The Effect of UVC Irradiation on the Mechanical Properties of Chitosan Membrane in Sterilization Process

N N Rupiasih\textsuperscript{1,2,*}, M Sumadiyasa\textsuperscript{1} and I K Putra\textsuperscript{1}

\textsuperscript{1}Department of Physics, Faculty of Mathematics and Natural Sciences, Udayana University, Denpasar, Bali 80361, Indonesia

\*Corresponding author e-mail: rupiasih@gmail.com

Abstract. The present study, we report about the effect of UVC irradiation on the mechanical properties of chitosan membrane in the sterilization process. The membrane used was chitosan membrane 2% which prepared by a casting method using chitosan as matrix and acetic acid 1% as a solvent. The UVC source used was germicidal ultraviolet (UVG) which widely used for sterilization purposes. Variation doses were done by the varying time of irradiation, e.g. 5 min, 15 min, 30 min, and 60 min. Those samples are named as S1, S2, S3, and S4, respectively. Chitosan membrane before irradiation namely S0 also used for comparative study. The effect of UVC irradiation on the mechanical properties of membranes has been examined by different techniques including FTIR, DMA, and the water uptake capability. The results showed that ultimate tensile strength (UTS) and moduli of elasticity (E) were increased by increasing the irradiation time. From FTIR analysis obtained that no new molecules were formed in irradiated membranes. The water uptakes capability of the membranes after irradiation was smaller compared with before irradiation, and among the irradiated membranes, the water uptake capabilities were increased by increasing the exposure time. These observations suggested that more care should be taken during the sterilization process and outdoor used of the membrane. The other side, the UVC irradiation can improve the mechanical properties of the membranes.

Keywords: chitosan membranes; short-wavelength ultraviolet (UVC); sterilization; mechanical properties; water uptake capability.

1. Introduction
Chitosan is a natural polymer derived by deacetylation of chitin. Chitin is a polysaccharide existing in the exoskeleton of crustaceans and insects, mollusk shells and fungal biomass [1, 2]. Chitosan is derived from the partial or full replacement of an N-acetyl group in chitin by an amine group; the process is called de-acetylation degree (DD) with value varying from zero to unity [3]. The amine and hydroxyl groups in chitosan polymer act as potential sites for intermolecular interactions take place. This characteristic has been extensively developed in various processes, for example, controlled drug release, sorption phenomena, and metal complexation [3-5].

Currently, UVG has been used widely for sterilization purposes. UVG irradiation is a disinfection method that uses short-wavelength ultraviolet (UVC) light to kill or inactivate microorganisms. It was used widely in medical sanitation, sterile work facilities, drinking, wastewater treatments, and air sanitation. Those facilities were enclosed and could be circulated, so the possibility of exposure to high radiation is large enough.
Many studies about photodegradation of structural modifications in chitosan-based systems induced by UV irradiation have been reported [3, 6]. The main photodegradation mechanisms involved rupture of glycosidic linkage and formation of a carboxylic group in the absence or presence of oxygen, and production of the hydroxyl group. The measurements of the static contact angle of chitosan films exposed to low-intensity UV lamps have revealed an enhancement in the surface energy with the exposure time [7]. This behavior has been associated with the increase of the surface polarity of films caused by the scission of glycosidic bonds and pyranose rings during the photo-oxidation process [3, 8]. A significant reduction of UV sensitivity has been detected in the study of UV effects on polymeric blends of chitosan matrix based. Chitosan-based blends show a lowering in the mechanical properties upon UV irradiation compared with pure chitosan films [3, 6]. The other sides, photo-irradiation-based techniques can be very useful to improve the performance of polymeric membranes in technical separations such as micro and ultra-filtration, gas separation, and as membrane adsorbers. Based on those backgrounds, thus it is importance to study about the effect of UVC irradiation on the mechanical properties of chitosan membrane which has been given during sterilization.

2. Materials and methods

2.1 Materials and membranes Preparation

Chitosan powder used was extracted from shrimp with a DD of 87.9% and solubility in acetic acid 1% is 99.4%. Acetic acid and NaOH were analytical grades (p.a.), and demineralized water was used in preparing solutions. Chitosan membrane 2% was prepared by a casting method using chitosan as matrix and acetic acid 1% as a solvent. The membrane solution was prepared by dissolving 5 g of chitosan powder in 250 ml of acetic acid 1%. The complete casting method described in Ref.1 and 2.

