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# WOUND DRESSINGS FILMS BASED ON THE CITRIC ACID MODIFIED STARCH

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The research focuses on obtaining polymer films based on citric acid-modified starch (MSt) in combination with polyvinyl alcohol (PVA) as a base for wound dressings with prolonged drug release. Starch modification was carried out with 0.5 and 1 mol/l citric acid solutions at a temperature of 40°C for 1.5, 2.0 and 2.5 hours. 10% solutions of MSt and PVA were mixed in ratios of 25:75, 50:50 and 75:25 to obtain films by the solution casting method. The influence of citric acid concentration and processing time on the physical-mechanical properties of the films was studied using an automated tensile testing machine ZwickRoell Z2.5TH1. The peculiarities of the interaction between PVA and MSt at different modification durations were determined by Fourier-transform infrared spectroscopy. It was established that the duration of modification and the concentration of citric acid affect the physical-mechanical properties of the films. It was found that increasing the concentration of citric acid contributes to obtaining stronger films. The duration of starch modification with citric acid does not significantly affect the sorption properties of the films, which were evaluated by the amount of water vapor sorption. The sorption properties of the films largely depend on the ratio of MSt and PVA. Thus, films with an MSt/PVA ratio of 75:25 demonstrate an optimal set of properties. The obtained films can be a base for wound dressings with prolonged drug release.

Keywords: modified starch, wound dressings, citric acid.

## INTRODUCTION

Wound healing is a critical aspect of healthcare, where effective wound dressings play a crucial role in facilitating healing and preventing complications. Traditional dressings often lack the capability for sustained drug release, necessitating frequent changes and potentially hindering the healing process. To address this limitation, researchers have developed advanced wound dressings capable of controlled and prolonged drug release (Dhivya *et al.*, 2015).

Starch is a natural and abundant polysaccharide, has garnered attention as a potential material for wound dressings due to its biocompatibility, biodegradability, and low cost (Falcão *et al.*, 2022). However, native starch exhibits certain limitations, including poor mechanical properties and rapid degradation. To overcome these challenges, starch can be modified to enhance its functionality and tailor its properties for specific applications (Torres *et al.*, 2013).

Citric acid is a natural organic acid, has emerged as a promising starch modifier. Citric acid reacts with the hydroxyl groups of starch, forming ester linkages that lead to the crosslinking of starch molecules (Yu *et al.*, 2005). This modification process can significantly improve the mechanical properties, water resistance, and stability of starch (Gonzalez Seligra *et al.*, 2016).

The introduction of an ester group into the cellulose backbone through the esterification reaction of hydroxyl groups imparts hydrophobicity to cellulose, making it more compatible with non-polar polymers and solvents. The use of carboxylic acids, such as citric acid (CA),


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for cellulose modification offers a less environmentally aggressive approach. CA serves as a cost-effective and stable esterification agent, capable of altering the hygroscopic nature of cellulose or nanocellulose through direct chemical modification, thereby enhancing hydrophobicity. Moreover, as emphasized by several authors, it is an esterification agent that can overcome the toxicity and cost associated with other esterification agents. Several authors have also reported the use of anhydrides as esterification agents, such as succinic, acetic, butyric, and hexanoic anhydride.

CA, being a tricarboxylic acid, reacts with cellulose through the attachment of a carboxyl group via esterification with a cellulose hydroxyl group. Further reaction via esterification with another cellulose hydroxyl group can lead to cross-linking between cellulose chains, resulting in cellulose with increased hydrophobicity.

Polyvinyl alcohol (PVA) is a synthetic polymer known for its excellent film-forming ability, biocompatibility, and non-toxicity. PVA is widely used in various biomedical applications, including wound dressings (Dash *et al*., 2011).

### Research Objectives

In this study, polymer films based on citric acid-modified starch (MSt) in combination with polyvinyl alcohol (PVA) were developed. The aim of this research is to create a composite material that leverages the individual advantages of both components, resulting in films with desirable properties for wound dressings with prolonged drug release. The influence of various modification parameters, such as citric acid concentration and modification time, on the physical, mechanical, and sorption properties of the films have been researched. The interaction between MSt and PVA using FTIR spectroscopy also have been investigated to gain insights into the molecular structure and properties of the composite films.

It is planned to improve wound treatment technologies by optimizing the composition and properties of polymer films based on starch, offering innovative solutions for long-term drug delivery and improving the results of wound healing.

## MATERIALS AND METHODS

### Starch Modification

Potato starch (CAS 9005-25-8) modification was conducted using two different concentrations of citric acid (CAS 77-92-9) solution (0.5 mol/l and 1 mol/l). For each concentration, the modification was performed at a constant temperature of 40°C but with varying reaction times of 1.5, 2.0, and 2.5 hours. This approach aligns with previous studies demonstrating the effectiveness of citric acid in altering starch properties (Yu *et al*., 2005). Different reaction times were chosen to investigate the effect of the modification duration on the final characteristics of the film.

