Influence of monomer concentration on the morphology, contact angle, water uptake, and antibacterial activity of grafted cellulose obtained from peel durian

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Abstract. The objective of the current study is to evaluate and determine the effect of monomer concentration of 2-[acyloyloxyl] ethyltrimethylammonium chloride (CIAETA) on the grafting copolymerization of oxidized cellulose which isolated from peel durian. Four concentrations of CIAETA were used in this study, e.g., 40, 50, 60, and 70%. Several analyses were performed to determine the material characteristic, e.g., degree of grafting, Fourier Transform Infrared (FTIR) Spectroscopy, surface morphology, contact angle, degree of swelling, and antibacterial activity. The result showed, monomer concentration plays a significant role to the physical and surface morphology of DAC-CIAETA. The degree of grafting of CIAETA was found in the range of 15-31%, and at the concentration of 50% the grafted oxidized cellulose has 30.4% of degree of grafting. SEM images showed the pore volume has linear correlation to the monomer concentration, it increased the surface roughness. Also, the contact angle confirmed the hydrophilicity and degree of swelling of grafted oxidized cellulose was increased that linear to CIAETA concentration. DAC-g-CIAETA was found antibacterial active against Staphylococcus aureus, Staphylococcus epidermis, and Candida albicans than DAC.

Keywords: modifications, polymer, grafting, cellulose, morphology

INTRODUCTION

Grating polymerization between cellulose and monomer is one technique to modify natural properties of cellulose for the wide application. This technique had been utilized since 1960s for preparing modified cellulose’ surface[1], prepare new derivate of grafted cellulose [2], grafting cellulose and poly(vinyl alcohol), PVA [2][3], copolymerization between in the presence of Mn3+ as initiator [4][5]. Other modifications have also been done by researcher to develop new cellulosic materials.[6][7][8]

Technically, the grafting copolymerization is affected by several factor, e.g., reaction temperature, contact time, solvent, initiator, and monomer concentration.[9][3][10]. In the previous study, [11] we already done the grafting of quaternary ammonium salt, called as CIAETA or [2-(acyloxyloxy) ethyl] trimethylammonium chloride, on the surface of oxidized cellulose (DAC, dialdehyde cellulose) under a specific condition, e.g., 2-[acyloyloxyl] ethyltrimethylammonium chloride (CIAETA) 50%, temperature 80°C, contact time 180 min in the presence of potassium persulfate as initiator [11], which produced a material which has 30.4% of degree of grafting. Another study revealed, a material which has 61.3% of degree of grafting could be obtained by modifying cellulose using methyl acrylate monomer under this following condition: monomer concentration 0.68 mol/L, temperature 50°C, contact time 115 minute in the presence of initiator, potassium persulfate.

Those mentioned previous study [11] indicated that the reaction parameter have important role for obtaining an optimized reaction. Different reaction condition will produce a different result. Based on this literature review, the objective of this current study is to determine the effect of one parameter, in this case
monomer concentration of CIAETA, in the grafting copolymerization of oxidized durian peel cellulose. Several characterizations have been performed to evaluate the properties of the obtained material, e.g., degree of grafting, FTIR, surface morphology analysis, contact angle, degree of swelling, and antibacterial activity.

**METHODOLOGY**

**Material**

Durian peel acquired from the nearby market in Medan, Indonesia. Sodium metaperiodate and CIAETA were purchased from Sigma Aldrich and analytical grade. Acetone (90 wt.%), NaOCl (98 %), NaOH (98 %), HNO3 (98 wt.%), and Methanol (70 wt.%) were purchased from Merck Chemical and analytical grade. Strain of Candida albicans, Staphylococcus aureus, and Staphylococcus epidermidis, were obtained from Laboratory of Microbiology, Faculty of Medicine, Universitas Prima Indonesia. All chemicals were used without further purification.

**Methods**

**Grafting of CIAETA onto cellulose**

5 g of oxidized cellulose with sodium metaperiodate (NaIO4: cellulose by ratio 0.6) [11] was dispersed in distilled water for 4 h into three-neck round flask heated up to 50 °C after 30 min heating, potassium persulfate (5% of monomer weight) and 25 mL CIAETA with variant concentration 40, 50, 60, and 70% were added into the solution to initiate the reaction. Grafting reaction was carried out at 80 °C under nitrogen atmosphere for 3 h, then the dispersion was cooled and methanol/acetone mixed solution was added to separate the treated monomer and the grafted cellulose. The obtained of grafted cellulose fiber was dried in vacuum oven.

