Antimicrobial Properties of [2-(Acryloyloxy)Ethyl]-Trimethyl Ammonium Chloride and Maleic Anhydride Surface Grafted-Cotton Fibers

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Abstract: Antimicrobial compound of [2-(acryloyloxy)ethyl]-trimethyl ammonium chloride (AETAC) can be bound into polymer backbones to produce various antimicrobial polymeric materials. In this work, cotton cellulose (CCell) fibres was modified in a laboratory scale reflux-reactor for 2 hours in toluene (TL) as solvent with addition of maleic anhydride (MA). TL solution of antimicrobial compound of AETAC and ammoniumpersulphate ($(NH_4)_2S_2O_8$) as initiator was added dropwise and the reflux was further continued for 2 hours. The reaction mixture with optimum weight ratio (CCell/MA/AETAC: 100/20/20) was then cooled down, filtered and wash thoroughly using distilled water and dried in oven vacum to constant weight at 80°C. The AETAC/MA-modified Cellulose (AETAC/MA-g-CCell) was then characterised using infrared spectroscopy (FTIR) for chemical structure identification of the reaction products. Antimicrobial properties of the modified cellulose was tested using: *Aspergillus niger* and *Staphylococcus aureus*. Results of FTIR spectra of the AETAC/MA-g-CCell after exhaustive Soxhlet extraction in toluene still showed stable absorption peak of AETAC/MA carbonyl group (>C=O) at 1736 cm^{-1} and dissapearance of bond absorption peak of acryloyl group (>C=C<) at 1470 cm^{-1}. The AETAC/MA-modified cotton cellulose showed marginal antimicrobial activity against *Aspergillus niger*, however the modified cellulose showed excellent antimicrobial activity against *Staphylococcus aureus*.

1 INTRODUCTION

Cotton being globally distributed across Asia, North America and Western Africa. According to data from the International Cotton Advisory Committee in 2015 more than 80 countries around the world plant cotton, mostly in Asia and America. More than half of the clothes people wear are made of cotton fiber, because it is can used to make a soft-textile (Yanjun, 2019).

One of the problems in the use of natural fiber-based textile product such as cotton is the growth of insect and microorganism, such as bateria and fungi. Natural fiber such as cellulosic and protein-based ones are more danger because of the chemical bonds that may easily be broken down by microorganism. Cotton fabrics are suitable matrices for the growth of fungi, particularly Aspergillus niger. Some studies have been worked by gamma irradiation for inactivation of Aspergillus niger in aged cotton (Donna, 2019).

Cellulose has three ractive hydroxyl group per anhydroglucose repeating unit that form and inter- and intramoleculer hydrogen bonds. These bonds strongly influence chemical reactivity of cellulose (Wasilla, 2010). Modified cotton cellulose was studied widely as antimicrobial agent. The monomer (3-acrylamidopropyl) trimethylammonium chloride was used to treat a cotton fibers by grafting copolymerization. Antimicrobial properties was run by transferring oxidative chlorine to their cells and then further oxidizing the cellular systems and causing the expiration of cells (Ying, 2014).

Besides that compound, there was also [2(acryloyloxy)ethyl]-trimethyl ammonium chloride (AETAC) used as antimicrobial agent. In previous work, researcher studied chemical modification of

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wool fabrics in order to get antimicrobial textile. Anionic sulphonate groups were introduced onto a wool fibre surface by grafting with polystyrene sulphonate, which enabled binding of cationic quaternized chitosan by ionic bonding. A bioactive quaternary ammonium polymer, poly[2-acryloyloxy)ethyl]trimethylammonium chloride, was grafted onto chitosan to enhance chitosan's limited antimicrobial activity (Hasan, 2015).

In this work, we studied about modified cotton cellulose (CCell) fibres in a laboratory scale. AETAC/MA grafting onto cotton cellulose was run by ammonium Persulphate as initiator. It was characterized using infrared spectroscopy (FTIR) and scanning electron microscope (SEM) for chemical structure. Antimicrobial properties of modified cotton were investigated using Aspergillus niger and Staphylococcus aureus. The expected outcome of this work is obtaining new antimicrobial cotton cellulose.

