

Study of Effect of Weight Ratio on Copolymerization of Chitosan and Acrylamide

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Abstract

In this research, chitosan copolymer synthesis with acrylamide has been carried out by varying weight of chitosan and acrylamide, namely 2:3, 3:2 and 1:1 using a microwave oven. The copolymers characterization was carried out using FTIR, XRD, SEM and TGA/DTA. The results of the synthesis of chitosan copolymer with acrylamide were obtained the largest percentage of grafting at a ratio of 2:3. From the results of FTIR analysis showed that the copolymer had been successfully synthesized. XRD analysis showed that the copolymers synthesized have amorphous properties compared to chitosan. The results of SEM analysis, the copolymers had a porous structure. Thermal analysis showed that the copolymers have better thermal stability than chitosan. The swelling ability of the CA23 copolymer was higher than that of the CA32 and CA11 copolymers. The chitosan-acrylamide copolymer which was synthesized in a ratio of 2:3 has better properties.

Keywords: Chitosan, copolymer, acrylamide, synthesis, grafting, copolymerization

Abstrak (Indonesian)

Pada penelitian ini telah dilakukan sintesis kopolimer kitosan dengan akrilamida dengan memvariasikan berat kitosan dan akrilamida yaitu 1:1, 2:3, dan 3:2 dengan menggunakan oven microwave. Kopolimer dikarakterisasi menggunakan FTIR, XRD, SEM dan TGA/DTA. Hasil kopolimerisasi kitosan dengan akrilamida diperoleh persentase grafting terbesar pada perbandingan 2:3. Dari hasil analisa FTIR menunjukkan bahwa kopolimer yang disintesis dengan perbandingan berat tersebut telah berhasil disintesis. Hasil analisis XRD menunjukkan kopolimer yang disintesis memiliki sifat amorf dibandingkan dengan kitosan. Dari analisis SEM terlihat kopolimer yang telah disintesis memiliki struktur berpori. Analisis termal menunjukkan bahwa kopolimer memiliki stabilitas termal yang lebih baik daripada kitosan. Kemampuan pengembangan kopolimer CA23 lebih tinggi dibandingkan kopolimer CA32 dan CA11. Kopolimer dengan perbandingan kitosan dan akrilamida 2:3 memiliki sifat yang lebih baik.

Kata Kunci: Kitosan, kopolimer, akrilamida, grafting, kopolimerisasi

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INTRODUCTION

Nowadays the use of chitin and chitosan has grown widely. In the industrial sector, chitosan plays a role, among others, as a polyelectrolyte coagulant for processing liquid waste, binder and absorber of metal ions, paper minerals, cosmetic industry, agriculture and food, cement industry, pharmaceutical industry and absorption of dye.

Chitosan is a polysaccharide polymer that is naturally non-porous so its use is restricted [1]. Besides, chitosan is insoluble in organic solvents but soluble in acidic solutions pH (≤ 6.5) [2]. Chitosan has hydroxyl and amino groups so that it is possible to be

modified to improve solubility, water absorption, adsorption ability and resistance to thermal [3]. Several chemical modifications of chitosan include impregnation, crosslinking method, copolymerization and formation of composite [4]. The cross-linking agent can stabilize chitosan in acidic solutions and can improve its mechanical properties. The crosslinking will increase the adsorption capacity and resistance to extreme media conditions. However, the crosslinking method has the disadvantage that the adsorption capacity will decrease slightly as a result of several functional groups (amino and hydroxyl) bound by the cross linker so that they cannot interact with pollutants.

Another method is the grafting method. By doing grafting, it can add functional groups to the chitosan so that it will increase the number of places for adsorption so that it can increase the adsorption capacity [5].

Several researchers have reported an increase in adsorption ability after grafting due to the inclusion of new functional groups into chitosan. The graft copolymerization of chitosan with aspartic acid has included to an increase in the adsorption properties for Nd(III) [6]. Meanwhile, the chitosan-acrylamide copolymer has also been synthesized by previous researchers using the $\text{NH}_4\text{S}_2\text{O}_3$ initiator [7, 8].