### Film Preparation

10% (w/v) solutions MSt and polyvinyl alcohol (PVA 17-99) were prepared to obtain films of varying composition. This concentration was selected based on previous research indicating suitable film-forming properties for both starch and PVA (Mali *et al*., 2005). Then these solutions were mixed in three different ratios (w/w): 25:75, 50:50, and 75:25 (MSt:PVA). To form films from these mixtures the solution casting method was employed as widely used technique for obtaining polymer films due to its simplicity and versatility (Gutiérrez *et al*., 2015).

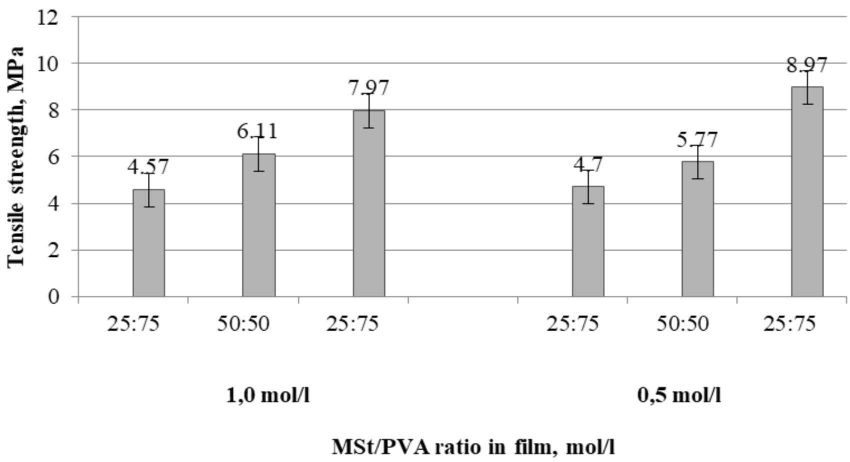
### Characterization and Analysis

The tensile strength and elongation at break of the films were evaluated using an automated tensile testing machine ZwickRoell Z2.5TH1. These properties are crucial in understanding the film's ability to withstand stress and deformation, which are relevant for wound dressing applications (Bergo *et al*., 2007; Ghanbarzadeh *et al*., 2010; Ibrahim *et al*., 2019). Molecular interactions between modified starch (MSt) and polyvinyl alcohol (PVA) within the films, Fourier-transform infrared (FTIR) spectroscopy was used.

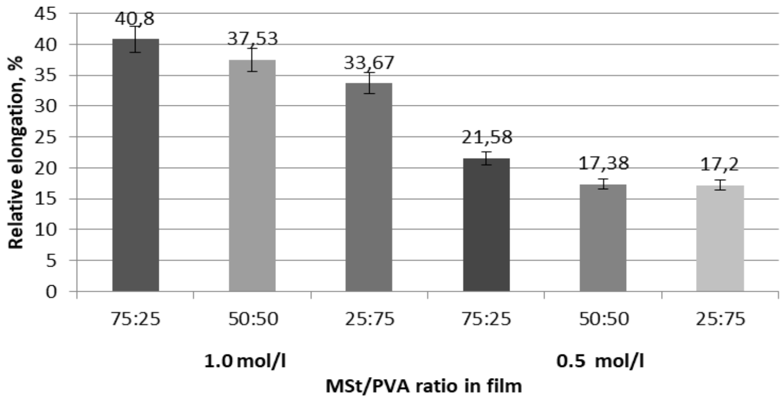
## RESULTS AND DISCUSSIONS

### Evaluation of Mechanical Properties

For each film sample, five replicate specimens were prepared according to standard testing methods (ASTM D882) (Anseth *et al*., 1996). By analyzing the tensile strength and elongation at break data, valuable insights into the mechanical behavior of the film and its suitability for wound dressing applications can be gained (Fig.1). Higher tensile strength values signify a stronger and more durable film, while higher elongation at break values indicate a more flexible and deformable film.




a)




b)

Figure 1. Tensile strength (a) and elongation (b) of film on different ratios of MSt/PVA

Processing time and citric acid concentration also influence the physical-mechanical properties of the films. It was determined that samples with a citric acid concentration of 0.5 mol/l have a tensile strength ranging from 4.7 to 8.97 MPa, and a relative elongation at break ranging from 17.2 to 21.58%. For samples treated with citric acid at a concentration of 1 mol/l, the tensile strength ranges from 4.57 to 7.97 MPa, and the relative elongation at break ranges from 33.67 to 40.8%.

Based on the research results, it can be established that with an increase in starch processing time, functional groups are added that influence the PVA crosslinking process. With an increase in concentration, the resulting films are more elastic.

**Fourier-Transform Infrared (FTIR) Spectroscopy Analysis**

To further investigate the molecular interactions between modified starch (MSt) and polyvinyl alcohol (PVA) within the films, Fourier-transform infrared (FTIR) spectroscopy was used.

The spectra were analyzed to identify characteristic absorption bands associated with MSt, PVA, and potential new bonds formed due to the modification process (Fig.2).