2 MATERIALS AND METHODS

2.1 Materials

Cotton cellulose was obtained from fabric cotton. Toluene, maleic anhydride, ammonium persulphate ($(NH_4)_2S_2O_8$), aceton, PDA (Potatoes dextrose agar), NA (Nutrient agar), DMSO, Aspergillus niger and Staphylococcus aureus.

2.2 Methods

Cotton cellulose (10,0 g) was carried out in toluene solution and refluxed for two hours with addition of maleic anhydride (MA) at 60-70ºC. Thereafter, the solution was filtered, washed with acetone and dried to obtain modified cellulase. Toluene solution of antimicrobial compound of AETAC and ammonium persulphate ($(NH_4)_2S_2O_8$) as initiator was added dropwise and the reflux was further continued for 2 hours. The reaction mixture with optimum weight ratio (CCell/MA/AETAC: 100/20/20) was then cooled down, filtered and wash thoroughly using acetone and dried in oven vacuum to constant weight at 60ºC. The AETAC/MA-modified Cellulose (AETAC/MA-g-CCell) was then characterized using infrared spectroscopy (FTIR) and scanning electron microscope (SEM) for chemical structure identification of the reaction products.

2.3 Antimicrobial Activity

Antimicrobial activity of modified cotton cellulose was investigated against two differential microbe names Aspergillus niger and Staphylococcus aureus bacteria by agar disc diffusion method. In this method, the antibacterial activity of AETAC/MA-modified cotton cellulose against Aspergillus niger manifested using PDA (Potatoes Dextrose Agar) medium solid agar petri dish and against Staphylococcus aureus bacteria using NA (Nutrient Agar). The sample were sterilized by autoclaving at 115ºC for 30 minutes, thereafter, placing on Aspergillus niger and Staphylococcus aureus agar plates and incubating for 24 h at 37ºC. AETAC/MA-modified cotton cellulose sample were cut about 5 mm on each side. The inhibition zones were measured.

3 RESULTS AND DISCUSSION

3.1 Synthesis and Characterization of AETAC/MA-g-Ccell

The FTIR spectra were used to analyze the bonding between cellulose and AETAC/MA. The broad peak at 3326 cm^{-1} was due to stretching of hydroxyl (-OH) groups, it is assigned to the cellulose structure. (Ling et al, 2018) In this section, cotton cellulose was modified by addition of 0.5, 1, 1.5, or 2 gram maleic anhydride under the same reaction conditions. The optimum condition was additional of 2 gram of maleic anhydride (Figure 1).

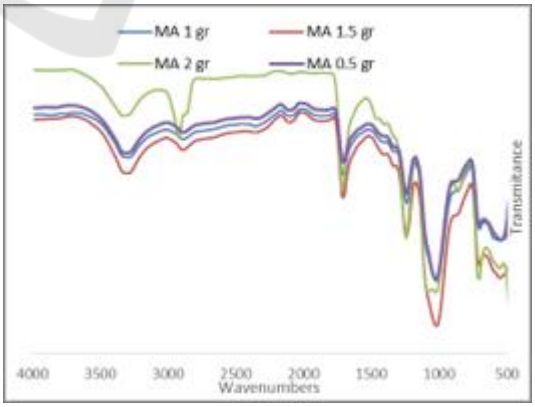

Figure 1: FTIR spectra of MA-g-Ccell.

This optimum condition was obtained by comparing the absorption peaks between C-C-O stretching around the number of waves 1242.94 cm^{-1}

and C = O stretching around the wave number 1709.05 cm^{-1} with a consecutive value of 0.2399; 0.2460; 0.2325; 0.4493 for the addition of maleic anhydride 0.5; 1 1.5 to 2 grams.

After the addition of Maleic Anhydride and followed by reflux for 2 hours, then the sample was dried in the oven with a temperature of 60ºC. The dried sample was added by ammonium Persulphate as the initiator, where this compound would produces radical compounds of cellulose cotton that has been grafted using Maleic Anhydride. Then the addition of AETAC [2-(Acryloyloxy) ethyl]-trimethyl ammonium chloride as an antimicrobial compound. The added AETAC volumes are 1, 2 and 3 mL. Optimum condition was achieved in addition of 2 mL AETAC, this can be seen from the highest absorption in the number of waves 1717.36 cm^{-1}. In the addition of 3 mL AETAC obtained the absorption intensity of its smaller function group, it was likely because AETAC was added too much, so that there was a clotting on the specimen and causing a smaller grafting condition. It can be seen from the resulting dry sample having clumps of cotton cellulose due to too much volume of AETAC addedThe figure below shows the functional groups of AETAC / MA-g-Cell with optimum conditions at the addition of 2 mL AETAC.

