IOP Conf. Series: Materials Science and Engineering **188** (2017) 012051 doi:10.1088/1757-899X/188/1/012051

The copolimeryzation synthesis and swelling capacity of cellulose-poly superabsorbent (acrylic acid-co-acrylamide) based on rice straw

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Abstract. A superabsorbent has been synthesized by copolymerization of rice straw cellulose as the back bone with the composition of 0.724 mol/L acrylamide and 1.429 mol/L acrylic acid as the monomers, 2.32 mmol/L N, N'-methylene-bis-acrylamide as the crosslinker, and 7.94 mmol/L potassium persulfate as the initiator. The rendement of cellulose obtained from rice straw isolation is 33.55% with the size of 34.06 nm nanocrystalline cellulose, obtained from XRD diffraction pattern. The copolymerization results in the spectrum characterization of Cellulose-Poly superabsorbent (AA-co-AM) with FTIR shows OH stretching vibration, NH and C=O stretching of monomer acrylic acid and acrylamide at wave number about 3343 cm^{-1} and 1600 cm^{-1}. The surface morphology analyzed with SEM shows the superabsorbent has rough surface morphology compared to acrylic acid-acrylamide copolymer. The results of grafting efficiency increases with the increasing amount of the reacted monomer. The characterization of result shows that the grafting process of acrylic acid-acrylamide on cellulose has been formed. The swelling capacity of superabsorbent in water is 691.18 g/g, and 765.58 g/g in urea. This result is quite satisfactory and can be applied for slow release superabsorbent.

1. Introduction

In recent years, research has been done to study the superabsorbent and its application in agricultural. Usually, the synthesis of superabsorbent is based on acrylic acid and acrylamide monomer. However the materials are expensive and can be hazardous to the environment [1]. Therefore, superabsorbent polymers which have biodegradable properties started to be developed. The synthesis of superabsorbent from waste wheat straw has been done, using acrylic acid and acrylamide as monomer, dimethyl-diallyl-ammonium chloride as initiator, and N, N'-metilenbisakrilamida (MBA) as crosslinking agent [1]. Utilization of mulberry twig waste as materials for the superabsorbent has been studied [2]. Ma *et al.* [3] has successfully synthesized the superabsorbent with the addition of inorganic materials. The addition of inorganic substances will create a higher thermal stability superabsorbent. Cellulose polymer is one of the most abundant, renewable, and biodegradable materials among the natural polymers. Cellulose can be converted into nanocellulose. Compared to other ordinary cellulose, nanocellulose has a smaller diameter which makes it has many unique properties, such as high mechanical strength and large surface area [4]. The cellulose can be isolated from rice straw, which contains 43-49% cellulose, 25-28% hemicellulose, lignin 15.8%, 12.5% silica, resin, gum, protein, and mineral compounds [5]. In this research, the cellulose is isolated from rice straw, and will be used to synthesize the superabsorbent.

2. Material and methods

2.1. Materials
Rice straw was obtained from Bukittinggi, Indonesia. Acrylic acid and acrylamide (Nippon Shokubai) were used as monomers. Toluene (Merck Co) and ethanol (Merck Co) were used to extract the cellulose from rice straw. Hydrogen peroxide (Merck Co) and potassium hydroxide (Merck Co) were used as the impurity removal from rice straw cellulose. Potassium persulfate (Merck Co) was used as initiator, and N,N′-methylenebisacrylamide (Sigma) as crosslinker.

2.2. Isolation of cellulose and synthesis of superabsorbent
The isolation of rice straw cellulose was performed according to the reported method by Fan *et al*. [6, 7]. The rice straw was washed with warm water at temperature 40°C to remove impurities and solutes then dried at 60°C. The dried and cleaned rice straw was then grinded into powder. 10 grams of the powder was extracted with a mixture of toluene: ethanol at a ratio of 2 : 1 for 72 hours with maceration method while stirring with a stirrer to eliminate the extracted substances, wax, pigment, and oil. Then the straw powder was filtered and dried at 50°C for 24 hours. Removing the hemicellulose and lignin was done by adding 350 mL KOH and H_2O_2, and then stirred at room temperature. The precipitate was washed to neutral pH and then dried in an oven at 50°C until completely dry and the weight constant was obtained. The dissolution process of rice straw cellulose and synthesis of superabsorbent was performed as reported by Cay *et al.* [8] and Helmiyati *et al.* [9].

3. Results and discussion

3.1. Isolation of cellulose from rice straw
The average of cellulose rendements can be seen in table 1. From table 1, it can be seen the rendement of cellulose obtained after isolation is 33.55%. The rendement of cellulose obtained in this work is smaller compared to Fan et al with the rendement of 58.0% [6], and Jiang *et al*. [10] with the rendement of 35.06%. This difference was caused by rice straw source.