Specifically, the appearance of new absorption bands in the ester carbonyl region (around 1730-1750 $cm^{-1}$) would indicate the formation of ester bonds between the hydroxyl groups of PVA and the carboxyl groups of citric acid in the modified starch. Judging by the curves, these peaks appeared at first, and gradually disappeared, which indicates their participation in the interaction. On the upper curve (75:25 MSt/PVA, 1 mol/l), the peak is larger, on the lower one (25:75 MSt/PVA, 0,5 mol/l) it is almost absent due to scale of modification and percentage of MSt in films, that indicates successful modification.

This esterification reaction is expected to contribute to the cross-linking of starch molecules and the enhanced mechanical properties observed in the films.

Furthermore, changes in the intensity and position of absorption bands associated with hydroxyl groups (around 3200-3600 $cm^{-1}$) could provide information about the extent of hydrogen bonding interactions between MSt and PVA. These interactions play a crucial role in determining the film's overall structure, stability, and sorption properties.

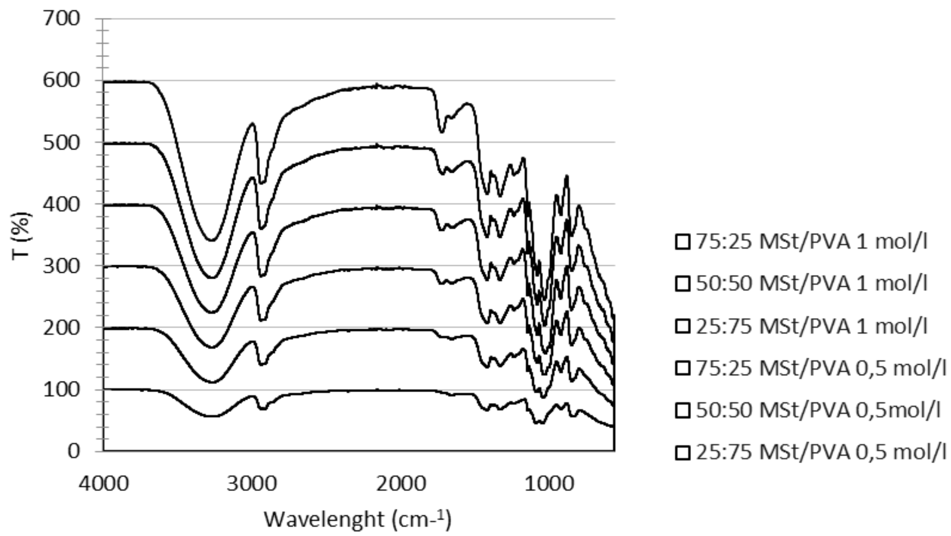



Figure 2. FTIR spectra of films with different MSt/PVA ratios and modification conditions

All six graphs exhibit a similar profile with a broad minimum in the range of 1000-1700 $cm^{-1}$, which corresponds to the vibrations of C-O and C-C bonds in the polymer chains, thus indicating successful modification. A deeper minimum signifies greater absorption and, consequently, a higher concentration of these bonds. In the spectrum of the 75:25 MSt/PVA 1 mol/l sample, a small peak (maximum %T) is also observed in the 3300-3500 $cm^{-1}$ region, which corresponds to the vibrations of O-H bonds. This may indicate the presence of residual water molecules in the modified material.

By comparing the FTIR spectra of films with different MSt/PVA ratios and modification conditions, it is possible to discern the influence of these factors on the molecular interactions and, consequently, the properties of the resulting films.

## CONCLUSION

This research investigated the development of polymer films based on citric acid-modified starch (MSt) and polyvinyl alcohol (PVA) for potential application in wound dressings with prolonged drug release. The study systematically evaluated the effects of citric acid concentration and modification time on the physical-mechanical properties and sorption characteristics of the films.

The results demonstrated that the modification process significantly influenced the film properties, with higher citric acid concentrations and longer modification times leading to improved mechanical strength and elasticity. FTIR analysis confirmed the formation of ester bonds between MSt and PVA, indicating successful cross-linking and enhanced structural integrity.

Processing time and citric acid concentration also influence the physicomechanical properties of the films. It was determined that samples with a citric acid concentration of 0.5 mol/L citric acid had tensile strength of 4.7-8.97 MPa and elongation at break of 17.2-21.58%. Samples with 1 mol/L citric acid had tensile strength of 4.57-7.97 MPa and elongation at break of 33.67-40.8%.

Based on the research results, it can be established that with an increase in starch processing time, functional groups are added that influence the PVA crosslinking process. With an increase in concentration, the resulting films are more elastic and stronger. Films based on modified starch are more homogeneous and transparent.

Among the studied formulations, films with an MSt/PVA ratio of 75:25 exhibited the most favorable combination of properties, including optimal mechanical performance and sorption characteristics. These findings suggest that the developed films hold significant promise as a novel material for wound dressings, offering potential advantages in terms of drug delivery and healing outcomes.

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