



Effect of Chemical Cross-Linking on the Swelling and Degradation Rates of Chitosan-Copper Complex/PVA Electrospun Nanofibers

Amir Parvinnasab*, Sharareh Shahroudi, Erfan Salahinejad

Faculty of Materials Science and Engineering, K. N. Toosi University of Technology, Tehran, Iran

*(amirars14@gmail.com)

Abstract- Chitosan-copper complex/PVA electrospun nanofiber mats were cross-linked with 6 and 12% glutaraldehyde (GA) for 12 and 24 h to study their effects on swelling and degradation until 21 days. Results showed that increasing GA concentration and cross-linking time reduces swelling from 186% for the non-cross-linked mats to 100% for the mats treated with 12% GA for 24 h after the first day. Degradation also decreased from 48% weight loss for non-cross-linked to 3% for the most extensively cross-linked mats. This study demonstrated that chemical cross-linking limits swelling and degradation of the chitosan-copper complex/PVA nanofibers by restricting the polymer chain mobility.

Keywords – Chitosan-copper complex, Electrospun mat, Chemical Cross-linking, Glutaraldehyde, Swelling, Degradation rate.

I. INTRODUCTION

Electrospinning is a versatile technique for fabricating non-woven nanofiber mats that have gathered significant interest for biomedical applications due to their high surface area-to-volume ratio and biomimetic structure [1]. Chitosan, a natural polysaccharide, is widely used for electrospinning due to its biodegradability, biocompatibility, and ability to chelate metal ions. This allows the incorporation of ions like copper which exhibit antimicrobial properties. However, poor mechanical strength and rapid degradation limit their long-term applications [2]. To address these limitations, chemical cross-linking is normally employed. While cross-linking improves stability, it can negatively impact desirable features like swelling and biodegradation behaviors [3]. The degree of cross-linking should therefore be optimized. Glutaraldehyde is commonly used for cross-linking of polymers like chitosan and PVA due to its ability to react with amine and hydroxyl groups. However, the effect of cross-linking concentration and time using glutaraldehyde on electrospun chitosan-copper complex/PVA nanofiber mats has not been examined.

In this study, chitosan-copper complex/PVA electrospun nanofiber mats were prepared via an electrospinning method. For the first time, the effect of glutaraldehyde concentration (6 and 12%) and cross-linking time (12 and 24 h) on swelling and degradation rates was examined, providing novel insights for stabilizing these fibers through optimized glutaraldehyde cross-linking for biomedical uses.

II. MATERIALS AND METHODS

Chitosan (medium molecular weight, 85% deacetylation degree), PVA (medium molecular weight, 99% hydrolyzed), glacial acetic acid, sodium hydroxide, anhydrous Cu (II) chloride, and glutaraldehyde solution (25% in water), all of analytical grade were used in this work.

Chitosan-copper complexes were prepared by an in situ precipitation method according to ref. [4]. These precipitants were dissolved in 2% v/v acetic acid and then blended with PVA (Table 1). The Nanoazma electrospinner was used for the electrospinning process. The electrospinning distance was 14 cm, the applied voltage was 30 kV, the flow rate was 0.4, and the collector speed was 800 rpm. Finally, the electrospun nanofibers were exposed to different concentrations of GA to be cross-linked with their vapor for different times.



Table 1. Specification of the samples prepared in this work

Sample names	Ch-Cu Complex (% wt)	PVA (%wt)	Volume Ratio (Ch-Cu Complex:PVA)	Glutaraldehyde Concentration (%)	Crosslinking Time (h)	Color in charts
Ch-Cu/PVA	3	7	30:70	0	-	●
Ch-Cu/PVA-6G12	3	7	30:70	6	12	●
Ch-Cu/PVA-6G24	3	7	30:70	6	24	●
Ch-Cu/PVA-12G12	3	7	30:70	12	12	●
Ch-Cu/PVA-12G24	3	7	30:70	12	24	●

III. RESULTS, DISCUSSION AND CONCLUSION

The swelling and degradation rates of the electrospun nanofibers are illustrated in Fig. 1. After one day of exposure, the degree of swelling decreased from 186% for the untreated mats to 100% for the Ch-Cu/PVA-12G24 sample. This downward trend persisted over the subsequent days, with the mentioned sample exhibiting the greatest reduction in the swelling degree of 53% until 21 days. Concerning the degradation rate, an increase in the glutaraldehyde concentration and exposure duration led to a decrease in the degradation rate. The untreated mats exhibited a degradation rate of 48% after the initial day, completely degrading within 21 days. However, the Ch-Cu/PVA-12G24 sample, with the highest glutaraldehyde concentration and cross-linking time, only experienced a 12% reduction in weight until 21 days.

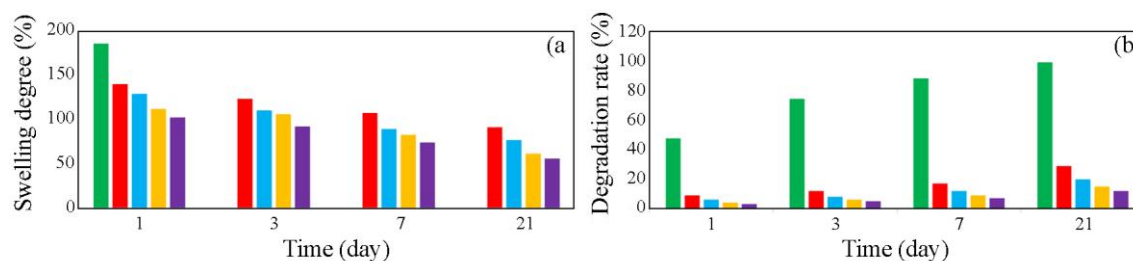


Fig. 1: (a) Swelling and (b) degradation rates of the samples cross-linked under the different conditions.

This decrease in the swelling and degradation rate can be attributed to the formation of covalent bonds between the polymer chains. This process enhances chemical stability and mitigates vulnerability to enzymatic or chemical degradation. Glutaraldehyde reacts with functional groups present in chitosan and PVA, leading to the formation of stable cross-links. These cross-links serve to limit the motion of the polymer chains, thereby diminishing the amount of free space accessible for water absorption and impeding water penetration into the fibers with hydrophilic functional groups [5,6].

In this work, chitosan-copper complex/PVA nanofiber mats were fabricated and cross-linked with glutaraldehyde at varying concentrations and times. This allowed for the systematic modulation of swelling and degradation behaviors. Tailoring the cross-linking conditions provides a means to design mats with stability profiles that meet demands of different biomedical applications, such as sustained ion release. This work establishes a method for customizing the durability of these fiber systems through glutaraldehyde treatment.

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