2.2 UVC irradiation and characterizations

Dry membrane was cut into different sizes for various characterization techniques. Some membranes were kept before irradiation as a comparative study, named as S0 and some membranes were irradiated by UVC radiation. The UVC source used was UVG. Variation doses were done by the different time of irradiation, e.g., 5 min, 15 min, 30 min, and 60 min. Those samples are named as S1, S2, S3, and S4, respectively. Various methods have been used to characterize the effect of UVC irradiation on the mechanical properties of membranes including FTIR, DMA (dynamic mechanical analysis), and the water uptake capability. FTIR spectra were recorded using an IR Prestige-21 FTIR spectrometer, Shimadzu. Spectra were taken with a resolution of 4 cm\(^{-1}\) in the range of 400 to 4000 cm\(^{-1}\). The mechanical strength of membranes was measured using DMA following the standard method ASTM D3039. The sample is rectangular with a cross-section of 5 x 0.5 mm\(^{2}\) and length 20 mm. All measurements were conducted at room temperature and in dry condition.

Water uptake experiment was done by following protocol described in Ref. 1. The water uptake of the membrane was calculated using the following formula, where \(m_{\text{dry}}\) is the mass of dry membranes and \(m_{\text{wet}}\) is the mass of wet membranes [1].

\[
\text{Water uptake } (\%) = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100%
\]

3. Results and discussion

Figure 1 show IR spectra of chitosan membranes S0, S1, S2, S3, and S4. All spectra showed a similar pattern; in the figure, only S0 is labeled, and other spectra are written in Table 1. The S0 spectrum obtained was similar to the spectrum obtained in our previous study and also has been reported by others [1-3].

For membrane before irradiation (S0, Fig. 1), IR spectrum shows the absorption bands at around 3475, 2920 and 2880 cm\(^{-1}\) are characteristic of stretching vibrations of –OH, –CH\(_2\), and –CH\(_3\) groups, respectively. The absorption bands at 3370 and 1580 cm\(^{-1}\) represent of stretching and bending vibrations of –NH\(_2\) amine group. The absorption band at around 1630 cm\(^{-1}\) corresponds to –C=O stretching of carbonyl group which is related to the presence of N-acetyl units due to the
DD value around 87.9%. The peaks at 1409 and 1328 cm\(^{-1}\) related to the vibrations of –OH and –CH groups in the pyranose ring. The strong peak at 1047 cm\(^{-1}\) associates to the anti-symmetric stretching of C–O–C glycosidic linkage. This result is by earlier studies [1-3, 8, 9].

![Figure 1. IR spectra of chitosan membranes: S0, S1, S2, S3, and S4](image)

For membranes after irradiation (S1, S2, S3, and S4), it observed some changes in the absorption bands of the stretching –OH group and the bending –NH2 group. Both bands were shifted to higher or lower frequencies. More can be seen in the data Table 1. These observations indicated that photodegradation and photo-cross-linking or photo-grafting process occurred in the membranes simultaneously [3, 8, 10] which depended on the irradiation time exposures. This also can be described from the ratio \(A_{3475}/A_{1580}\) and \(A_{1047}/A_{1580}\) IR spectra of chitosan membranes as shown in Table 2, where \(A_{3475}, A_{1580},\) and \(A_{1047}\) are the absorbances of hydroxyl-stretching, amine-bending bands and glycosidic-stretching respectively [3, 8]. From this analysis, we observed an increase around 1% to 2.3% in the ratio \(A_{3475}/A_{1580}\) and increase or decrease around 0.7% to 2.3% in photodegradation process occurs along the entire membranes as a consequence, a change in membrane properties found.

