silver nanoparticles can provide antibacterial properties to the coating [2]. The developed coatings could find applications in textiles, biomedical applications or water filtration [3].

METHODOLOGY

In the present work, a previously developed and optimized coating for PVDF filtration membranes was employed to be tested on other materials. Materials tested include flat sheet polyamide, Kevlar fibers, Spectra yarn, cotton woven fabric, glass filaments, melamine formaldehyde foam, copper-coated polyester nonwoven, nanofibrous polyamide membrane. Materials were immersed in the coating solution for a given time, left for drying, and checked under scanning electron microscope.

To give the coating new functional groups and properties, an attempt was made to replace previously used tris(2-aminoethyl)amine with chemical substrates such as aminothiol, alkanolamine, carboxylic acid, and different amines. Cysteamine, ethanolamin, citric acid, and diethylenetriamine were used for this experiment. The reaction between catechol and cysteamine was optimized. FTIR analysis of the resulting coating was performed. Different reaction conditions were tested, such as initial concentration of pyrocatechol, molar ratios, temperature and pH effect. In Table 1 shown tested conditions.

Table 1: Tested reaction condition for catechol – cysteamine coating

Time [h]	Pyrocatechol concentration [mmol]	Molar ratio (CAT: CYST)
24	1	0.5:1 1:1 1:1.5 1:2
10	1	1:1 1:1.5 1:2
	2.5	1:1 1:1.5 1:2
	4	1:1 1:1.5 1:2
	5	1:1 1:1.5 1:2

RESULTS AND DISCUSSION

The developed CAT-TRIS coating covered tested materials. The surface of melamine formaldehyde foam, polyamide, cotton and polyester were covered completly. Selected materials covered by the coating are shown in the Figure 1.

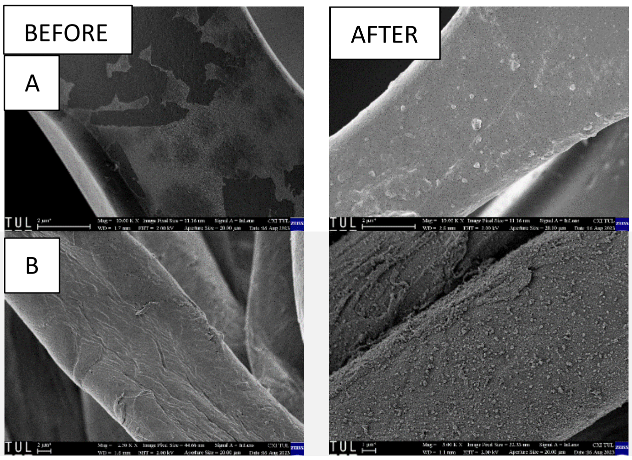

Figure 1: Coating on different materials. A) melamine formaldehyde foam, B) glass fibers, C) cotton woven fabric.

Other tested materials have also been covered, but adjusting the appropriate reaction conditions would be necessary first.

Attempts were made to obtain new catechol-based coatings with different chemical substrates such as aminothiol, alkanolamine, carboxylic acid, and different amines. Previously used Tris(2-aminoethyl)amine was replaced by cysteamine, ethanolamin, citric acid and diethylenetriamine. It was observed, that only citric acid did not result in a coating formation. That can lead to the conclusion that the presence of an amine group is required to initiate the reaction. The more terminal amino groups present, the faster the reaction starts and proceeds. Coating formed when catechol reacted with the cysteamine, ethanolamin, and diethylenetriamine. The modification attempted to cover the hydrophobic surface of PVDF nanofibrous and flat sheet membranes. Reaction with cysteamine resulted in complete coverage of both types of membranes, with diethylenetriamine only the flat sheet type. In the case of reaction with ethanolamine, none of the membranes tested were covered. It can be deduced from this that the resulting coatings differ in their properties and adhesion to different materials. To confirm this, it is necessary to check how these coatings cover other materials.