In this research, a polymerization reaction has been done, namely grafting between chitosan and acrylamide. Copolymer synthesis is influenced by the concentration of the initiator, the number of monomers, temperature and reaction time. In this study, copolymer synthesis was carried out by varying the weight of chitosan and acrylamide, namely 2:3, 3:2 and 1:1. By varying the weight of chitosan with acrylamide, it will be possible to know the optimum conditions for the weight ratio of chitosan and acrylamide which can produce a large adsorption ability by looking at the largest swelling ability. In addition, it will be known in what ratio produces a large percentage of grafting.

The copolymerization of chitosan with acrylamide in microwave with mass variations of chitosan and acrylamide i.e. 2:3, 3:2 and 1:1 has not been reported. The best copolymer results can later be used in dealing with water pollution problems such as contamination of heavy metals, dyes, sulphate pollution and so on. Besides, it can also be applied in reducing the BOD and COD values from wastewater. In addition, chitosan has been widely studied as a bio adsorbent to overcome dye waste [8]. However, this study only focuses on copolymer synthesis and its characterization.

MATERIALS AND METHODS

Materials

The sample of chitosan with value of de-acetylation degree is 87.5% from the local product (Indonesia), acrylamide for synthesis from Merck (Germany), ammonium persulfate from AR (China), glacial acetic acid was obtained from Merck (Germany), technical methanol from the local product (Indonesia) and distilled water. These chemicals were used without purification.

Methods

Synthesis of copolymers

Some chitosan is dissolved in 2% acetic acid solution and put in a container made of Teflon. Then added acrylamide. The variations of chitosan and

acrylamide were carried out, namely 2:3, 3:2; 1:1. The total sample weight in each comparison is the same, namely 2.5 g. Then, the initiator is added to the sample and stirred until it is completely mixed. Then put the Teflon container into a microwave oven with 70% power. The reaction was stopped after the gel was formed. After the reaction was complete, the reaction mixture is poured into excess methanol while stirring until a precipitate is formed.

Precipitated copolymers were washed three times with acetone to remove the formed homopolymers. Finally, the copolymers were dried at 40°C to constant weight. The copolymers formed were analyzed using FTIR, XRD, SEM and TGA/DTA. The grafting percentage (%G) of the copolymers was calculated according to the following equation: [10].

$$\% G = \frac{\text{grafted polymer}}{\text{weight of substrate}} \times 100 \quad (1)$$

Characterizations

FTIR characterization was carried out on copolymers with various weight ratios, namely 2:3, 3:2 and 1:1 using SHIMADZU-8400 model. X-ray diffraction (XRD) analysis was carried out on copolymers at various weight ratio of chitosan and acrylamide using an XRD device using $\text{Cu K}\alpha$ monochromatic radiation. From the XRD analysis, a diffractogram will be obtained. XRD analysis was performed using the Rigaku MiniFlex600. SEM analysis was done on copolymers of CA23, CA32 and CA11 using SEM ZEISS EVO MA 10.

Thermal Gravimetric Analysis (TGA)/Differential Thermal Analysis (DTA) analysis were carried out on chitosan and copolymers CA23, CA32 and CA11 using Hitachi/TGA/DTA 7300. The analysis was carried out using nitrogen gas at temperature of 30°C-600°C. The heating rate was 10/min.

Swelling Tests

A total of 0.1 grams of copolymer was dispersed into 100 ml of distilled water and left for 1 hour at room temperature. Then the unabsorbed water is filtered and left until no water drops fall. Then weighed to a constant weight. Percent swelling is calculated using the following equation: [16]

$$\text{Swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

where W_s is samples that have experienced swelling, W_d is dried copolymer.