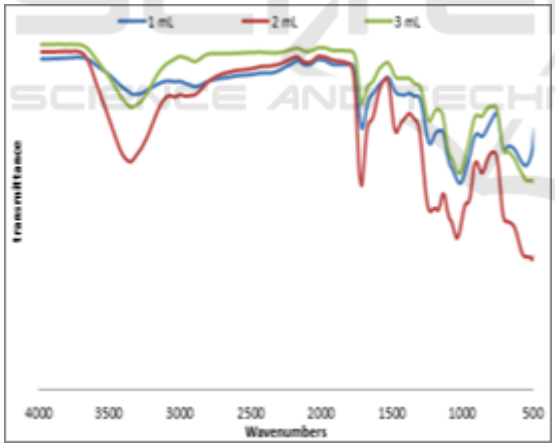

Figure 2: FTIR spectra of AETAC/MA-g-Ccell.

The graft AETAC/MA onto cotton cellulose were synthesized by using ammonium Persulphate (APS) as initiator. Persulphate ion initiate free radical sites on the cellulose. The mechanism by which the initiator ion react with cellulose materials has been widely studied (Hassan, 2015). Comparable between FTIR spectrum of MA-g-Ccell and AETAC/MA-g-Ccell were shown in Figure 2. Absorption occurred at ~1717 cm^{-1} (C=O stretching vibration of the ester group) and disappearance of bond absorption peak of acryloyl group (>C=C<) at 1470 cm^{-1} suggested that AETAC and MA have been successfully grafted onto cellulose backbone (Ling, 2018). Factors affecting graft including initiator concentration, monomer concentration and reaction time have been well investigated (Bledzki, 1997).

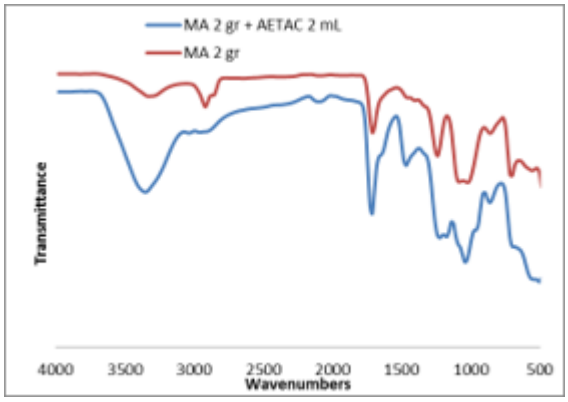

Figure 3: FTIR spectra of MA-g-Ccell and AETAC/MA-g-Ccell.

Free OH stretching vibrations (no hydrogen bonds) have occurred in the 3700-3500 cm^{-1} region while absorption of the OH bound hydrogen band has been seen in the 3450 - 3200 cm^{-1} region as a rather strong and wide band. Therefore, based on data obtained from the table, only hydrogen bonds occured.

The results of the SEM analysis could provide information about the shape and surface changes of a sample being tested. If there has been a change in a sample in the form of for example curves, fractures, and structural changes, the material tends to experience energy changes. Changed energy can be emitted, reflected and absorbed and converted into electron waves that can be captured and read the results on SEM photographs.One potential challenge is the modification of cotton cellulose to see the morphology and structure of the fiber, which can destroy the physical properties and integrity of the structure.

The surface morphology of untreated cellulose and AETAC/MA-modified cotton cellulose were shown in Figure 3. By comparing the two images, almost no major changes in the morfology of sample surfaces could be observed. The surfaces of both samples were flat and smooth, on which natural structure (Liduo, 2019). The morphology of modified cotton cellulose is more flat than fabric cotton fibre. Esterification reaction of grafting process were not destroying the fibre. The results indicated the modification process was efficient and

did not cause any damage to cotton fbre microstructure. The image below shows a SEM photo of commercial cotton and modified with the antimicrobial component of AETAC.

