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PREPARATION AND THERMAL ANALYSIS OF DURIAN PEEL CELLULOSE GRAFTED WITH POLY (2-[ACRYLOYLOXYL]-ETHYL TRIMETHYL AMMONIUM CHLORIDE/CHITOSAN NANOCOMPOSITES AS ANTIMICROBIAL APPLICATION

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ABSTRACT

In this work, facile preparation and low-cost utilizing durian peel organic waste as a cellulose (DPC) source and copolymerization grafted between 2-[acryloyloxyl]-ethyl trimethylammonium chloride (AETAC) and chitosan were developed. Accordingly, a grafting yield of 21.9 % was obtained. In addition, to further understand the characterization of grafted cellulose with AETAC and cellulose grafted with AETAC and chitosan through techniques, including FTIR, SEM, XRD, TGA, and contact angle confirmed the grafting of AETAC and chitosan monomers onto cellulose backbone (DPC-g-AETAC-co-chitosan). The morphology grafting process resulted in the DPC-g-AETAC-co–chitosan with wrinkle structure, coarse surface, and formation of pores, resulting in a crystallinity index slightly reduced from 36.58 to 19.3 %, however, DPC-*g*-AETAC-co-Chitosan increased in thermal stability. In addition, DPC-*g*-AETAC-co-chitosan demonstrated excellent antibacterial and antifungal ability against *S. aureus*, *S. epidermis*, and *C. albicans*.

Keywords: Cellulose, Chitosan, Durian Peel, Antifungal, Antibacterial.

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INTRODUCTION

Cellulose and chitosan have been categorized as biopolymers in a group of polysaccharides. Cellulose is a biopolymer, that has many advantages, including biocompatibility, easily modified, biodegradable, and low-cost.[1,2] Cellulose is obtained from the repeated unit of β-D-anhydroglucopyranose that is linked through the covalent bond of the acetal group at C4 and C1 (β-1,4-glycoside). Chitosan has a similar structure to cellulose, the difference is the presence of an amine group at C-2 at β-D-glucose. Chitosan is obtained by partial deacetylation of the chitin structure that is mostly found in the exoskeleton of *crustaceans*. Those biopolymers can be found in abundance amount in nature, are able to degrade, are non-toxic, and can be grouped as renewable materials. Over those advantages, those biopolymers have several disadvantages, i.e. with the high densities of the hydroxyl group these biopolymers are least reactive due to the presence of intra and inter0hydrogen bonding; not soluble in water, low dimensional stability, and low thermoplasticity stability, low antimicrobial activity.[3,4] The amine reactive group of chitosan acted as Lewis acid and was able to show antimicrobial properties only in an acid medium.[5,6,7,8] Due to resolve the disadvantages of these biopolymers, a modification through a chemical process is the only solution to improve their properties. Modification through combining two or more macromolecules can be used to create a macromolecule with a bulky network that has high porosity and this kind properties will be extremely helpful to entrap the microorganism in the porous structure of materials. Many efforts have been devoted to incorporating antibacterial agents into cellulose such as chitosan,[9] cetyltrimetylammonium bromide,[10] 2-aminoethyl methacrylates,[11] bis(2-chloroethyl) amine.[12] Antimicrobial polymers are materials that can kill or inhibit microbial growth on the surface or around the environment. In recent decades, research into polymer materials as antimicrobial materials has been extensively and widely applied. Most of the cell walls of negatively charged bacteria, containing the compound phosphatidylethanolamine (70%) as the main component, and most of the positively charged antimicrobial polymers, polymers with the ammonium quaternary group are widely developed as their

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biocide polymers.[13] Antimicrobial peptides (AMP) for example oligopeptides with a varying number (from five to over a hundred) of amino acids. AMP has a broad spectrum of targeted organisms ranging from viruses to parasites.[14] Chitosan[15], Polyethylenimine (Branched), Polyguanidines, N –halamines, and Acrylate derivatives.[15] This work aims to utilize durian peel organic waste as a source of cellulose (DPC) and grafted copolymerization between 2-[acryloxyl]-ethyl trimethylammonium chloride (AETAC) and chitosan at low cost.