3.2. Diffraction pattern of rice straw cellulose by XRD
The diffraction patterns of rice straw cellulose is shown in figure 1. In figure 1 it can be seen the peaks of the cellulose are obtained at about 22.4° with a sharp peak. The peak at 22.4° called intensity of crystalline, and the peak at 18.25° called intensity of amorphous. The crystallinity degree of cellulose is 72.753%, means cellulose is semi crystalline and the calculation by Scherrer's law obtained the size of crystal cellulose of 34.06 nm which indicated the nanocrystal size.

3.3. FTIR spectra of superabsorbent
Figure 2 shows the FTIR spectra of rice husks, acrylate acid-acrylamide copolymer (AA-AM copolymer) and Cellulose-Poly (AA-co-AM). Figure 2c shows the infrared absorptions of Cellulose-Poly superabsorbent (AA-co-AM). The main absorption band shows stretching vibration of OH and NH from monomer at 3343 cm^{-1}, while at 1600 cm-^{1} indicates the C=O stretching vibration of the carbonyl

Table 1. Rendement of cellulose

Weigth of rice straw (g)	Weight of rendement (g)	Rendement of cellulose (%)
10.00	3.10	31.01
10.01	3.49	34.84
10.00	3.17	31.69
10.01	3.67	36.64
Average of cellulose rendement (%)		33.55

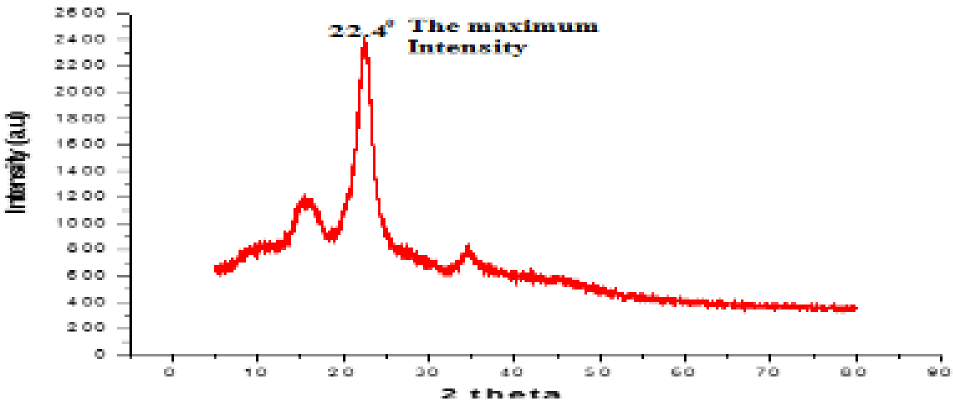

Figure 1. XRD diffraction pattern of rice straw cellulose

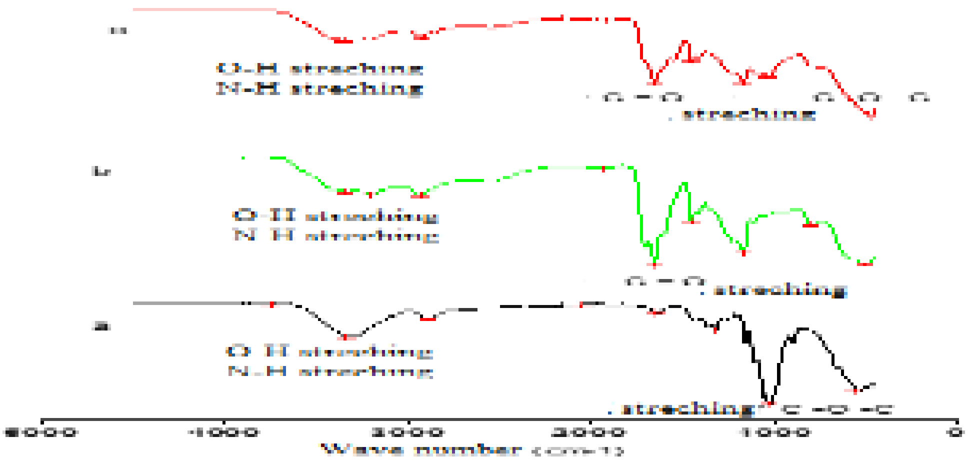

Figure 2. Spectra of FTIR (a) rice straw (b) copolymer AA-AM, and (c) cellulose-poly (AA-co-AM)

group of acrylic acid and acrylamide. Overall, it was found that the spectrum of the superabsorbent is a combination from spectrum straw cellulose (figure 2a) and copolymers (AA-AM) (figure 2b). It indicates that theacrylic acid and acrylamide has been successfully grafted on the cellulose.

