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Studies on the Cellulose Extraction and Film Preparation from Coconut Meat Residue

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Abstract

The project aims to study cellulose extraction of coconut meat residue (CMR) The method was performed in 3 steps:

1. Lignin extraction by refluxing in 4% w/v NaOH to obtain CMR-1
2. Oxidation by refluxing in 0.5 M $K_2S_2O_8$ to obtain CMR-2
3. Acid hydrolysis by refluxing in 6 M H_2SO_4 to obtain CMR-3

The extracted cellulose was totally washed and dry at 50 °C. CMR-1, CMR-2 and CMR-3 were further analyzed by scanning electron microscopy, Fourier transformed infrared spectroscopy, thermogravimetric analysis and X-ray diffraction. From SEM analysis, the cleaner and finer fibers were obtained after being hydrolyzed by acid. The FT-IR spectra of all CMR samples show the characteristic absorption peaks of cellulose and also the presence of carboxylic groups at 1750 and 1655 cm^{-1}. The TGA data showed that the start temperature in the cellulose degradation region was decreased as the number of extraction steps was increased. The highest crystallinity was obtained in CMR-3. For film preparation, CMR-3 was mixed with 1% sodium alginate solution and subsequently stirred for 6 hours to obtain homogeneous solutions. The solution was poured into the petri dish and left in the oven at 50 °C for 6 hours to obtain the CMR film. It was then analyzed by scanning electron microscopy, thermogravimetric analysis and X-ray diffraction. SEM image showed the good homogeneity of the CMR film. The thermal stability of cellulose in the film was increased as evidenced from TGA data. While the crystallinity of cellulose in CMR film was decreased significantly.

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Introduction

There has been an increasing interest in the development and applications of sustainable bio-based polymer films in place of petroleum-based plastic films due to the environmental problems caused by the synthetic plastic (Khan *et al*., 2014; Reddy *et al*., 2013). The biomaterials, especially biopolymers, for film production have been intensively studied. Various biopolymers such as polysaccharides, proteins, and lipids obtained from plant and animal resources have been studied as an alternative use of non-biodegradable packaging materials since they are abundant, renewable, inexpensive, environmentally friendly, biodegradable and biocompatible (Tang *et al*., 2012). Among these materials, polysaccharides are of interest due to their good film forming property, good mechanical and gas barrier properties compared to other biodegradable materials (Rhim *et al*., 2013). Various polysaccharides such as chitosan (Li *et al*., 2009), thermoplastic starch (Savadekar *et al*., 2014), agar (Reddy *et al*., 2014), carrageenan (Rhim *et al*., 2014), and carboxymethyl cellulose (Ghanbarzadeh *et al*., 2011) have been studied to make biodegradable packaging films. Cellulose is an abundant, self-generating biomass which is created through photosynthesis in trees, bamboo, grass, reeds, and other plants. With an annual production of 1.5×10^{12} tons, cellulose has been considered an inexhaustible and sustainable raw material (Klemm *et al*., 2005).

Coconut is one of the main agricultural crops of Thailand. Every year, a variety of food and related products are made from this crop producing high quantity of coconut meat residues. This waste contains cellulose which can be extracted by various chemical means. In this research, the extraction methods of the cellulose from coconut meat residues was investigated. The extracted cellulose was also attempted for film fabrication. The spectroscopic studies on the extracted cellulose and cellulose films were also reported.

Experimental

The cellulose extractions were performed in three steps as in 1-3.

1. *Cellulose Extraction from coconut meat residue using NaOH*
    1. Weigh 20 g of coconut meat residue.
    2. Add 300 mL of 4% w/v sodium hydroxide solution.
    3. Reflux the mixture at 100 °C for 2 hours.
    4. Filter, wash and dry the fiber at 50 °C for 6 hours.
    5. Repeat step 2-4 for 2 times to obtain CMR-1. Weigh and calculate yield.

2. Oxidation of the cellulose using $K_2S_2O_8$

For CMR-1

1. Weigh 1 g of CMR-1.
2. Add 100 mL of 0.1 M $K_2S_2O_8$ solution.
3. Reflux the mixture at 60 °C for 1 hour.
4. Filter, wash and dry the fiber at 50 °C for 6 hours to obtain CMR-2 (0.1 M). Weigh CMR-2 (0.1 M) and calculate yield.
5. Repeat step 1-4 with the change in concentrations of $K_2S_2O_8$ solutions to 0.25 M and 0.5 M to obtain CMR-2 (0.25 M) and CMR-2 (0.5 M) respecively.

