OPTIMIZATION OF CATECHOL-BASED SURFACE MODIFICATION

[1]Izabela Joanna GALLUS, [2]Daniel KARTHIK

[1]*Technical University of Liberec, Faculty of Mechatronics, Informatics and Interdisciplinary Studies, Liberec, Czech Republic, EU, izabela.gallus@tul.cz*

[2]*Technical University of Liberec, Department of Material Engineering, Faculty of Textile Engieenering, Liberec, Czech Republic, EU, daniel.karthik@tul.cz*

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Abstract

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. By adding suitable agents to the coatings, it is possible to control the properties of the surfaces by giving them new properties. For example, the addition of silver nanoparticles can provide antibacterial properties to the coating. The developed coatings could find applications in textiles, biomedical applications or water filtration. The coating of catechol with Tris(2-aminoethyl)amine (TAEA) for various textiles was performed. Various combinations of catechol with different chemical substrates i. e. diethylenetriamine (DETA), ethanolamine (ETA), cysteamine was carried out and optimization of catechol - cysteamine coating was performed.

Keywords: Surface modification, coating, catechol, materials functionalization, optimization

1. INTRODUCTION

Catechol coatings, also known as catechol-functionalized coatings or catechol-based coatings, are a class of synthetic materials widely employed in various applications, particularly within the realms of materials science, chemistry, and bioengineering. These coatings are intentionally engineered to replicate the remarkable adhesive qualities of catechol, a natural compound abundantly present in the adhesive secretions of specific marine organisms, notably mussels [1]. The utilization of catechol coatings has garnered considerable attention due to their unique adhesive characteristics [2], rendering them indispensable in a myriad of applications, as follows:

- Bioadhesives: Catechol coatings have been instrumental in the development of bioadhesives for medical purposes, such as tissue repair and wound closure. These coatings exhibit an exceptional capacity to adhere to biological tissues, offering a biocompatible alternative to traditional adhesives and sutures [3], [4].
- Underwater adhesion: Renowned for their aptitude to adhere to wet surfaces, including underwater substrates, catechol coatings find valuable application in marine and underwater settings. They are used to create coatings for underwater sensors and materials designed for deployment in marine environments [5].
- Surface modification: Catechol coatings serve as a potent tool for the modification of surface properties across a wide array of materials. This leads to improved adhesion to other materials, elevating durability and bolstering resistance against environmental factors [2].
- Antifouling and anitmicrobial coatings: Catechol-based coatings have been the subject of extensive exploration with the objective of formulating antifouling and antimicrobial coatings [3], [6], [7].

- Drug delivery: The potential of catechol coatings in drug delivery systems is the focus of ongoing research. These coatings can be meticulously designed to release drugs or therapeutic agents at a controlled rate [3].

The adhesive attributes of catechol are attributable to its ability to form robust and reversible bonds with a diverse range of surfaces through interactions such as hydrogen bonding, coordination chemistry, π-π stacking [1], [2], [7], [8].Catechol-functionalized coatings are meticulously engineered to harness these adhesive properties, offering a versatile foundation for diverse applications. The evolution of catechol-based coatings remains an active domain of research with the overarching goal of expanding their utility within biotechnology, medical devices, and materials engineering. In this study, an investigation was conducted to determine whether the CAT-TAEA coating could effectively cover various materials. The study also aimed to explore whether catechol could be used to create coatings with different chemical derivatives and to optimize the coating process between catechol and cysteamine.

2. METHODOLOGY

In this study, a previously developed and optimized CAT-TAEA coating for PVDF filtration membranes was tested on a variety of other materials. The tested materials included flat sheet polyamide, Kevlar fibers, Spectra yarn, cotton woven fabric, glass filaments, melamine formaldehyde foam, copper-coated polyester nonwoven, and nanofibrous polyamide membrane. The process involved immersing these materials in the coating solution for a specified duration, allowing them to dry, and subsequently examining them under a scanning electron microscope. To introduce new functional groups and, consequently, new properties to the coating, attempts were made to replace the previously used tris(2-aminoethyl)amine with different chemical substrates, including aminothiol, alkanolamine, carboxylic and different amines. These replacement substrates included cysteamine, ethanolamine and diethylenetriamine. The reaction between catechol and cysteamine was optimized, and FTIR analysis was conducted on the resulting coating. Several reaction conditions were explored, including variations in the initial concentration of pyrocatechol, molar ratios, temperature, and the effect of pH. **Table 1** provides an overview of the tested conditions.

