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Optical Constant Determination of Crosslinked Chitosan-Polyethylene Glycol (PEG) using Attenuated Total Reflection Method by Surface Plasmon Resonance Phenomenon

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Abstract. Application of chitosan as a sensing layer for heavy metal ions in surface plasmon resonance (SPR)-based sensor with Kretschmann configuration has been done extensively using polypyrrole and glutaraldehyde. The deposition methods that are very widely used in depositing chitosan onto the sensing surface are spin coating, electrodeposition and dip coating (for SPR based fiber optic sensor). The deposition technique of chitosan-polyethylene glycol (PEG) composite material as sensing layer in SPR based sensor by using the drop-casting method has not been done to the best of our knowledge. In order to use chitosan-PEG composite material as a sensing layer for heavy metal ion detection, it is necessary to determine the optical constant of chitosan-PEG which is deposited by the drop-casting method. The refractive index of chitosan-PEG with mass composition 0.4 grams chitosan and 0.04 grams PEG was determined by attenuated total reflection (ATR) method by utilizing surface plasmon resonance phenomenon on the prism/silver/chitosan-PEG interfaces in Kretschmann configuration. The refractive index then was extracted from the ATR curve by using Winspall software. Based on the experimental result, it was found that the ATR curve was shifted from 44.3° to 68.9° with the presence of a chitosan-PEG layer deposited onto the silver surface, about 0.01 ml in solution form. From the fitting result, it was found that the refractive index of chitosan-PEG was $n = 1.32$.

1. Introduction

The use of crosslinked chitosan with a polymer as a detection layer for heavy metal ions had been studied before [1–12]. From the results, it was found that the methods which were used to produce crosslinked chitosan thin film are spin coating, electrodeposition, and dip coating methods. To the best of our knowledge, the use of the drop-casting method to produce the thin film layer has not been reported. Therefore, the development of surface plasmon resonance (SPR)-based sensor using crosslinked chitosan-polyethylene glycol (PEG) composite that is dropcasted onto the metal thin film surface to form a thin film layer needs to be studied as an alternative method.

The essential information needed in SPR-based sensor when developing an active sensing layer is its refractive index before it sense an object [13]. Basically, the detection mechanism of SPR-based sensor is the shift of ATR curve when another material such as heavy metal ions and biomolecules were detected by the sensing layer. This shift is a result of the changing of the refractive index on the sensor surface [14]. ATR curve then can be used to extract the optical constant and thickness of thin films. Therefore, in order to use chitosan-PEG composite material as a sensing layer for heavy metal ion detection, it is necessary to determine its optical constant.



The chemical structure of chitosan is poly (β -1-4)-2-amino-2-deoxy-D-glucopyranose produced by partial or full alkaline N-deacetylation of chitin until its degree of deacetylation is more than 50%. The amino group in chitosan structure contributes to chelate heavy metal ions, and the electrostatic force in its structure depends on the protonation of the amino group in acid solution [2]. Several studies have been done to observe the ability of chitosan to adsorb heavy metal ions by a chemical mechanism [15–17]. The crosslinked compounds that were used in SPR-based sensor for the detection of heavy metal ions were polypyrrole [1, 6, 9] and glutaraldehyde [3–5, 7–8, 10]. Meanwhile, the chitosan-PEG composite material using drop-casting method which we used in developing SPR-based sensor to detect heavy metal ion have not been studied yet. Hence, here we report our study of chitosan-PEG composite material optical constants by determining them using ATR method by utilizing SPR phenomenon in Kretschmann configuration.

2. Materials and Methods

Chitosan with high molecular weight and degree of deacetylation 80-84% was purchased from Biotech Surindo (Cirebon-Indonesia), acetic acid 96% was purchased from CV. Progo, and distilled water was purchased from CV. General Labora. The silver with 99.99% purity and polyethylene glycol 4000 were purchased from Sigma Aldrich. Prism with refractive index of $n = 1.503$ at 632.8 nm was purchased from UD. Nirwana Abadi (Surabaya-Indonesia), and the glass cover slips 24x50 mm with thickness 0.13-0.16 mm was purchased from Menzel-Glaser.

To prepare the chitosan solution, 0.4 g of chitosan was dissolved in 50 mL 1% acetic acid made by dissolving it in the distilled water until the concentration achieved. The solution was then stirred about four hours at 60°C. After that, the 0.04 g polyethylene glycol was added to the solution and then stirred for another two hours at the same temperature. The silver was deposited onto the surface of the prism using Thermal Evaporator Edward Coating System E 610. Then the drop-casting method was used to produce a sensing layer from chitosan-PEG composite material. About 0.01 ml of the solution was placed on the surface of silver thin film and then the glass cover slip was placed on the top of the chitosan-PEG solution.

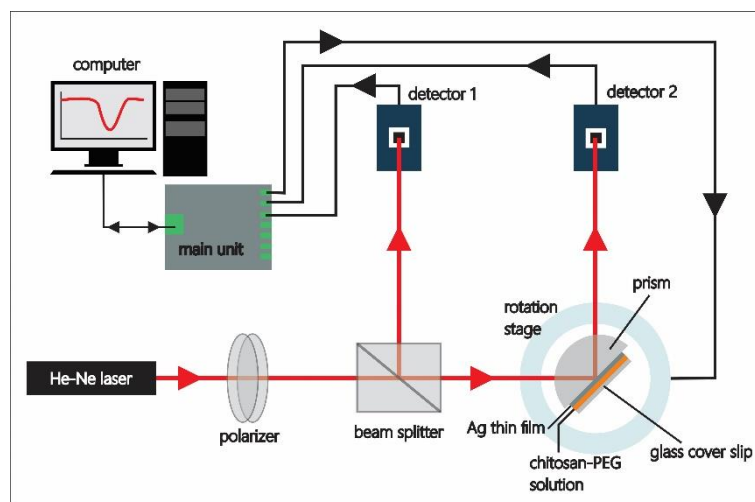


Figure 1. The experimental setup in Kretschmann configuration.