3. Acid hydrolysis using dilute H_2SO_4

1. Weigh 0.5 g of CMR-2.
2. Add solution of conc. H_2SO_4:H_2O (1:1 v/v).
3. Reflux at 55 °C for 2 hour.
4. Filter, wash and dry the fiber at 50 °C for 6 hours to obtain CMR-3. Weigh CMR-3 and calculate yield.

4. Characterization of the cellulose extracts

All samples were analyzed by scanning electron microscopy (SEM), Fourier transformed infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and X-ray diffraction (XRD)

5. Preparation of CMR film

1. Weigh 0.5 g of sodium alginate.
2. Add 50 mL of distilled water.
3. Stir for 40 minutes until the mixture was well mixed.
4. Weigh 0.25 g of CMR-3 and add into sodium alginate solution
5. Stir for 6 hours until the homogeneous mixture was obtained.
6. 20 mL of the mixture in step 5 was poured into petri dish.
7. Dry at 50 °C for 6 hours to obtain dry film.
8. 5 mL of 0.5 M $CaCl_2$ was slowly poured onto the dry film.
9. Remove the film from the petri dish, wash and dry the film at 50 °C for 6 hours to obtain CMR film.
10. The film was then analyzed by scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and X-ray diffraction (XRD).

Results and Discussion

1. Cellulose extraction from coconut meat residue

Coconut meat residue was refluxed in 4% NaOH for 2 hours to obtain CMR-1. It was further reacted with various concentrations of $K_2S_2O_8$ to obtain CMR-2. The fiber was then hydrolyzed by diluted sulfuric acid to obtain CMR-3. The yield for each step was calculated by using the equation below:

Formula: $$\text{Percent yield} = \frac{W_{before} - W_{after}}{W_{before}} \times 100$$

W_{before} = Weight before each extraction step

W_{after} = Weight after each extraction step

The yield percentage for each extraction step was averaged from three experimental runs and summarized in Table 1. Lignin, hemicellulose and silica were removed using NaOH to obtain CMR-1. The average yield from this process was 68.61. Reaction with $K_2S_2O_8$ helps remove residual lignin which is strongly attached to the cellulose surface. The proper concentration of $K_2S_2O_8$ for producing highly crystalline cellulose fiber is 0.5 M. The amorphous cellulose was further removed by dilute sulfuric acid. The crystallinity index of cellulose extract from each step will be presented in 2.3.

Table 1 Yield percentage of the cellulose extracts from coconut meat residue

Sample		**% yield (±S.D.)**
CMR-1		68.61 (±0.17)
CMR-2	0.1 M	16.78 (±0.08)
	0.25 M	21.22 (±0.10)
	0.50 M	30.72 (±0.14)
CMR-3		59.09 (±0.19)

When the $K_2S_2O_8$ solution is subjected to heat treatment, the cleavage of the peroxide bond of $S_2O_8^{2-}$, the weakest bond, is expected to generate two SO_4^{-} radical ions. In the presence of proton in solution, hydrogen peroxide will also be formed. As cellulose fibers were immersed in an $K_2S_2O_8$ aqueous solution, the free radicals produced would penetrate into amorphous region of cellulose and co-hydrolyze the 1,4-β bond of the cellulose chain in this region, resulting in a large weight loss of celluloses. On the other hand, together with hydrogen peroxide, these free radicals were capable of oxidizing CH_2OH in the C_6 position to form -COOH groups on the cellulose surface (Lam *et al*., 2012). All details are shown in Figure 1. For acid hydrolysis, amorphous cellulose was further removed as seen from the higher value of crystallinity index of CMR-3.