EXPERIMENTAL

Grafting of AETAC and Chitosan Monomers onto Cellulose

The oxidized DPC by following a similar process to our previous report.[16] The oxidized cellulose (5 g) was dispersed in distilled water for 4 h into a three-neck round flask heated up to 50 ºC for 30 min. Potassium peroxydisulfate (5 wt%) was added to the solution to initiate the reaction. 25 ml of AETAC 50% was added to it drop-wise with vigorous stirring and continuous purging with nitrogen. The grafting reaction was carried out at 80 ºC under a nitrogen atmosphere for 3 h and 4 g of chitosan (100 ml) with 1% solution acetic acid was added to polymer suspension and the grafting reaction was carried out at 80 ºC under nitrogen atmosphere for 3 h. Subsequently, the dispersion was cooled down to room temperature, and a methanol/acetone (1:1) mixed solution was added to separate the unreacted monomer and the grafted cellulose. The obtained grafted cellulose fiber was dried in a vacuum oven.[17]

Characterization

The Characterization of pristine and grafted cellulose was determined by following similar techniques to our previous report,[15] including FTIR, SEM, XRD, TGA, and antimicrobial activity

Contact Angle

The contact angle is measured by direct measurement of droplets (sessile drop) using a goniometer with a high-speed CCD camera resolution of 120 fps (1980 x 1080 pixels).

RESULTS AND DISCUSSION

The DPC was isolated via a modified conventional bleaching method.[18] AETAC and chitosan were chemically attached with (R-N(CH3)$^+$) and (R-NH2) groups through free radical polymerization from sulfate groups in this study as a means of enhancing the antibacterial activity of the DPC. In Fig.-1, you can observe how cellulose changed after being oxidized and grafted. As demonstrated in Fig.-1 with a grafting yield of 21.9%, the oxidized DPC-g-AETAC-co-chitosan that was produced could be easily diffused in water.

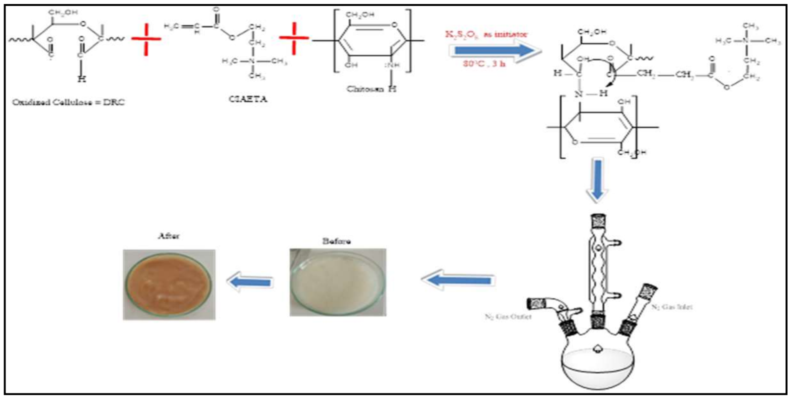


Fig.-1: Synthetic Process for Oxidized DPC-g-AETAC-Co-Chitosan is Shown Schematically

Figure-2 shows the transmittance of DPC can be compared with characteristic peaks at 3332, 2907, 1640, 1028, and 887 cm^{-1}, respectively, which are attributable to the O-H, C-H, C=O, C-O-C, and C-C stretching, to define the indication to confirm the occurrence of the grafting process. After the grafting process, the band centered at 1729 cm^{-1} was associated with the C=O ester group molecular structure.[15,19] Another characteristic of AETAC modification at 1476 and 1217 cm^{-1} corresponds to the vibration of the trimethyl group of quaternary ammonium salt[20] and C-C-N asymmetric.[15,22] These further demonstrated that AETAC molecules were chemically bonded to the oxidized DPC surface and may greatly increase the density of positive surface charges (R-N(CH_3)$^+$). The presence of a new band at 1535 cm^{-1} indicated the chitosan was successfully grafted onto oxidized cellulose fiber. This band was ascribed as the stretching vibration of the N-H group that was mostly found around 1630-1510 cm^{-1}.

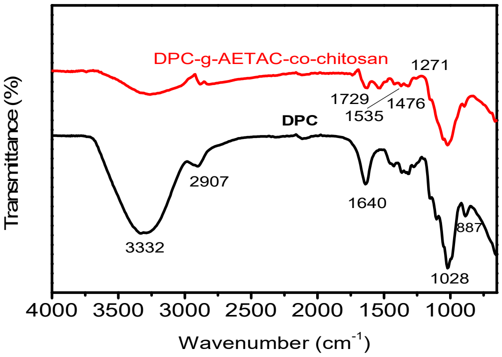


Fig.-2: FT-IR Spectra of DPC and DPC-*g*-AETAC-Co-Chitosan

The surface morphology of oxidized DPC, before and after surface modification by grafting AETAC and chitosan, that is clearly different in the SEM image shown in Figure-3. Contrarily, the DPC-g-AETAC-co-chitosan morphology was wrinkled, coarse, and pore-filled, suggesting that AETAC and chitosan had formed a crosslinked on the DPC molecules, increasing the surface density of the grafted DPC's fibrous ribbons.