Table 1 Tested reaction condition for catechol-cysteamine coating

Time (h)	Pytocatechol concentration (mmol/L)	Molar ratio (CAT:CYST)
24	5	0.5:1, 1:1, 1:1.5, 1:2
10	5	1:1, 1:1.5, 1:2
	12,5	1:1, 1:1.5, 1:2
	20	1:1, 1:1.5, 1:2
	25	1:1, 1:1.5, 1:2

3. RESULTS

3.1 CAT-TAEA coating for various materials

Based on the experimental procedure described in the previous section, the different substrates, including flat sheet polyamide, Kevlar fibers, Spectra yarn, cotton woven fabric, glass filaments, melamine formaldehyde foam, copper-coated polyester nonwoven, and nanofibrous polyamide membrane were treated with pyrocatechol and the SEM images of the resulting substrates shown in **Figure 1**. It can be observed that for melamine foam, cotton fibers, glass fibers and flat-sheet polyamide, a not noticeable amount of CAT-TEAE coating is formed on the surface. In the case of Kevlar fibers, Spectra yarn and copper coated polyester nonwoven, we are unable distinctly observe the formation of any coating on the surface, however, we cannot be completely certain that there is absolutely no coating, as there was mild coloration that was observed post treatment. In order to determine the coverage, further analyses would have to be performed. However, the study shown that CAT-TEAE can be potentially coated on various types of materials and contribute to their functionalization with new properties.

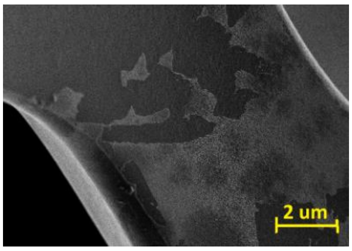
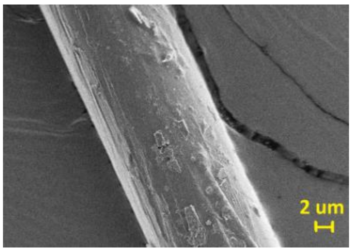
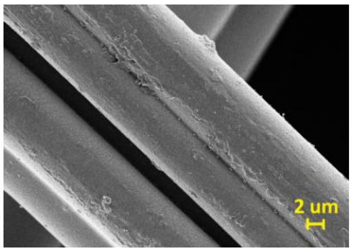
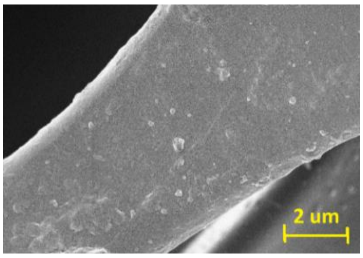
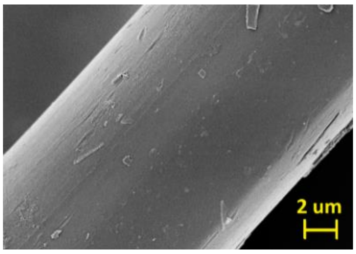
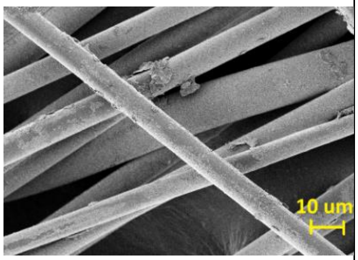
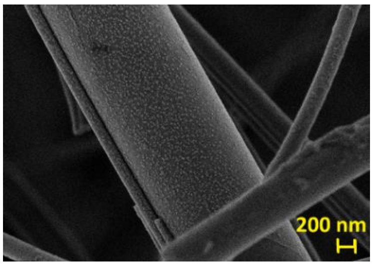
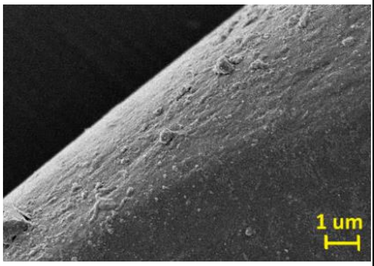
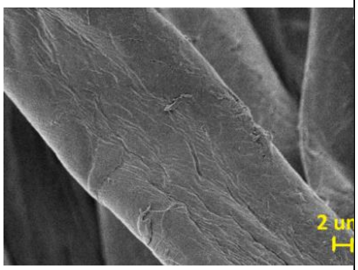
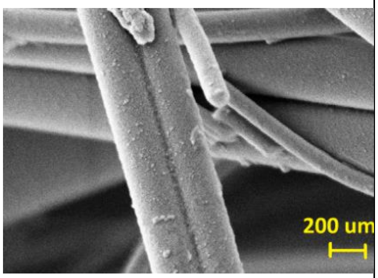
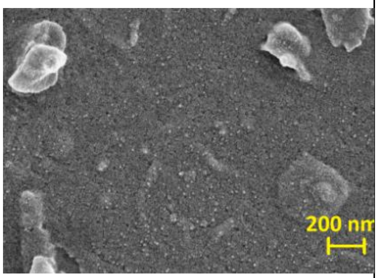
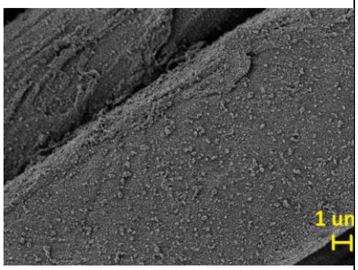
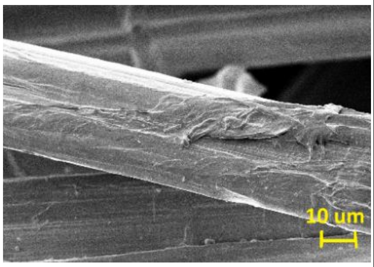
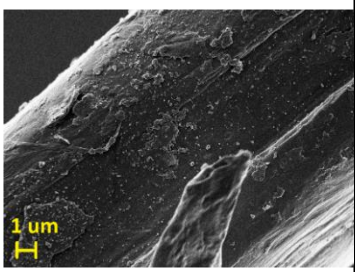
Substrate	**Melamine formaldehyde foam**	**Kevlar fibers**	**Copper-coated polyester nonwoven**
Before coating			
After coating			
Substrate	Glass filament	Flat sheet polyamide	Cotton
Before coating			
After coating			
Substrate	Spectra yarn		
		Before coating	**After coating**