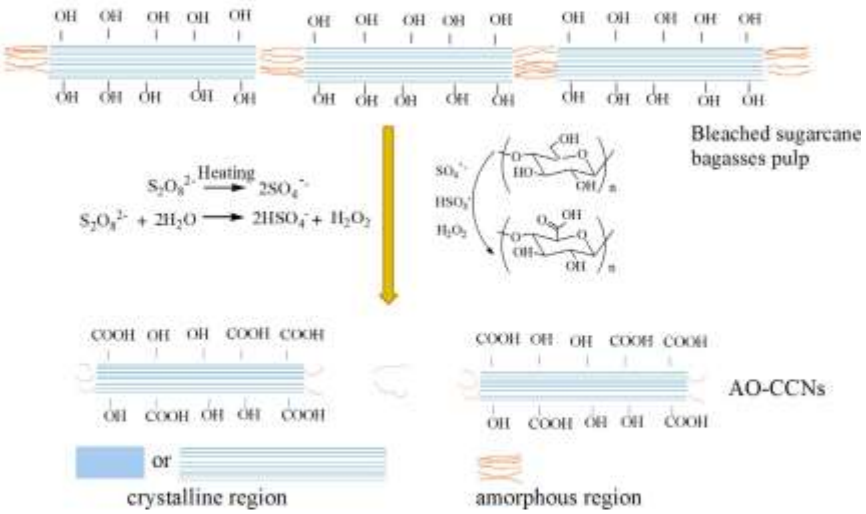
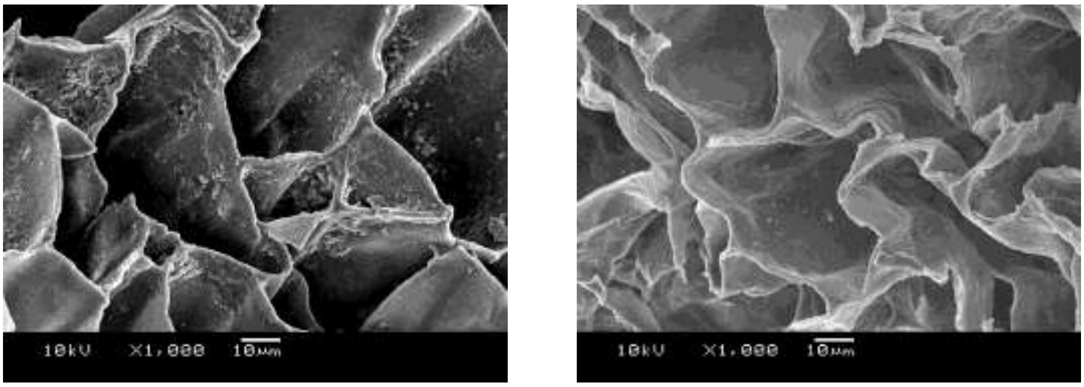


Figure 1 The detailed reaction between cellulose and $K_2S_2O_8$ (Zhang *et al*., 2016)

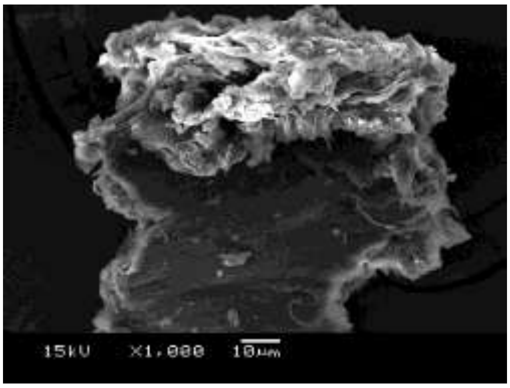
2. *Characterization of the cellulose extracts*

2.1 Scanning Electron Microscopy

The SEM images of CMR, CMR-1, CMR-3 are presented in Figure 2. After being reacted with NaOH, the fiber surface is cleaner. While its folding morphology is similar to the untreated fiber (see Figure 2 (a) and (b)). After being hydrolyzed by sulfuric acid, the folding morphology is broken as in Figure 2 (c).



(a) (b)