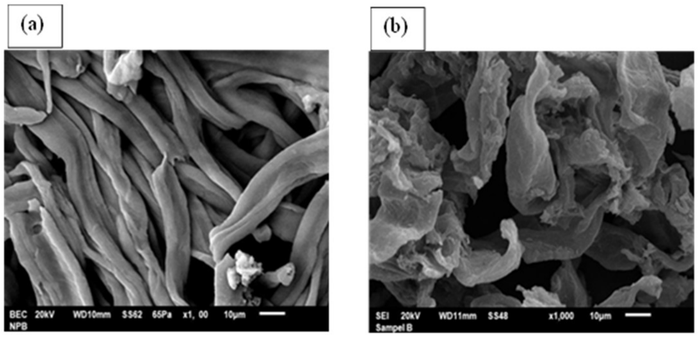


Fig.-3: SEM Images of Oxidized DPC (a) before and (b) after Grafted with AETAC Dan Chitosan

The diffractogram of DPC and after surface modification of oxidized DPC grafted AETAC and chitosan can be seen in Fig.-4. In the lattice plane 101, 101, and 002 all cellulose sample was found at 2θ of 14.3, 16.7, and 21.69°. Based on Eq. (2), pristine DPC has a higher crystallinity index of 26.19 % compared to that of grafted cellulose (DPC-g-AETAC-co-Chitosan) (19.3%). These results indicated that grafted process of AETAC dan chitosan onto the surface of cellulose distorted the crystallinity phase of cellulose. This distortion effect can be caused by the crosslinked formation among the AETAC, chitosan, and oxidized DPC.[2]

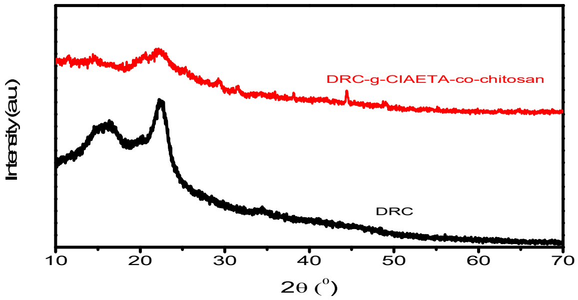


Fig.-4: XRD Spectra of Pristine DPC and DPC-*g*-AETAC-co-chitosan

Thermogravimetry Analysis

TGA analysis was used to compare the thermal stability of DPC before and after modification. The TGA and DTA curves of ungrafted and grafted DPC are shown in Fig.-5a and 5b, respectively. Three peaks of degradation can be observed in the thermogram of DPC after grafting. Those peaks were found at 230.36, 250.13, and 304.61°C where each peak indicated the degradation of one component, i.e., AETAC, chitosan, and cellulose, respectively. The weight loss of each peak was about 23.63, 29.21 and 44.53%. respectively.

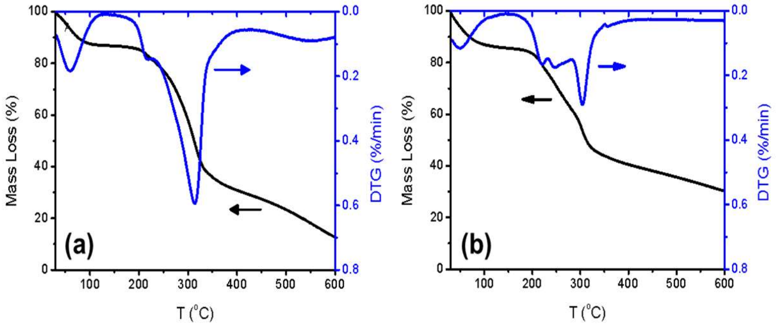
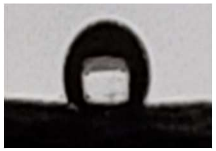