The early focus was on the reaction of catechol with cysteamine. This reaction takes a long time to initiate but proceeds quickly once it starts. It can be inferred that the reaction occurs autocatalytically. Attempts were made to speed up the reaction initiation by changing the pH value (to 1, 4 and 9) and increasing the reaction temperature. However, none of the factors tested resulted in acceleration of the reaction. A by-product formed during the coating formation is probably responsible for the autocatalysis. It is necessary to identify the chemical structure of the resulting coating to identify it. FTIR analysis of catechol-cysteamine-coated PVDF membranes was performed, the graph is shown in Figure 2.

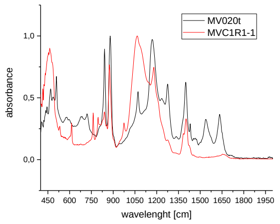

Figure 2: FTIR spectrum for pristine and coated catechol-cysteamine flat sheet PVDF membrane.

The overlapping peaks in the original and modified samples are from PVDF. The new peak appearing in the modified sample in the 1150-1085 range is from the ether group (-C-O-C-). This suggests that the generation of ether bonds are crucial during the formation of coating. In addition, hydroxyl groups and a catechol-derived benzene ring are visible on the spectrum.

Optimizing the catechol-cysteamine reaction allowed nanofiber PVDF membrane coating conditions to be chosen. Too long a reaction time created a thick membrane coating, clogging the pores. However, low initial reactant concentrations formed spherical coating agglomerates. The optimal coating was achieved by sustaining the reaction for 10 hours, using a molar ratio of 1:1.5 and an initial catechol concentration of 4 to 5 mmol.

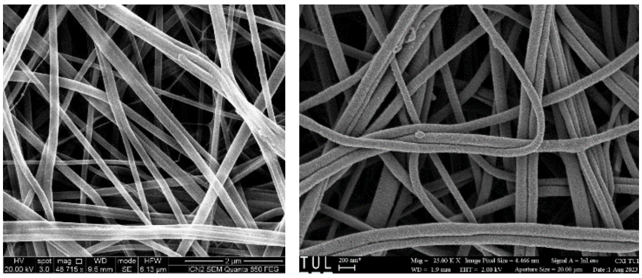

Figure 3: Nanofiborus PVDF membrane before (left) and after (right) CAT-CYS coating with optimized reaction conditions.

CONCLUSION

CAT-TRIS potentially coat a variety of materials, including cotton, polyamide, polyvinylidene fluoride, Spectra yarn, polyester, and melamine formaldehyde foam. New properties can be achieved for coated materials since coating may interact with particular molecules. By experimenting with various monomers, one may manipulate and control the features of the coating. Catechol reacts with the amine groups of numerous different compounds. Choosing the right substrate can adapt coating characteristics to specific purposes or uses. It has been demonstrated that it is feasible to study and characterize how pyocatechol behaves on diverse surfaces, paving the path for its use in various industries including composites, biopolymers, tissue engineering, biosensors, etc.

ACKNOWLEDGE

This work was supported by the Student Grant Competition of the Technical University of Liberec under the project No. SGS-2021-3027. The authors acknowledge the assistance the Research Infrastructure NanoEnviCz provided, supported by the Ministry of Education, Youth and Sports of the Czech Republic under Project No. 2021-12-22.

REFERENCES

[1] Q. Lyu, N. Hsueh, and C. L. L. Chai, “The Chemistry of Bioinspired Catechol(amine)-Based Coatings,” *ACS Biomater. Sci. Eng.*, vol. 5, no. 6, pp. 2708–2724, Jun. 2019, doi: 10.1021/acsbiomaterials.9b00281.

[2] T. Naseem and T. Durrani, “The role of some important metal oxide nanoparticles for wastewater and antibacterial applications: A review,” *Environ. Chem. Ecotoxicol.*, vol. 3, pp. 59–75, Jan. 2021, doi: 10.1016/j.enceco.2020.12.001.

[3] W. Zhang *et al.*, “Catechol-functionalized hydrogels: biomimetic design, adhesion mechanism, and biomedical applications,” *Chem. Soc. Rev.*, vol. 49, no. 2, pp. 433–464, 2020, doi: 10.1039/C9CS00285E.