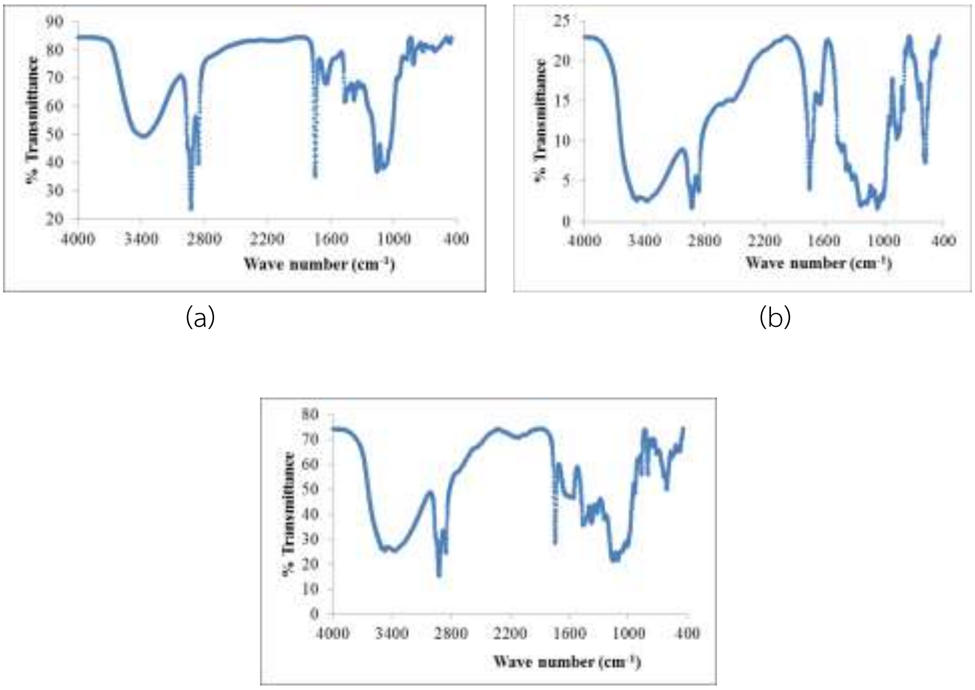


(c)

Figure 2 SEM images of (a) CMR (b) CMR-1 (c) CMR-3 with the magnification of 1000

2.2 Fourier Transformed Infrared Spectroscopy (FT-IR)

The FT-IR spectra of all samples are shown in Figure 3. The functional group analysis of cellulose in CMR samples was summarized in Table 2. All samples show the signals of carboxylic groups at ~ 1750 and 1655 cm^{-1} indicating the presence of trace fatty acid in the fiber. However in the case of CMR-2 and CMR-3, these peaks may include the carboxylic groups from oxidized cellulose (see Figure 1).



(a) (b)

(c)

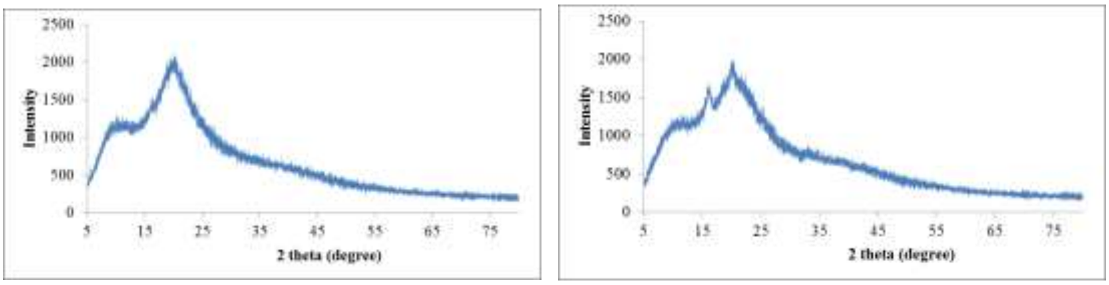
Figure 3 IR spectra of (a) CMR (b) CMR-2 (c) CMR-3

Table 2 Analysis of IR spectra of CMR samples

Mode of vibration	Wave number (cm^{-1})
$\nu_{O\text{-}H}$	3350
$\nu_{C\text{-}H}$	2901
$\delta_{O\text{-}H}$	1638-1643
$\delta_{C\text{-}H}$	1429
$\nu_{C\text{-}C}$ and $\nu_{C\text{-}O}$ (Skeletal vibration)	1319
$\nu_{C\text{-}O}$ (antisymmetric bridge stretching)	1164
$\nu_{C\text{-}O\text{-}C}$ (pyranose ring skeletal vibration)	1127-1000

2.3 X-ray Diffraction

All CMR samples were analyzed by X-ray diffraction technique. The XRD results of CMR and CMR-1 are presented in Figure 4.