RESULTS AND DISCUSSION

Synthesis of copolymers

In this research, chitosan copolymer synthesis with acrylamide was carried out with the weight variation of chitosan and acrylamide was 2:3; 3:2 and 1:1. In each of these weight ratios, the total sample weight is the same. Copolymers with a ratio of chitosan to acrylamide 2:3 are given the symbol CA23, 3:2 is given the symbol CA32 and 1:1 with the symbol CA11. Copolymers were synthesized using a domestic microwave at 70% power. The chitosan copolymer with acrylamide was obtained by grafting copolymerization reaction using ammonium persulfate initiator. In a previous study, the synthesis of acrylamide copolymer with chitosan with the ratio of chitosan to acrylamide was 1:4 and also used ammonium persulfate as the initiator but with variations in microwave power [11]. The copolymerization process carried out for all treatments showed that the formation of the copolymer was indicated by the formation of a gel. The resulting gel is yellow, which is the same as the previous study [11].

The time required for each copolymer in the weight variation of chitosan and acrylamide was not so different. In the CA23 copolymer, the time needed to form the copolymer was about 9 min. For copolymers with a variation of weight of chitosan and acrylamide 3:2 (CA32) and 1:1 (CA11), the time required to form the copolymers were about 10 minutes. The percentage of grafting obtained can be seen in Table 1.

Table 1. The effect of ratio of the weight of chitosan with acrylamide on percentage of grafting.

Sample	G (%)
CA23	85.49
CA32	70.64
CA11	73.45

Table 1 shows that the highest percentage of grafting was obtained at a weight ratio of 2:3. Whereas at a ratio of 3:2 the percentage of grafting was lower, this was due to the increasing number of chitosan in the mixture, it would impede the interaction between chitosan and acrylamide. With more polymer (chitosan) it can inhibit the graft copolymerization reaction between chitosan and acrylamide due to steric hindrance and limit the movement of molecules due to high viscosity [17].

Characterization of copolymers

FTIR Analysis

FTIR analysis was carried out to determine the functional groups present in the CA23, CA32 and CA11 copolymers. FTIR spectra for copolymers CA23, CA32 dan CA11 can be seen in Figure 1.

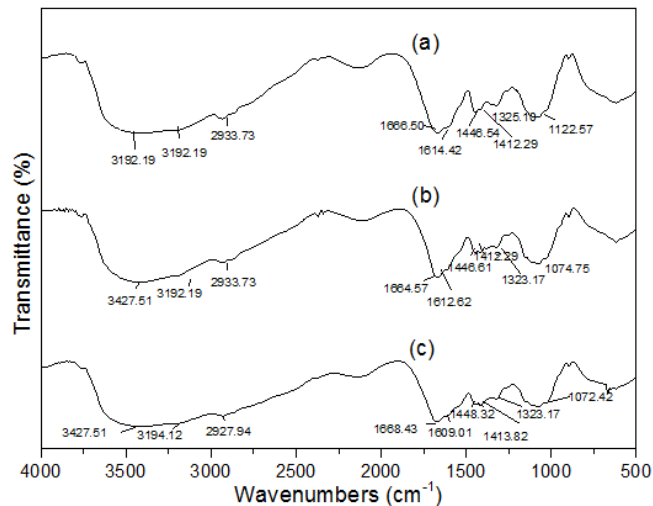


Figure 1. Spectra FTIR of (a) CA23 (b) CA32, (c) CA11.

From Figure 1, it can be seen that there is a similarity in the FTIR spectrum from previous studies, namely using a ratio of chitosan to acrylamide, which is 1:4 [11]. Figures 1 (a), 1 (b), and 1 (c) and represent the FTIR spectrum of chitosan acrylamide copolymer with a ratio of 2:3; 3:2 and 1:1. From the spectrum, it can be seen that the wave number indicating the presence of a C=C double bond does not appear. This indicates that a copolymerization reaction has occurred. Another thing that indicates that copolymerization has occurred is the appearance of C-N absorption at wave number 1412.29 cm^{-1} on copolymers CA23, 1412.29 cm^{-1} on copolymers CA32 and 1413.82 cm^{-1} on copolymers CA11. The absorption peak appeared with a small intensity due to the overlap between the C-N stretching vibrations of acrylamide and chitosan in the copolymer. The C-N uptake peak of chitosan and acrylamide copolymers that has been reported by previous researchers appears at the wave number 1411.69 cm^{-1} [12]. From Figure 1 it can be concluded that chitosan and acrylamide with various mass ratios of 2:3, 3:2 and 1:1 have been successfully copolymerized by microwave heating at 70% power.