Figure 1 Tested substrate before and after CAT-TAEA coating

3.2 Catechol coating with different chemical substrates

Efforts were made to develop new catechol-based coatings using various chemical substrates. Tris(2-aminoethyl)amine, which had been previously used, was replaced with cysteamine, ethanolamine and diethylenetriamine. It is assumed that the presence of an amine group is a prerequisite to initiate the reaction. Moreover, the reaction's initiation and progression were found to be faster when more terminal amino groups were present. When it comes to coating hydrophobic surfaces, such as PVDF nanofibrous and flat sheet membranes, different reactions resulted in varying degrees of success. Cysteamine led to complete coverage of both membrane types, while diethylenetriamine only coated the flat sheet membrane. In the case of ethanolamine, none of the tested membranes were effectively covered. These outcomes suggest that the resulting coatings possess distinct properties and exhibit varying levels of adhesion to different materials. To confirm this conclusively, further investigation is required to determine how these coatings interact with other materials. **Figure 2** presents visual difference between catechol-based coatings.

Figure 2 Formed coatings between catechol and 1) tris(2-aminoethyl)amine, 2) cysteamine, 3) diethylenetriamine and 4) ethanolamine

3.3 Optimization of catechol – cysteamine coating

The early focus of the study was on the reaction between catechol and cysteamine. This reaction exhibited a slow initiation period but once initiated, it proceeded at a relatively rapid rate. It is likely that the reaction occurs autocatalytically, meaning that a product of the reaction accelerates its own progress. Attempts were made to expedite the initiation of the reaction by altering the pH value (tested at 1, 4, and 9) and by increasing the reaction temperature, but none of these factors resulted in an acceleration of the reaction. It is probable that a by-product formed during the coating formation contributes to the autocatalytic nature of the reaction. To identify this by-product, it is crucial to determine the chemical structure of the resulting coating. In this regard, FTIR analysis was conducted on the catechol-cysteamine-coated PVDF membranes, and the resulting graph is depicted in **Figure 3E**. In the spectra, the overlapping peaks common to both the original and modified samples belong to PVDF. Notably, a new peak in the modified sample's spectrum appeared in the 1150-1085 range, indicating the presence of ether groups (-C-O-C-). This suggests that the generation of ether bonds is a critical aspect of the coating formation. The spectrum also reveals the presence of hydroxyl groups and a catechol-derived benzene ring.