(a) (b)

Figure 4 XRD of (a) CMR (b) CMR-1

The crystallinity index (I) of each sample was calculated by the following equation :

$$I = \frac{I_{22^\circ} - I_{15^\circ}}{I_{22^\circ}} \times 100$$

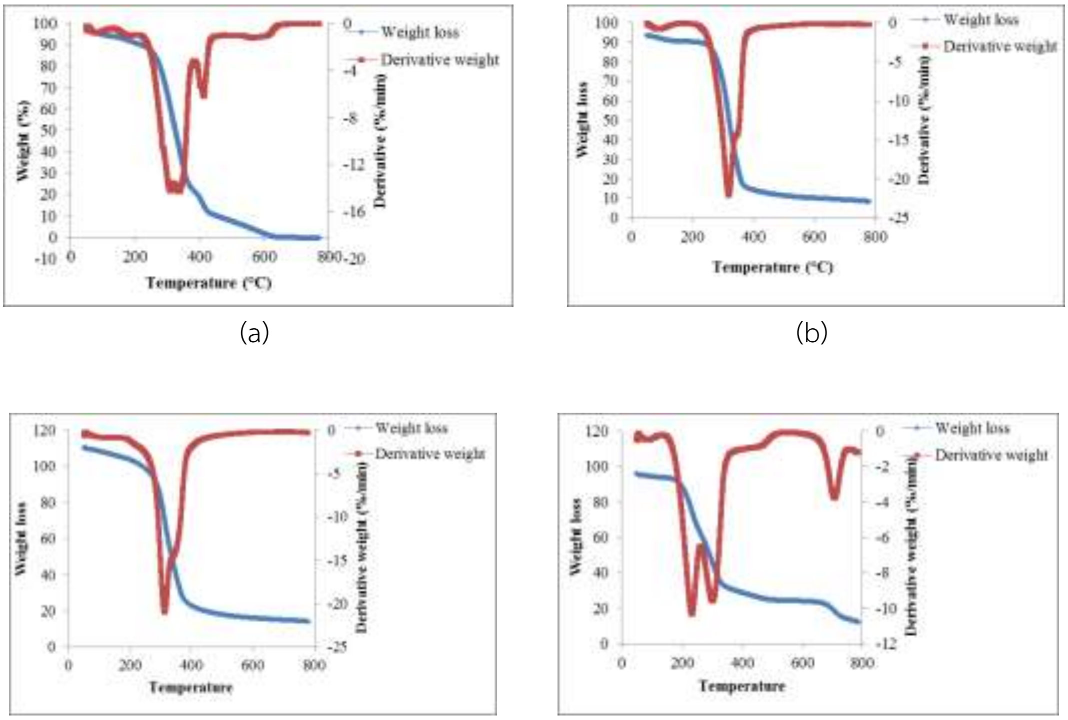
The results are tabulated in Table 3. The amorphous phases of CMR, CMR-1, CMR-2 (0.1 M) and CMR-2 (0.25 M) are dominant. However $K_2S_2O_8$ and H_2SO_4 can help increase the crystallinity of coconut fiber. The best concentration of $K_2S_2O_8$ to produce highest crystallinity is 0.5 M.

Tabel 3 Crystallinity index of coconut meat samples

Sample		Crystallinity Index (%)
CMR-1		-
CMR-2	0.1 M	-
	0.25 M	-
	0.5 M	6.06
CMR-3		8.98

2.4 Thermogravimetric Analysis (TGA)

Thermal analysis of all samples was performed and the results are presented in Figure 5. The thermograms of CMR samples were analyzed and tabulated in Table 4.



(a) (b)

(c) (d)

Figure 5 TGA of (a) CMR (b) CMR-1 (c) CMR-2 (d) CMR-3

Table 4 TGA analyses of CMR samples

Sample	Decomposition step	Temperature (°C)			% Weight loss	
		Start	End	Tp	Each	Total
CMR	1st	49.07	142.83	77.97	3.37	96.89
	2nd	142.83	217.23	183.33	3.60	
	3rd	217.23	386.59	335.07	68.97	
	4th	386.59	435.48	411.75	10.04	
	5th	435.48	639.14	568.68	10.91	
CMR-1	1st	49.33	175.78	88.221	3.21	78.59
	2nd	175.78	385.48	318.64	75.38	
CMR-2	1st	49.58	176.84	105	5.03	83.68
	2nd	176.84	503.01	313.18	78.65	
CMR-3	1st	49.08	145.98	83.34	2.20	82.38
	2nd	145.98	261.77	231.94	31.40	
	3rd	261.77	408.02	301.03	33.77	
	4th	408.02	556.89	415.57	4.07	
	5th	556.89	762.94	707.01	10.94	

From the data in Table 4, the first decomposition step with the start temperature ~ 50 °C is the evaporation of water. The yellow-highlighted row indicates the initial disintegration of cellulose. The start temperature of this step seems to be decreased as the number of extraction steps is increased as seen in CMR (217.23 °C), CMR-1 (175.78 °C), CMR-2 (176.84 °C) and CMR-3 (145.98 °C). However, CMR-3 shows the additional cellulose disintegration steps with higher start temperatures indicating the presence of thermally stable crystalline cellulose.