XRD Analysis

XRD analysis was performed for chitosan, CA23, CA32 and CA11 copolymers. XRD analysis results can be seen in Figure 2.

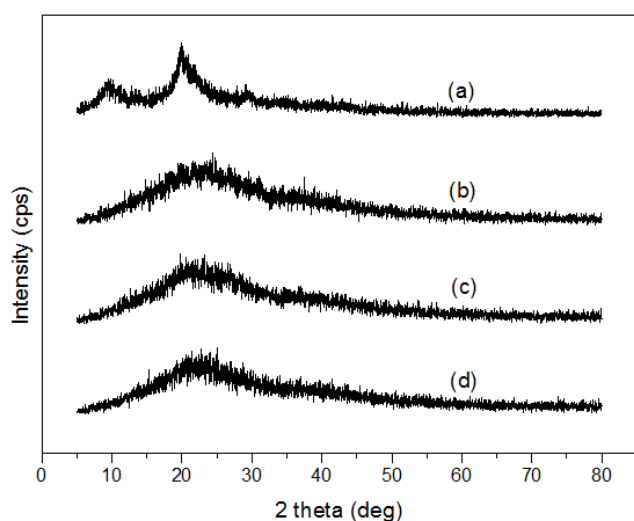


Figure 2. X-ray diffraction of (a) chitosan (b) CA23 (c) CA32 (d) CA11.

Figure 2 (a) is a XRD of chitosan. The chitosan XRD shows three peaks, namely at an angle of $2\theta = 9.53^\circ$, angle $2\theta = 19.62^\circ$ and $2\theta = 29.29^\circ$. Previous researchers found two chitosan peaks at an angle of 2θ , namely at 11.5° and 20° . These peaks indicate that chitosan is crystalline. The crystalline peak in chitosan is caused by the intermolecular and intramolecular forces between hydroxyl and amino acids in chitosan. The structural order in the chitosan molecule makes it crystalline [13].

In Figures 2 (b), (c), and (d) it can be seen, the diffractogram show a wide peak at an angle of 2θ and a decrease in intensity. The peak at an angle of $2\theta = 9.58^\circ$ did not appear on the copolymer of acrylamide and chitosan. Figure 4 (b) is a CA32 diffractogram showing a wide peak at $2\theta = 22.90^\circ$. Meanwhile, the CA23 and CA11 diffractograms showed 2θ peaks at 23.36° and 22.80° , respectively. From the diffractogram of chitosan and acrylamide copolymers in all weight ratios, it showed that the chitosan and acrylamide copolymers showed amorphous properties. The intensity decreases with increasing chitosan content in the copolymer, this is due to the reduced occurrence of intramolecular and intermolecular bonds between hydroxyl and amino acids in chitosan caused by grafting between chitosan and acrylamide.

SEM Analysis

SEM analysis was carried out on samples of CA11, CA23 and CA32. Figure 3 is the result of SEM analysis of the CA23, CA32 and CA11 copolymers. From Figure 3 shows that the morphology of CA23, CA32 and CA11 copolymers have porous structure. This is consistent with studies that have reported that

copolymer of chitosan with acrylamide copolymer showed the porous structure [14].