3.4. Surface morphology of superabsorbent

Figure 3a shows the surface morphology of Cellulose-Poly superabsorbent copolymerization (AA co AA) in porous form, more uniform and rough compared to figure 3b. This is due to grafting process of acrylic acid and acrylamide monomer to cellulose, so the superabsorbent network was formed more tightly and the pores can be utilized to absorb water and fertilizer when carried out the swelling process. Figure 3b shows a more smooth surface morphology of acrylic acid-acrylamide copolymer without cellulose. This is similar to the results conducted previously [10].

3.5. Swelling capacity

The swelling characteristics of the superabsorbent were measured by gravimetric analysis [11]. Superabsorbent was synthesized with different conditions to get different swelling capacity. The results of the analysis with orthogonal show the sequence of swelling influence factors in water and urea are MBA>AM>AA>KPS. MBA crosslinking agent is the most important factor, followed by the monomer AM, and AA, then the KPS initiator. Based on the experimental results, the optimum combination for the synthesis of Cellulose-Poly superabsorbent copolymerization (AA co AA) are [AA] with the

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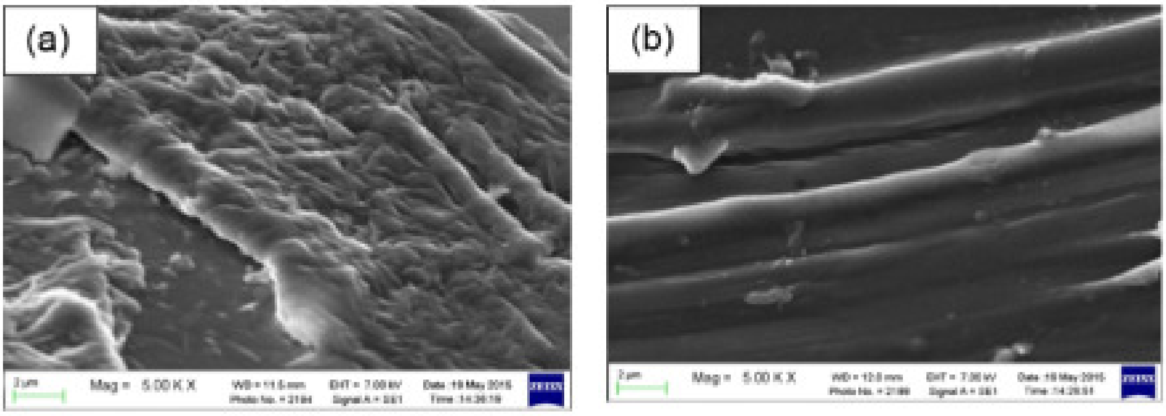

(a) (b)

Figure 3. SEM micrograph of (a) Cellulose-Poly Superabsorbent (AA-co-AM) and (b) Copolymer AA-AM

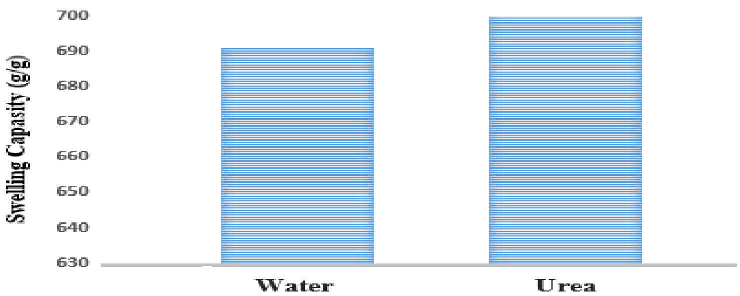

Figure 4. Swelling capacity cellulose poly (AA co AA) superabsorbent on the water and urea

concentration of 1.429 mol/L, followed by 0.724 mol/L [AM], 2.32 mmol/L [MBA], and 7.94 mmol/l [KPS]. The synthesized superabsorbent has swelling capacity in the water and urea of 691.18 g/g and 765.58 g / g, respectively, as can be seen in figure 4.

4. Conclusions

The cellulose has been isolated from rice straw and can be separated from the lignin and hemicellulose with the average rendement of 33.55%, and the size of cellulose crystal at 34.06 nm, which indicated nanocrystal size. Cellulose isolation was used as the backbone in the synthesis of superabsorbent. The result of grafting was characterized by FTIR and SEM. The optimum condition of the Cellulose-Poly superabsorbent synthesis (AA co AA) were 1.429 mol/L acrylic acid, 0.724 mol/L acrylamide, 2.32 mmol/L MBA crosslinking agent,and 7.94 mmol/L KPS initiator, with the capacity of swelling in water and ureawere 691.18 g/g and 765.58 g/g, respectively.

Acknowledgements

The authors would like to thank Universitas Indonesia for funding this research through PITTA Grant Universitas Indonesia with contract No: 2045/UN2.R12/HKP.05.05/2016.

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