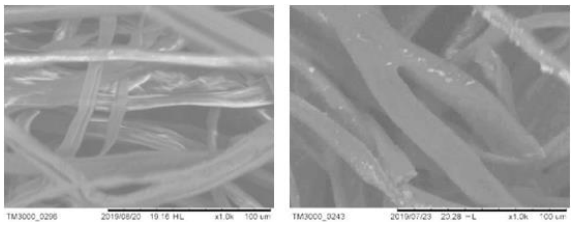

Figure 4: SEM image of (a) untreated cellulose and (b) AETAC/MA-modified cotton cellulose.

3.2 Antimicrobial Properties

Based on the Ministry of Trade of the Republic of Indonesia that the fungus that can live on used clothing is *Aspergillus* sp and *Candida* sp. *Aspergillus* sp found in nature as saprophytes, grows in tropical areas with high humidity. Types of *Aspergillus* sp that can cause disease in humans are *Aspergillus flavus* and *Aspergillus niger*, all of which are transmitted by inhalation transmission.In the antimicrobial activity test conducted to determine the inhibition of the antimicrobial component of AETAC against the fungus *Aspergillus niger* and *Staphylococcus aureus* bacteria. Bacteria and molds were rejuvenated first, then microbial suspensions were made. The modified surface cotton was moistened using DMSO, performed three times with unmodified as standard. After incubating for 24 hours for bacteria and 48 hours for fungi, a zone of inhibition was indicated which indicates the antimicrobial inhibition of modified cotton. The difference in incubation time between fungi and bacteria was caused by differences in the growth rate of both, where the bacteria in this test have a faster growth rate compared to fungi so that the zone of inhibition of the fungus has not been seen after 24 hours and can be clearly observed after 48 hours of incubation. Below was a picture of an antimicrobial test against the fungus *Aspergillus niger* (AN) and the bacterium *Staphylococcus aureus* (SA) with A as the standard of unmodified cotton.

Evaluation of antimicrobial properties done by inoculating *Aspergillus niger* and *Staphylococcus aureus* on agar plate. The zone of inhibition or regions where the growth of the microbial was inhibited around the samples were measured by investigating radius of the zone. The AETAC/MA-modified cotton cellulose showed excellent antimicrobial activity against *Staphylococcus aureus* and *Aspergillus niger*. The results are shown in Figure 4, AETAC/MA-modified cotton cellulose produce large zone of inhibition against *Aspergillus niger* after 48 hours incubation and produce zone of inhibition against *Staphylococcus aureus* after 24 hours. The average radius of "Zone of Inhibition" for AETAC/MA-modified cotton cellulose were 9.5 mm for *Aspergillus niger* and 12.3 mm for *Staphylococcus aureus*. Below is a figure of an antimicrobial test against the fungus *Aspergillus niger* (AN) and the bacterium *Staphylococcus aureus* (SA) with A as the standard of unmodified cotton.

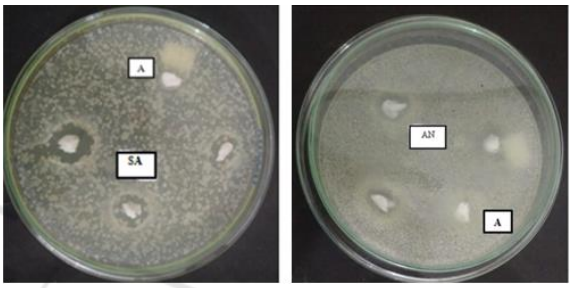

Figure 5: Representing of "Zone of Inhibition" for Staphylococcus aureus (SA) and Aspergillus niger (AN) with A is untreated cotton cellulose.

4 CONCLUSIONS

In this work, [2-(acryloyloxy)ethyl]-trimethyl ammonium chloride (AETAC) and maleic anhydride were grafted on cotton cellulose surface for changing the properties of cotton. FTIR spectra of the AETAC/MA-g-CCell after exhaustive Soxhlet extraction showed stable absorption peak of AETAC/MA carbonyl group (>C=O) at 1736 cm^{-1} and disappearance of bond absorption peak of acryloyl group (>C=C<) at 1470 cm^{-1}. SEM images showed that the surfaces of both samples were flat and smooth, on which natural structure. The results indicated the modification process was efficient and did not cause any damage to cotton fibre microstructure. The resulting material showed excellent antimicrobial activity against *Staphylococcus aureus* and *Aspergillus niger*.

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