Figure 1 shows the experimental setup for obtaining ATR curves from SPR phenomenon. The ATR curves were obtained by measuring the reflected power of He-Ne laser beam ($\lambda = 632.8$ nm from ThorLabs P945488 with maximum power < 4 mW) by varying the angle of incident. The optical setup

consist of an optical stage driven by stepper motors with total resolution of 0.01, a polarizer, beam splitter, and the reflected beam was detected by sensitive photodiode.

To extract the refractive index from ATR curves, we used Winspall software (SPR simulation). The complex refractive index of silver thin film based on a study by Johnson and Christy [18] for He-Ne laser beam and the refractive index of the prism $n = 1.503$ were used as a input parameter to fit the experimental data. After the chitosan-PEG solution was deposited onto the silver thin film surface, we used trial value of the refractive index chitosan-PEG solution until the simulated ATR curve fits well with the experimental once.

3. Result and Discussion

The ATR curves of prism/silver thin film (Ag) and prism/Ag/chitosan-PEG obtained in this study is shown in Figure 2. Based on experimental and simulation fitting results, it was found that the optical constant of the silver thin film was $0.056 \pm i3.442$, and the thickness of the silver thin film was $d = 46.1$ nm. This result is similar with the optical constant obtained by Johnson and Christy [18].

It was shown in Figure 2 that the prism/Ag ATR curve have a narrow and deep profile which implies the SPR phenomenon in dielectric (prism) and silver thin film interface has a high sensitivity towards refractive index change on the sensor surface. The SPR phenomenon occurs when the surface plasmon wave (SPW) on the interface between silver and air coupled to the evanescent wave on the interface between prism and silver thin film layer.

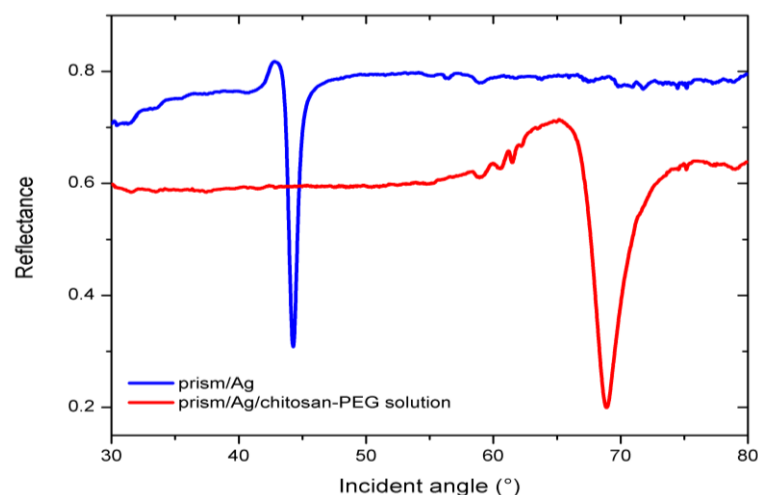


Figure 2. ATR curve of prism/Ag and prism/Ag/chitosan-PEG systems

After the chitosan-PEG solution was placed on the top of silver thin film and covered with a glass cover slip, the ATR curve was measured and it shown in Figure 2 According to the results, it was found that the ATR curve was shifted from 44.3° to 68.9° with minimum reflectance difference was 0.1082. The shift of the ATR curve shows that the refractive index of chitosan-PEG solution caused the intersection between dispersion relation curves of SPW with photon wave from the laser shift to the right (higher value). This implies that SPR angle shifted to the higher value, as can be seen in Figure 2.

From the fitting result, it was found that the refractive index of chitosan-PEG was $n = 1.32$. Regarding to the explanation above, this value caused the resonance angle shifted to higher value, since it has a higher refractive index than that of the air. It also implies that the SPR phenomenon occurs the presence of chitosan-PEG on the sensor surface, therefore this material can potentially be developed as an active sensing layer. Furthermore the ATR curve of prism/Ag/chitosan-PEG was wider and deeper than the ATR curve from prism/silver thin film system that implies the evanescent field enhancement from silver thin film [19].

4. Conclusions

In this study, the optical constant of crosslinked chitosan with polyethylene in solution form have been obtained using ATR method by utilizing SPR phenomenon on the interface between silver and chitosan-PEG interface. The resonance angle shifted to higher value to the right since the refractive index value of chitosan-PEG caused the intersection between dispersion relation curves of SPW and photon wave shifted to higher value. It means that there was a evanescent field enhancement from silver thin film. From the fitting result, the refractive index of chitosan-PEG composite solution was $n = 1.32$, which can potentially be developed as an active sensing layer for developing SPR-based sensor as a heavy metal ions detection. Therefore, further investigation regarding the ability of the composite in detecting heavy metal ions need to be conducted.

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