**Table 1.** The main bands observed in chitosan membranes: S0, S1, S2, S3, and S4

| Functional Groups                                      | Wavenumbers Observed (cm\(^{-1}\)) |
|--------------------------------------------------------|-----------------------------------|
| –OH stretch                                            | 3475 3482 3479 3471* 3475          |
| –CH\(_2\) stretch                                      | 2920 2934 2934 2934* 2943          |
| –CH\(_3\) stretch                                      | 2880 2887 2878 2878* 2869          |
| –NH\(_2\) amine group stretch and bend                  | 3370 and 3395 and 3388 and 3374* and 3388 and 3388 and |
| –C=O stretch of carbonyl group                          | 1580 1581 1581 1555* 1537          |
| –OH and –CH groups in the pyranose ring                 | 1409 and 1393 and 1393 and 1393* and 1383 and 1383 and |
| The anti-symmetric stretch of C–O–C glycosidic linkage  | 1328 1337 1337 1328* 1337          |

Ref. 1-3. *: Peak is very weak.
The UTS, modulus of elasticity and elongation-at-break are presented here to characterize the mechanical properties of the chitosan membranes, as shown in Fig. 2. UTS is the maximum tension that can be supported by the membranes until the moment it breaks. Elongation-at-break is a measure of flexibility of the membranes before breaking. These measurements are important once the mechanical properties of membranes or films depend on the filmogenic nature of the material used, which is directly related to its structural cohesion [11].

**Table 2.** The ratio $A_{3475}/A_{1580}$ and $A_{1047}/A_{1580}$ IR spectra of chitosan membranes: S0, S1, S2, S3, and S4

| Sample | $A_{3475}/A_{1580}$ | $A_{1047}/A_{1580}$ |
|--------|---------------------|---------------------|
| S0     | 1,000               | 0,916               |
| S1     | 1,000               | 0,917               |
| S2     | 1,007               | 0,896               |
| S3     | 1,010               | 0,923               |
| S4     | 1,023               | 0,893               |

Figure 2a and b showed that UTS and E moduli increased by increasing the irradiation time, where $\varepsilon$ is increased up to irradiation of 15 min then decreased. These mean that UVC irradiation affected the mechanical properties of chitosan membrane in doses dependent manner. There has been membrane modification (functionalization) during the sterilization process, which includes photo-cross-linking of membranes and photo-grafting of membrane surfaces, either via “grafting-from” or “grafting-to” ways [10]. The crosslinking reactions occurred in competition with chain scission. Thus the modifications of the chemical structure will cause the changes of the mechanical property of the membrane; they will also contribute to the development of entirely novel membrane-based materials [10, 12].

**Figure 2.** a) Ultimate tensile strength (UTS) and b) elongation-at-break ($\varepsilon$) and elastic moduli (E)

The water uptakes of all membranes, at various times, were investigated and the results obtained as shown in Fig. 3a and 3b. It showed that the dynamic of water uptake is highly affected by the UVC irradiation which depending on the irradiation time given. The dynamical of water uptake is due to varies changes in the chemical structure of the entire membrane [3, 13] which showed by IR spectra. The water uptake of S0 is reached a maximum after 24 h while the water uptake of S1, S2, and S3 reached a maximum after 1 h and S4 after 6 h. They were reached maximum faster compared with S0. Figure 3b showed the water uptake capabilities of irradiated membranes were smaller compared with S0, but among the irradiated membranes, the water uptake capability was increased by increasing the exposure time. The UVC irradiation affected the water uptake capability of chitosan membranes in doses dependent manner. This result is in agreement with the tensile modulus obtained by DMA test. It can be described that might occur the competition between chain scission, which initiated by UVC irradiation and crosslinking reactions that changed the chemical
structure of irradiated membranes. The crosslinking have increased the strength of the membrane, so it reduced the water uptake capability.

![Graph showing water uptake over time for membranes S0, S1, S2, S3, and S4.](image)

**Figure 3.** Water uptake of all membranes: S0, S1, S2, S3, and S4. a) Water uptake as a function of time and b) The maximum percentage of water uptake (%) of each membrane

4. Conclusion

This study demonstrated that the mechanical properties of chitosan membranes were greatly affected by UVC irradiation within the short time of irradiation (i.e., 5 min). It affects the mechanical properties of chitosan membranes which strongly depends on the time of irradiation. These observations suggested that more care should be taken during the sterilization process and outdoor use of the membrane. The other side, the UVC irradiation can improve the mechanical properties of the membranes.

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