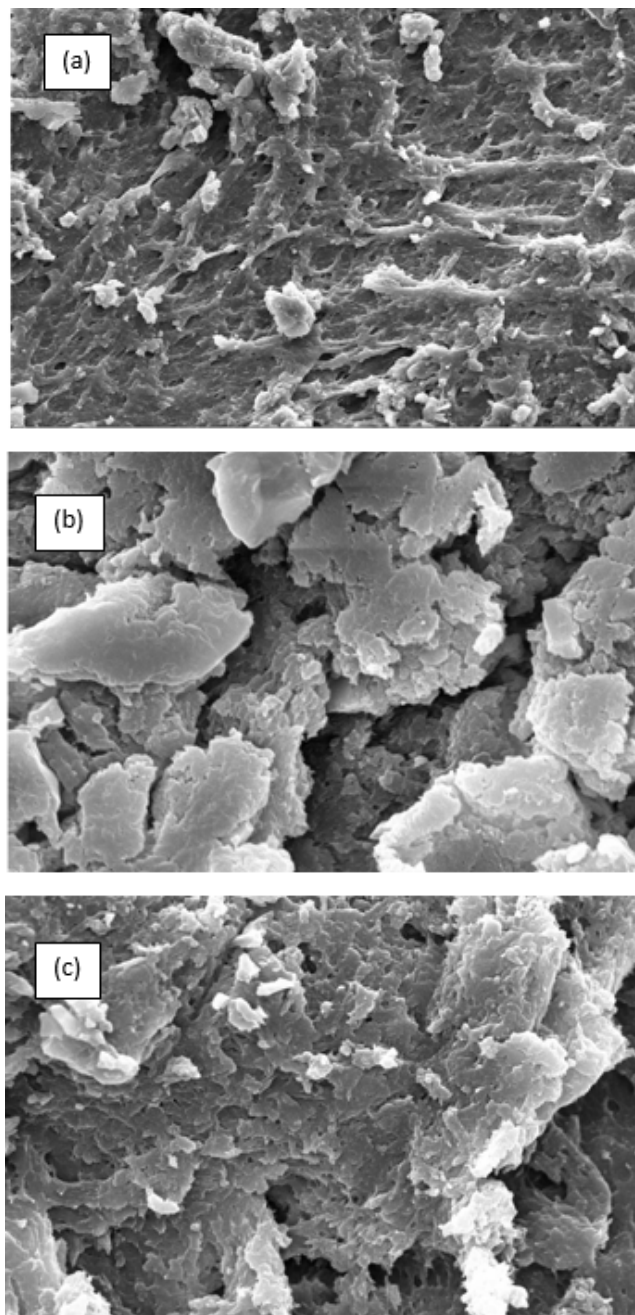


Figure 3. SEM analysis (a) CA23 (b) CA32 (c) CA11 (10.000x)

The CA23 copolymer has a more porous structure than the CA11 and CA32 copolymers. This is because the CA23 copolymer occurs more copolymerization reactions between chitosan and acrylamide which is also evidenced by the percentage of grafting obtained. While the CA11 copolymer appears to have more pores than the CA32 copolymer. This is because the chitosan content in CA32 which is more than acrylamide causes the copolymerization reaction to be blocked. SEM

analysis of chitosan and acrylamide has been reported in previous studies, where the SEM analysis results of chitosan before copolymerization with acrylamide did not show any pores [11]. Copolymers with a more porous structure will have a better adsorption capacity when used as an adsorbent.

TGA-DTA Analysis

TGA-DTA analysis was carried out on chitosan and copolymers of CA23, CA32 and CA11. TGA-DTA analysis to see the thermal properties of the copolymers that have been synthesized. The results of the TGA-DTA analysis were shown in Figure 4.