Optimization of the catechol-cysteamine reaction led to the identification of the most suitable coating conditions for the nanofiber PVDF membrane. Excessive reaction time resulted in an overly thick coating layer on the membrane, potentially leading to pore clogging (**Figure 3D**). Conversely, a low initial concentration of reactants led to the formation of spherical coating agglomerates (**Figure 3B**). The most effective coating of the material was achieved with a 10-hour reaction time, a molar ratio of 1:1.5, and an initial catechol concentration of 4-5 mmol, obtained coating presented in **Figure 3C**.

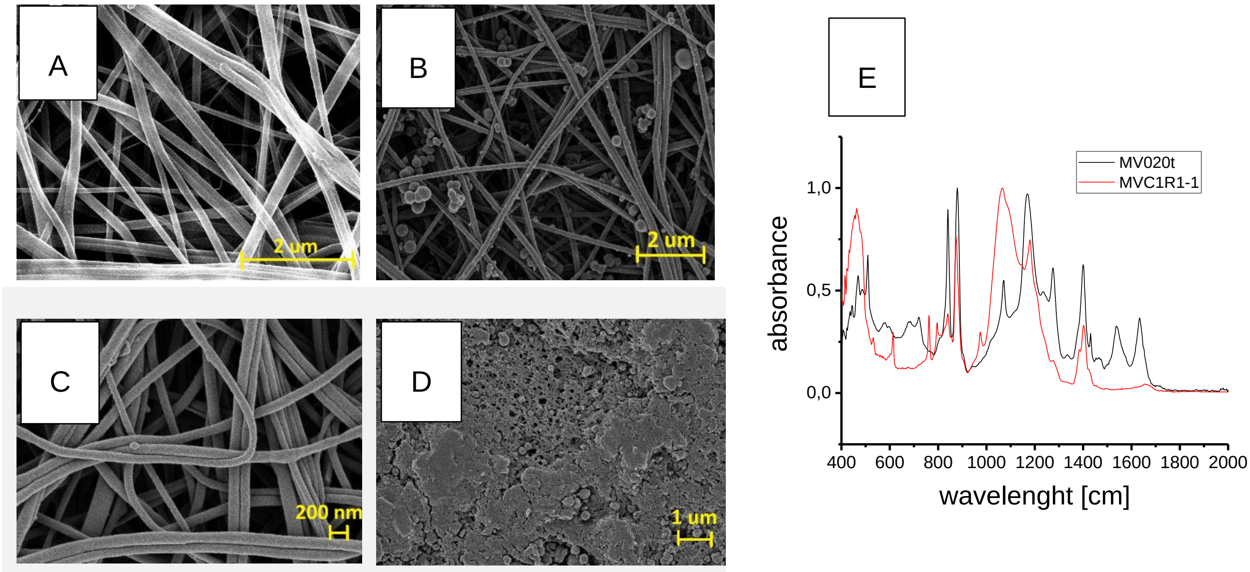


Figure 3 SEM images of a) pristine PVDF nanofibers b) PVDF nanofibers during optimization c) coated PVDF nanofibers after reaction optimization d) clogged flat sheet PVDF membrane after too long treatment. E) Comparison of FTIR spectrum of pristine and coated catechol-cysteamine flat sheet PVDF membrane

4. CONCLUSION

The CAT-TRIS coating has demonstrated its ability to effectively coat a variety of surfaces, including cotton, polyamide, polyvinylidene fluoride, polyester, and melamine formaldehyde foam. This versatility allows for the acquisition of new properties for the coated materials, as the coating can be integrated with specific molecules. Furthermore, the coating's properties can be manipulated and controlled by altering the monomers used. Catechol exhibits reactivity with different chemical groups that contain amine functionalities. By carefully selecting the appropriate substrate, it becomes possible to tailor the coating properties in line with specific goals or intended applications. This study has affirmed that it's feasible to explore and characterize the behavior of pyrocatechol on a range of surfaces. This capability potentially opens up a wide spectrum of applications, encompassing fields like composites, biopolymers, tissue engineering, biosensing, and more.

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