

Microwave-Assisted Modified Cellulose from Corn Husk: Effects of Reaction Conditions on Degree of Substitution and Film Properties

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Abstract: This study was focused on synthesis of cellulose from corn husk in LiCl/DMAc solvent system by esterification reaction under microwave energy at various microwave power and reaction time using lauroyl chloride and N,N-Dimethyl 1-4-Amino Pyridine (DMAP) as an esterifying agent and a catalyst, respectively. The obtained modified cellulose powder was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and proton Nuclear Magnetic Resonance (¹H-NMR) analysis. The Degree of Substitution (DS) value and thermal stability of modified cellulose were evaluated by ¹H-NMR and Thermogravimetric Analysis (TGA), respectively. Then the modified cellulose powder was transferred into film by casting method with chloroform. The optimum conditions for cellulose modification under microwave heating which yielded low, medium and high DS values along with reasonable %weight increase were obtained at 90' sec 320 W (DS 1.99), 150 sec 160 W (DS 2.44) and 60 sec 240 W (DS 2.73), respectively. The effects of DS values on the wettability, water absorption, gloss and tensile properties of the obtained modified cellulose film were analyzed. The results revealed significant effect of the DS values on the properties of esterified cellulose films that upon increasing the DS values, the gloss value and tensile properties increased while the wettability and water absorption decreased.

Key words: Corn husk, cellulose, degree of substitution, esterification, microwave

INTRODUCTION

Nowadays, synthetic plastics have become the important materials for everyday life. They are widely used for packaging applications because of their lightweight, inertness and low cost. However, synthetic plastics are made from petroleum resources which are non-renewable and becoming exhausted in the near future. In addition, they need over a hundred year to be degraded naturally, leading to the disposal problem of plastic wastes which are accumulated in nature substantially throughout the world. The development and utilization of biodegradable cellulose-based plastic film may be a good candidate for solving these problems.

Cellulose is the most abundant renewable raw material. It is estimated that about 5×10¹⁰ (Gourson *et al.*, 1999) tons of cellulose are generated each year throughout the world (Joly *et al.*, 2005). However, cellulose has limitation in its fabrication since it cannot be dissolved in common organic solvents and is not melt-processible due to the large amount of intra and intermolecular hydrogen bondings attributing to highly

crystalline structure. As a result, it cannot be converted into different shapes by injection molding or melt extrusion because it will be thermally degraded prior to obtaining the ability to flow. Nevertheless, after chemical modification, cellulose can be soluble in common organic solvents and is easy to process so it can have wide applications such as coating, laminates, composites and plastics (Freire *et al.*, 2006).

Typical reaction of cellulose modification is occurred by fatty acids substitution on hydroxyl group available on each anhydroglucose ring with esterification reaction. The success of cellulose modification can be evaluated from degree of substitution or DS value which is the parameter determining substituted value of hydroxyl group in cellulose structure. Theoretically, the DS value can be ranged from 0-3 depending on reaction system, catalyst, modifying agent, heating method and reaction time (Chauvelon *et al.*, 1998). The changes in DS values are strongly affected on the properties of modified cellulose such as solubility, swelling and biodegradability (Ishizu, 1991; Richardson and Gorton, 2003). Several researches have been investigated the key parameters for

cellulose modification such as molar ratio of the initial substances, quantity of catalyst, type of esterifying agent and heating method (Richardson and Gorton, 2003; Antova *et al.*, 2004; Heinze and Liebert, 2001).

Generally, the modification reaction of cellulose has been heated using conventional heat transfer equipment such as oil baths, heating jackets and hot plates. The conventional heating spends a long reaction time and uses a lot of energy to complete the modification reaction of cellulose (e.g., 5 h to 1 day or 2 day) (Satge *et al.*, 2004, 2002). Alternatively, many researches on the effectiveness of using microwave heating in modification processes have been reported. They have founded that the microwave heating can decrease the reaction time, give better yield assist in developing cleaner chemical reaction. In addition, the microwave heating can accelerate the modification reaction of cellulose better than the conventional heating and does not alter the chemical structure of modified cellulose (Gourson *et al.*, 1999; Marson and Seovd, 1999; Memmi *et al.*, 2006; Ratanakamnuan *et al.*, 2012; Santos *et al.*, 2015; Xu *et al.*, 2008).

Corn husk is an interesting source for cellulose production. It is an agricultural residue with a Thailand annual yield of 3.60 million tons. It is annually renewable, low cost and copious source for cellulose production. Corn husk has the following compositions: 38-40% cellulose, 44% hemicellulose, 7-21% lignin and 2.8-7% ash (Richardson and Gorton, 2003; Barl *et al.*, 1986). Therefore, it would be a good alternative to utilize corn husk as a raw material for cellulose film preparation.

In this research corn husk was used as a cellulose raw material and the microwave energy was selected as a heating source for the esterification reaction to reduce time and energy used. By varying microwave power and reaction time, modified cellulose with different DS values was obtained. The esterification reaction was carried out under microwave energy by using lauroyl chloride as an esterifying agent and N, N-Dimethyl-4-Aminopyridine (DMAP) as a catalyst in lithium chloride/N, N Dimethylacetamide (LiCl/DMAc) solvent system. The influences of DS values on physical and mechanical properties of modified cellulose film were investigated.