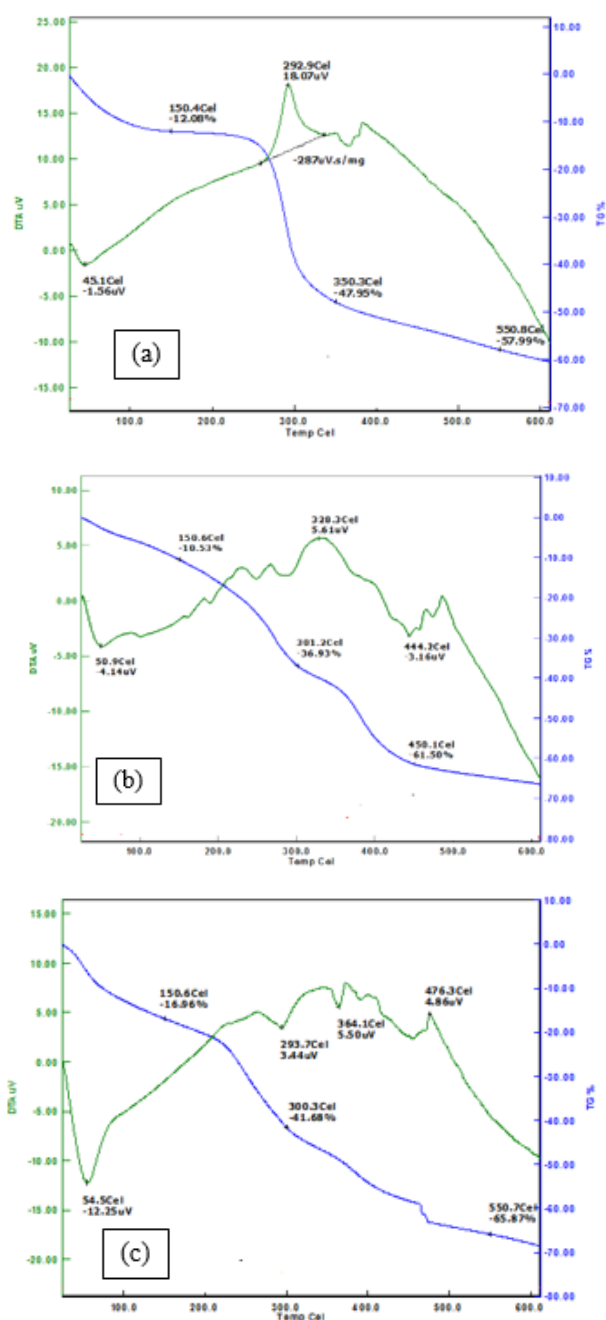


Figure 4. TGA/DTA curve of (a) chitosan (b) CA23 (c) CA32 (d) CA11

Figure 4 show that TGA chitosan is different from copolymers. TGA copolymers have two degradation stages whereas chitosan has one degradation stage. This shows that the copolymers have better thermal stability than chitosan. The chitosan undergoes weight loss due to evaporation from water up to 150° C and the next step is weight loss due to degradation of the glycoside bonds from chitosan [15], starting from 150 - 350° C. While the CA23 copolymer have a weight loss of 36.93% at a temperature of 301.2°C, CA32 at a temperature of 300.3° C with a weight loss of 41.68% and CA11 at a temperature of 300.9°C with a weight loss of 38.86%. The TGA results indicate that the copolymer CA23 is more stable than CA11 and CA32. This is supported by DTA data where the melting temperatures of CA23, CA32 and CA11 are 444.2; 364 and 392°C, respectively. The CA23 copolymer has a higher melting point.

Swelling Test

The swelling test or water absorption aims to see the swelling ability of the synthesized copolymers. In this study, the swelling test was carried out within 1 hour. In the swelling process, solvent molecules in this case water will be adsorbed on the surface of the copolymer molecules. The results of the swelling test can be seen in Table 2. From the table, it can be seen that the swelling ability of CA23 copolymer is higher than CA32 and CA11. This is due to the occurrence of electrostatic repulsion between the amine groups of chitosan and acrylamide in the copolymer chain [18]. The high swelling ability of CA23 indicates that the copolymer has a greater ability to absorb water. With the increasing percentage of grafting of the copolymer, it can be seen that the swelling ability is also getting bigger. Besides that, the CA23 copolymer has a more

amorphous structure so it is easier to absorb water. The SEM results also showed that the CA23 copolymer was more porous than the CA11 and CA32 copolymers.

Table 2. Results of swelling test

Sample	% Swelling
CA23	859
CA32	529
CA11	734

CONCLUSION

Synthesis of chitosan-acrylamide copolymer with the ratio of weight variation between chitosan with acrylamide, namely 2:3; 3:2 and 1:1 using microwave oven at 70% power, have been successfully synthesized based on analysis based on FTIR and XRD analysis. The highest percentage of grafting was obtained at a ratio of 2:3, namely the CA23. The resulting copolymer has a porous structure and is amorphous. CA23 copolymer has better thermal stability and has more pores than CA11 and CA32. This shows that CA23 has good thermal stability and better swelling capability between CA32 and CA11.

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