Optimization of Ceric Ammonium Nitrate and Ferrous Ammonium Sulfate in the Synthesis of Chitosan-Graft-Maleic Anhydride

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Abstract. Amongst various methods for chitosan modification, grafting process is one of the promising techniques to alter chitosan surface properties. Maleic anhydride (MA) was grafted onto chitosan in the presence of an initiator to produce chitosan-graft-maleic anhydride (CTS-graft-MA). In this study, we compared and optimized two types of initiators: Ceric Ammonium Nitrate (CAN) and Ferrous Ammonium Sulfate (FAS) with various ratios in the synthesis of chitosan-graft-maleic anhydride. Chitosan was dissolved in dilute acetic acid solution. Subsequently, the initiator was added into solution to initiate the reaction and maleic anhydride was added immediately afterward. The reaction was carried out for 45 minutes at 70 °C with 430 rpm of agitation. The results of Fourier Transformed Infrared (FTIR) spectroscopy showed an appearance of a new peak at 1705.07 cm⁻¹ which belongs to C=O bands for both initiators. To find out the optimum results from CAN and FAS, the back-titration method was performed. The optimum ratio for CAN is 2.51% with the acidic content 5.4421 mmol/gr, while FAS is 0.268% with the acidic content 4.4673 mmol/gr. In conclusion, CAN is more effective than FAS to initiate the grafting process on CTS-graft-MA.

1. Introduction
Chitosan is the most abundant natural polysaccharide after cellulose in terms of utilization and distribution [1]. Chitosan can be produced by deacetylation of chitin. It has various characteristics such as biocompatible, biodegradable, non-toxic degradable product, non-immunogenic, and non-carcinogenic [2]. Because of these characteristics, chitosan has been widely utilized in food, biomedical, water treatment, functional membrane, and flocculation process [3],[4]. Utilization of chitosan, however, is not easy since it cannot dissolve in water but is able to dissolve in diluted acid. There are several acids that usually used to dissolve chitosan such as acetic acid, formic acid, lactic acid, and propionic acid. However, in terms of formation of flexible and transparent film, only acetic acid and formic acid are favourable [5]. Therefore, to help modify the properties of chitosan, physical and chemical treatment can be applied. One of the most promising methods is by grafting process.

Chitosan can be grafted using several chemicals, which depends on the final expected properties. Maleic anhydride (MA) is widely used to be grafted into chitosan. Chitosan-graft-maleic anhydride (CTS-graft-MA) can be applied in several applications such as pervaporation [6], heavy metal adsorption [7], and biomaterials [8]. In pervaporation, CTS-graft-MA significantly increases the selectivity of water-ethanol pervaporation than unmodified chitosan. CTS-graft-MA can also be
utilized to adsorb copper (II) and lead (II) in wastewater treatment. The hydrophilicity of CTS-graft-MA due to the introduction of an additional carboxyl group into the chitosan backbone is also favorable in biomaterial application.

To produce CTS-graft-MA in a more efficient way, the use of initiator is needed. The reaction between the initiator and chitosan will produce free radicals, which makes the amine group of chitosan is more reactive to react with MA. Grafting is started by producing one or more free radicals in the chitosan chain and allows these radicals to react with polymerizable monomers [9]. Recently, a number of initiators have been developed for grafting such as Ferrous Ammonium Sulfate (FAS) [10], Ceric Ammonium Nitrate (CAN) [8], and Ammonium Persulfate (APS) [11].

Amino groups of chitosan can be covalently grafted with MA using CAN as an initiator. There are 3 steps in grafting process using CAN as an initiator: (1) the solvation of water into chitosan, (2) the formation of the complex between solvated chitosan and CAN, lastly (3) grafting initiation by radicals from the complex [12]. As an initiator, FAS can prevent homopolymerization for the preparation of chitosan-graft [10]. In particular, the use of FAS as a reducing agent has shown to be a convenient method of controlling the extent of grafting [13].

In this research, we compared CAN and FAS as the initiator for the grafting process of chitosan and maleic anhydride. In order to optimize the condition, the acidic content from several ratios of CAN and FAS was observed.

2. Materials and Methods

2.1. Materials

Chitosan low molecular weight (DD ≥ 75%; MW = 50,000-190,000 Da) was purchased from Sigma Aldrich, USA. Maleic Anhydride (MA) was purchased from Nacalai Tesque Inc, Japan and used without purification. Acetic acid (CH₃COOH), ferrous ammonium sulfate (FAS), and ceric ammonium nitrate (CAN) were purchased from Merck, Germany.