Fig.-5: TGA dan DTG Curves of (a) Pristine Oxidized DPC and (b) DPC-*g*-AETAC-Co-Chitosan

Contact Angle

The surface contact angle can be used quantitatively to determine the degree of wetting of the solid surface by the liquid and using the direct drop method (sessile drop).[23] The degree of surface contact angle of pristine and grafted cellulose (DPC-g-AETAC-co-chitosan) is shown in Table-1. The degree of contact angle of oxidized DPC before and after grafting during the first water drop was 94 ± 3° and 112 ± 8°, respectively. The higher contact angle of grafted oxidized DPC can be explained due to the crosslink between cellulose and the cationic hydrophobic of chitosan which was formed by Schiff base reaction as confirmed in FTIR analysis. The surface contact angle of the grafted DPC decreased from 112 ± 8 to 43 ± 3°. These changes indicated that the surface of the grafted cellulose was able to absorb water (hydrophilicity nature).[23] This effect is most likely influenced by the hydrophilic monomer AETAC bound to the cellulose. The ability of the grafted oxidized DPC to absorb water was also supported by water uptake (%) measurement data and SEM imaging which shows the presence of pores on the surface of the grafted cellulose.[30] This finding was in good agreement with the previous report,[15] where wool yarn fibers coated with Q-chitosan demonstrated surface contact angles of 122.2 and 52.7 ° at the duration of the 0 and 45 s, respectively.

Table-1: Surface Contact Angle of Pristine Oxidised and Grafted DPC

Sample	Contact angle			
	0 s	60 s	120 s	180 s
DPC		 75 ± 2°	 69 ± 2°	 56 ± 1°
DPC-g-AETAC-g-chitosan	 112 ± 8°	 43 ± 3°	 0	

Antibacterial and Antifungal Properties

Antibacterial and antifungal activities of cellulose before and after the grafting process against *S. aureus*, *S. epidermis,* and *C. albicans* were carried out. The inhibition zone of each treatment was summarized in Table-3, this data confirmed that the grafted cellulose has the highest antibacterial and antifungal activities compared to pristine oxidized DPC. The improvement of antibacterial and antifungal activities was mainly attributed due to the presence of AETAC and chitosan which are known to have the ability to inhibit the growth of bacteria and fungi. This result was confirmed by several previous studies after the grafting with chitosan, and MAETC, the obtained materials were able to inhibit *S. aureus*, *E. coli*, *B. cereus*, and *P. fluorescens*.[22,24]

Table-3: Summary of Diameter of Inhibition Zone of Pristine Oxidized and Grafted DPC Against S. Epidermis, S. Aureus Dan C. Albicans.

Antibacterial/antifungal	Sample	Diameter of inhibition zone (mm)			
		25%	50%	75%	100%
S. epidermis	Pristine	0	0	0	0
	DPC-g-AETAC [15]	0	6.15 ± 0.23	6.75 ± 0.31	7.02 ± 0.26
	DPC-g-AETAC-co-chitosan	6.35 ± 0.23	8.35 ± 0.32	8.85 ± 0.23	9.35 ± 0.39
Chloramphenicol		22.02			
S. aurous	Pristine	0	0	0	0
	DPC-g-AETAC [15]	0	7.15 ± 0.48	7.85 ± 0.53	8.30 ± 0.24
	DPC-g-AETAC-co-chitosan	7.35 ± 0.23	11.35 ± 0.42	11.85 ± 0.52	12.35 ± 0.34
Chloramphenicol		25.75			
C. albicans	Pristine	0	0	0	0
	DPC-g-AETAC [15]	8.00 ± 0.52	9.06 ± 0.41	11.0 ± 0.35	16.02 ± 0.37
	DPC-g-AETAC-co-chitosan	9.00 ± 0.48	13.06 ± 0.52	14.0 ± 0.45	18.02 ± 0.27
Chloramphenicol		7.56			

CONCLUSION

The modification of the cellulose surface through the grafting process in the presence of AETAC and chitosan has been successfully prepared with a yield of 21.9 %. This modification resulted in a reduced crystallinity index, higher thermal stability, hydrophilicity, and water uptake of cellulose. In addition, the antibacterial and antifungal of the modified grafted cellulose with AETAC and chitosan showed significant improvement with a large inhibition zone compared to pristine oxidized DPC. Our finding demonstrated the promising application of grafted cellulose for antimicrobial and wound-dressing applications.

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CONFLICT OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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