**Determination of grafting yield**

The grafted cellulose fiber was dried in vacuum oven at 60 °C until a constant weight was reached. The grafting yield (GY) was determined gravimetrically and calculated as follows according to previous report [10]:

\[ \text{GY} = \frac{W_2 - W_1}{W_1} \times 100\% \]  

Where \( W_1 \) is the weight of cellulose before and \( W_2 \) is the weight of cellulose after grafting.

**Experimental Analysis FTIR Analysis**

The spectra of the practical gathering of unblemished and united oxidized cellulose were used by an FTIR spectrophotometer utilizing Cary 630 FTIR Agilent. All acquired range was recorded in the accompanying condition: the goal of 4 cm\(^{-1}\) and wavenumber scope of 4000-650 cm\(^{-1}\) and checked multiple times.

**Surface morphological characterization**

The surface morphology characterization of cellulose and altered cellulose were resolved to utilize an examining electron magnifying lens (SEM) JEOL/EO JSM-6510 LA version 1.0.

**Contact angle analysis**

The wetting surface capability of the modified cellulose was determining by measuring the contact angle using sessile drop method using Ganiometer, CCD camera resolution 50 fps (1980 x 1080 pixel).

**Water Uptake Capability**

DAC-g-CIAETA were first gauged and \( m_0 \) absorbed refined water for various time points at 1, 2, 3, 4, 5, 6, and 7 h. After taking out the example pieces from the arrangement, the perfect tissue paper was utilized to eliminate unnecessary water on the outside of the test and the subsequent weight was recorded \( m_t \). The growing proportion of each example was determined by the Eq.(2).

\[ \text{Swelling ratio (\%)} = \frac{[m_t-m_0]}{m_0} \times 100\% \]  

**Antimicrobial activity**

Gram-positive bacterial, S. aureus and S. epidermidis, and C. albicans were utilized to decide the antimicrobial of united oxidized cellulose fiber disconnected from durian skin. The estimation was performed utilizing plate dispersion Kirby-Bauer (KB). The detach of microscopic organisms was refined on supplement agar (NA) medium, and parasites were refined on a potato dextrose agar (PDA) medium. Each segregate with a thickness of 108 was immunized into a physiological arrangement of NaCl 0.85%. The thickness of microbes and growths was resolved utilizing a standard arrangement of Mc. Farland. The grouping of adjusted cellulose was changed, for example 25, 50, 75, and 100%. Brooding was performed at 30 °C for 48 h [11].

**RESULTS AND DISCUSSION**

**Degree of grafting of DRC-g-CIAETA**

The grafting of CIAETA onto the oxidized cellulose surface was performed using free radical polymerization technique, as the initiator is sulfate radical obtaining from the thermal heterolysis of potassium persulfate. Mechanism of grafting of CIAETA onto Cellulose using KSP as the initiator in Figure 1.
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Formation of free radicals of Potassium Persulfate

\[ K_2S_2O_8 \rightarrow K^+ + S_2O_8^{2-} \]

\[ S_2O_8^{2-} \rightarrow 2SO_4^{2-} \]

Initiation

H- abstraction
DAC: Dialdehyde Cellulose

Propagation

Termination

Macro radical DAC - CIAETA

Figure 1. Mechanism of grafting of CIAETA onto Cellulose using KSP as the initiator
The effect of monomer concentration to the degree of grafting of the obtained material is shown in Table 1.

**Table 1. Degree of grafting of DAC-g-CIAETA**

| Cellulose | CIAETA | Temperature | Time (min) | Degree of grafting (%) |
|-----------|--------|-------------|------------|------------------------|
| 5         | 40     | 80          | 180        | 15.6                   |
| 5         | 50     | 80          | 180        | 30.4                   |
| 5         | 60     | 80          | 180        | 28.9                   |
| 5         | 70     | 80          | 180        | 26.3                   |

Those result confirmed that the concentration parameter affected the degree of grafting of DAC-g-CIAETA. The increase concentration of CIAETA from 40 to 50% significantly enhanced the degree of grafting of DAC-g-CIAETA. However, when the CIAETA concentration was in the range of 60-70%, the degree of grafting of DAC-g-CIAETA was decrease. This phenomenon can be caused by the polymerization technique that adopted in this study is classified as uncontrolled technique [15][16][17][10]. Another reason, when the CIAETA concentration was increase to 60-70%, the number of homopolymer that produced during the grafting reaction is also increase the competing reaction between the grafting and homopolymer formation is happen in the uncontrolled free radical polymerization. The homopolymer formed is separated by purification using acetone.

In the free radical copolymerization, monomer concentration is an important factor that influence the threshold value equivalent (TVE) of the optimum degree of grafting. Above TVE, the degree of grafting will decrease, and vice versa. The decrease of degree of grafting is caused by homopolymer formation and monomer decomposition as the thermal effect [18][19][20].