2.2. Film preparation

The method used in this research was similar to other studies with a slight modification [7]. About 0.6 grams of chitosan were dissolved in 30 mL acetic acid solution (1% v/v) followed by stirring with a magnetic stirrer at 70 °C to obtain a homogeneous solution. After that, the initiator (CAN or FAS) was added into the solution to initiate the reaction. The variations of CAN in this study were 0%; 0.83%; 1.67%; 2.51%; and 3.33% (% w/w), while for FAS 0%; 0.089%; 0.178%; 0.268%; and 0.357% (% w/w), with all ratio to chitosan weight. Immediately after, 0.3 grams of MA were added to the solution and the reaction was carried out for 45 minutes at 70 °C and 430 rpm. The obtained homogeneous solution then casted on a petri dish and dried overnight in an oven at 50 °C. In order to remove the excess of maleic anhydride, the dried film was washed by acetone (25% v/v).

2.3. Fourier Transform Infrared (FTIR) Spectroscopy

The functional groups of samples were measured by FTIR spectroscopy. The FTIR study was performed using SHIMADZU IR Prestige-21 in the range of 400 – 4000 cm⁻¹. All the samples were scanned with a resolution of 4 cm⁻¹ and 10 number of scans.

2.4. Acidic Content Measurement

In order to measure the amount of carboxyl group in CTS-graft-MA film, the back-titration method was performed [14]. The content of carboxyl groups (mmol/g) was determined by titration of 0.01 g sample dissolved in 10 mL NaOH solution (0.01 M) with HCl solution (0.005 M). The acidic content (AC) was calculated by equation (1) [15]:

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AC = \frac{C_{NaOH} \times V_{NaOH} - C_{HCl} \times V_{HCl}}{m_{sample}}
\]
3. Result and discussion

3.1. FTIR Spectroscopy

FTIR spectroscopic measurements were carried out to confirm the formation of grafting, based on changes in the chemical structure of chitosan. Figure 1 shows the FTIR spectra for (a) chitosan, (b) CTS-graft-MA using CAN initiator, and (c) CTS-graft-MA using FAS initiator. The chitosan FTIR spectrum (a) shows that peaks at 1643.4 cm\(^{-1}\) and 1558.48 cm\(^{-1}\) belong to amide I and amide II functional groups, while peak around 1373.32 cm\(^{-1}\) belong to C-N bond. This result is similar to other studies [10]. The results from figure 1(b) and (c) show the appearance of a new peak at 1705.07 cm\(^{-1}\) which belongs to C = O bands from the carboxyl group grafted on the chitosan backbone. The presence of the C = O band in each sample is confirmed that this method is successful in producing chitosan-graft-maleic anhydride [7]. The interaction of chitosan, initiator and maleic anhydride is illustrated in figure 2. Chitosan was oxidized by Ce(IV) to form a radical on its amine and hydroxyl group. Radical chitosan then reacted with maleic anhydride and produced chitosan-graft-maleic.

![Figure 1. FTIR Spectrum for pure CTS (a), CTS-g-MA using CAN (b), CTS-g-MA using FAS (c).](image)

![Figure 2. Schema of Interaction between Chitosan, Initiator, and Maleic Anhydride [7].](image)
3.2. Acidic Content Measurement
To find out the optimum results from CAN and FAS initiator, the back-titration method was performed. Grafting was started by the formation of free radicals in the chitosan chain. These free radical electrons allow initiation of copolymerization of chitosan with MA through ring-opening mechanism. The total acidic content of each sample is determined by back-titration using Equation (1). Different values of acidic content (AC) occur because of the variations in the initiator ratio. The acidic content result of CAN is shown in Figure 3(a). Higher ratio of CAN leads to an increase of the AC in the membrane due to the new carboxylic groups on the chitosan backbone. However, there is a ratio of CAN which gives the optimum value of AC. The optimum value of AC obtained when the CAN ratio is 2.51%. This result is similar to other studies that used eugenol to modify chitosan in the form of hydrogels [9]. The graft yield increase along with the ratio of CAN and decreased after reaching the optimum value. The use of CAN initiator ratio greater than 3.33% leads to damaged film. AC results from FAS initiator have similar trend. However, the optimum AC value of CAN is higher than the AC value of FAS. Therefore it can be concluded that CAN is more effective than FAS to initiate the grafting process on CTS-graft-MA.

![Figure 3. Acidic Content of CTS-graft-MA using CAN (a) and FAS (b).](image)

4. Conclusions
The CTS-graft-MA using CAN and FAS as the initiator is successfully produced and had been confirmed using FTIR. The results show an appearance of the new peak that belongs to the carboxyl group of MA for both initiators. CAN is more effective than FAS with the optimum value of AC was obtained with CAN ratio 2.51%. The use of the CAN ratio greater than 3.33% leads to damaged film.

Acknowledgment
This research was supported by Ministry of Education and Culture of Indonesia through PDUPT scheme with contract number No. 2573/UN1.DITLIT/DIT-LIT/LT/2019.

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