3. Film Fabrication and characterizations

The CMR film was fabricated by mixing CMR-3 with alginate solution. The surface morphology was analyzed by SEM and the results were presented in Figure 6. The image shows smooth surface with small bubbles as shown in Figure 6.

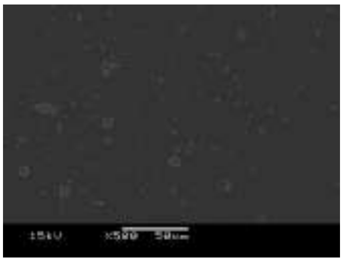


Figure 6 SEM images of CMR film with the magnification of 500

The interactions between the alginate and cellulose in CMR-3 *via* hydrogen bonds are proposed as in Figure 7. The formation of the ester bonds from carboxylate groups of alginate and hydroxyl groups of the cellulose is also plausible. However, the explicit conclusion cannot be drawn due to the lack of spectroscopic evidence on the ester bonds.

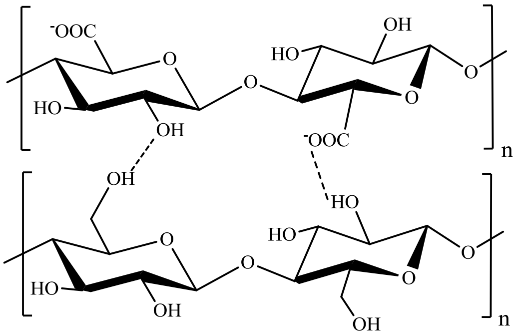


Figure 7 The proposed hydrogen bond interactions between alginate and cellulose in CMR film

The XRD pattern of the CMR film is very broad and the result is not presented in this work. The peak broadening was observed due to the more disorder of the cellulose chain arrangement in the film.

The TGA thermogram of the CMR film is shown in Figure 8. The analysis of the TGA data is tabulated in Table 5. The start temperature (yellow highlight) for the cellulose disintegration of CMR film (170.76 °C) is higher than that of CMR-3 (145.98 °C). The combination of CMR-3 with alginate helps increase the stability of the cellulose. This increased stability also causes the lower weight loss percentage of the film as compared to that of CMR-3.

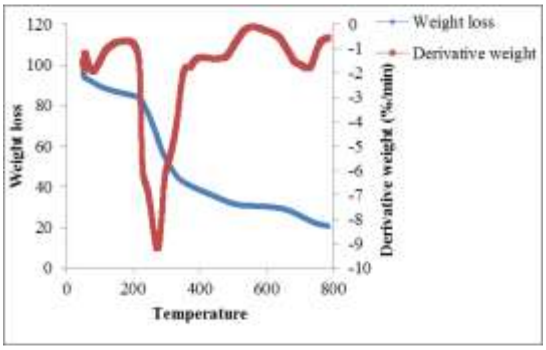


Figure 8 TGA thermograms of CMR-film

Table 5 TGA analyses of films and alginate

Example	Decomposition step	Temperature (°C)			% Weight loss	
		Start	End	Tp	Each	Total
CMR-film	1st	49	170.76	80.63	9.723	74.936
	2nd	170.76	358.55	272.31	44.322	
	3rd	358.55	552.93	361.25	11.009	
	4th	552.93	783.97	722.81	9.882	
Alginate	1st	42.88	174.41	103.73	14.810	78.156
	2nd	174.41	229.27	188.87	18.768	
	3rd	229.27	341.06	255.67	18.731	
	4th	341.06	455.84	406.95	13.072	
	5th	455.84	528.74	483.04	5.754	
	6th	528.74	679.27	663.68	4.342	
	7th	679.27	708.68	705.08	2.679	

Conclusion

The cellulose fiber was successfully extracted from coconut meat residue. The extraction processes include NaOH extraction to obtain CMR-1, oxidation by $K_2S_2O_8$ to obtain CMR-2 and acid hydrolysis to obtain CMR-3. CMR-3 was further mixed with alginate solution to yield CMR-film. The TGA results indicate the higher stability of the cellulose in the film. However the measurement on the film strength need to be done as the scientific support of using this biodegradable film in place of non-degradable synthetic plastic.

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