**FTIR**

The monomer concentration effect on the obtained product was also evaluated using FTIR, as in Fig. 2. The FT-IR spectrum shows that there is no significant change on the wavenumber shift and the band shape. The band was observed at 1729 cm\(^{-1}\) associated with the C=O ester group molecular structure [12]. Another characteristic of CIAETA modification at 1476 and 1217 cm\(^{-1}\) corresponds for the vibration of trimethyl group of quaternary ammonium salt [13] and C=C=N asymmetric [14]. These further confirmed that CIAETA molecules were chemically anchored onto oxidized DRC surface and may significantly enhance the density of positive surface charges (R-N(CH\(_3\))\(^{+}\)).

As in the previous study [11] those mentioned wavenumbers are new signal that only appeared after the grafting of CIAETA onto DAC. As the references, the FT-IR signal of neat DAC is found in the following wavenumber: 3332.2 cm\(^{-1}\) (ν\(_{\text{O-H, str}}\)), 2907.3 cm\(^{-1}\) (ν\(_{\text{C-H, str}}\)), 1640 cm\(^{-1}\) (ν\(_{\text{C=O, str}}\)), 1028.7 cm\(^{-1}\) (ν\(_{\text{C-O-C, str}}\)), 887.1 cm\(^{-1}\) (ν\(_{\text{C-C, str}}\)) [11].

**Figure 2. FT-IR spectrum of DAC-g-CIAETA that prepared at different concentration of CIAETA**

**Morphology analysis of DAC-g-CIAETA**

Figure 3 shows the micrograph image obtaining from SEM analysis before and after grafting process. A change on the topology surface of DAC was confirmed. The neat DAC has long band fiber with smooth surface. However, DAC-g-CIAETA has roughness surface than the previous one (750x magnification). The increase of CIAETA concentration significantly affected the morphology of material molecule.

**Contact angle analysis**

Table 2 shows the contact angle of DAC and DAC-g-CIAETA. The measurement was performed using sessile drop method, and the droplet contact angle was observed during this time: 0, 60, 120, and 180 s.

Table 2 confirms monomer concentration significantly affected the contact angle of modified material. The increase of CIAETA concentration affected on the decrease of contact angle. This result indicating the hydrophilicity of material is also increase. When the material has contact angle between 0 and 90\(^{\circ}\), the material can be said as hydrophilic material, above those value the material is hydrophobic [21][22][23]. The increase on hydrophilicity is caused by the...
distortion phenomenon as explained in the previous section. The presence of pore volume can facilitate the water molecule to diffusion into the fiber segments. The higher the pore volume, the lower contact angle that will be observed.

Table 2. Contact angle of DAC and DAC-g-CIAETA

| Sample          | Contact angle (°) |
|-----------------|-------------------|
| DAC             | 0° ± 0°           |
| DAC-g-CIAETA 40%| 94 ± 1°           |
| DAC-g-CIAETA 50%| 85 ± 3°           |
| DAC-g-CIAETA 60%| 75 ± 2°           |
| DAC-g-CIAETA 70%| 69 ± 2°           |

Antibacterial activity
Several concentrations of DAC-g-CIAETA were tested to determine its potential as an antibacterial agent against Staphylococcus aureus, Staphylococcus epidermis, and Candida albicans. As control, chloramphenicol was used to determine the capability of DAC-CIAETA.

Figure 3. SEM images of oxidized DAC before and after grafted with CIAETA

Figure 4. Degree of swelling of modified DAC in different concentration of CIAETA

The inhibition zone diameter that produced by DAC-g-CIAETA is shown in Table 3. The DAC-g-CIAETA which prepared with high CIAETA concentration shows the high antibacterial activity. As reported, CIAETA is a quaternary ammonium and classified as cationic surfactant which has antibacterial and antifungal activities. It able to interact through electrostatic interaction between cationic group from CIAETA and negative charge molecule which present in cell membranes.
This interaction then form a complex of surfactant-microbe, and able to disrupt the function of cell membranes and biological activities, indirect impact is it will lower the capability of microbe to perform self-multiplication [24][25].

CONCLUSION

Grafting copolymerization of oxidized cellulose in the presence of various concentration of CIAETA monomer shows it able to control the surface roughness, hydrophilicity, and biological activity of material. Degree of grafting is this study is in the range of 15-31%, with the highest percentage is found at the CIAETA concentration of 50%. The increase on CIAETA concentration the contact angle is found increase, as the impact its hydrophilicity of material also increases. The presence of CIAETA on the DAC surface improves the antibacterial activity of DAC.

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