MATERIALS AND METHODS

Experimental

Materials: Corn husk was obtained from local market in Bangkok, Thailand. Lithium Chloride (LiCl), N, N Dimethylacetamide (DMAc) and N,N-dimethyl-4 aminopyridine (DMAP) and lauroyl chloride were purchased from Fluka Analytical (Sigma-Aldrich,

Germany). Hydrochloric Acid (HCl), ethanol and chloroform were purchased from RCI Lab-Scan Asia Co., Ltd, Thailand. All chemicals and solvents were reagent grade and used without further purification.

Preparation of cellulose powder: Corn husk was soaked in distilled water at 80°C for 1 h and then in 0.5 M NaOH solution at 100°C for 4 h in order to remove lignin and hemicellulose from pulp. After that, the delignified corn husk pulp was bleached by 5% (v/v) H₂O₂ in 0.5 M NaOH at 80°C for 2 h and washed with distilled water until the pH of washing water become neutral. Next, the bleached corn husk pulp was hydrolyzed in boiling 2 N HCl for 4 h. Subsequently, the bleached pulp was filtered, washed with distilled water, dried in an oven at 60°C for 12 h and ground with the agitator for 3 min to obtain cellulose powder.

Esterification and film casting: The obtained cellulose powder was dissolved in 8% (w/v) LiCl/DMAc solution. After that, 0.9 equiv. of DMAP and 10 equiv. of lauroyl chloride were added into cellulose solution and the mixture was esterified in a domestic microwave oven. The microwave power output and reaction time were varied from 80-400 W and 30-180 sec respectively. At the end of esterification reaction, the product was purified by precipitation and washing with ethanol and dried in an oven at 60°C for 12 h. Finally, the modified cellulose films with different DS values were prepared by casting method with chloroform.

Characteriation of modified cellulose powder: The percentage weight increase of modified cellulose powder was evaluated by weighing the cellulose powder before and after modification reaction. It was calculated using the following equation:

$$\%WI = \frac{W_f - W_i}{W_i} \times 100$$

Where:

W_f = The final weight of sample after modification (g)

W_i = The initial weight of sample before modification (g)

Fourier Transform Infrared Spectroscopy (FTIR; Nicolet 7600 FT-IR, Thermo Fisher Scientific, Waltham, MA) was used to characterize the functional group of modified cellulose powder. FTIR spectra were scanned at a frequency range of 4000-400 cm⁻¹ with 32 consecutive scans at a resolution of 4 cm⁻¹. Proton Nuclear Magnetic Resonance Spectroscopy (¹H-NMR; Inova 500MHz, Varian, Vernon Hills, IL) was used to prove the chemical structure of modified Cellulose powder in Deuterated Chloroform (CDCl₃). All of the chemical shifts were reported in parts per million (ppm) using Tetramethyl

Silane (TMS) as an internal standard. In addition, ^1H -NMR Spectroscopy was used to evaluate the DS value by an integration of aliphatic chain protons and cellulosic sugar protons according to the following equation (Satge *et al.*, 2004):

$$\text{DS} = \frac{10I_{\text{CH}_3}}{3I_{\text{sugar}} + I_{\text{CH}_3}}$$

Where:

I_{CH_3} = The integration for the methyl protons of aliphatic chain end group

I_{sugar} = The integration of glucosidic protons

Thermal properties of samples were carried out by thermogravimetric analysis (TGA; TGA/SDTA 815e, Mettler Toledo, Greifensee, Switzerland) under nitrogen atmosphere from 30-800°C with a heating rate of 10°C min⁻¹. Prior to do the experiment, the sample was dried in vacuum oven at 60°C for 24 h. The decomposition temperature (T_d) was reported as the onset of weight loss of heated sample.

Characteriation of modified cellulose film: The wettability of modified cellulose film was analyzed by Contact Angle Measurement (CAM-Plus, Tantec, Schaumburg, IL) according to Tantac's Half-Angle method. A contact angle formed between a water droplet placed upon a sample surface is a measurement of hydrophobicity of the film samples. Liquid droplet (10 μL) was placed at ten different sites on the film surface. The contact angle at each position was measured and the average contact angle value and standard deviation were reported.

Water absorption capacity of modified cellulose film was measured according to the ASTM D570 standard method. The film samples were dried in a vacuum oven at 50°C for 24 h and then cooled in a desiccator before being weighed (W_i). After that, the film samples were fully immersed in container filled with distilled water at room temperature. After 24 h, the soaked films were taken off from the container, removed the surface water by wiping off with a dry cloth and immediately weighed (W_A). Then, these films were repeatedly soaked in distilled water and weighing until the equilibrium was obtained. The result of each film represents the average of five tests. The Water Absorption Capacity (WAC) was calculated as (Guohua *et al.*, 2006):

$$\text{WAC\%} = \frac{W_A - W_i}{W_i}$$

Where:

W_A = Weight of sample at absorbing equilibrium (mg)

W_i = Initial dry weight of sample (mg)

Gloss of film sample was determined by gloss meter (Micro-gloss 60°, BYK-Gardner, Geretsried, Germany) at

23±2°C according to the ASTM D523 standard method. Calibrations of dark standard holder were 95.1 units. Five positions of each film sample were tested to obtain the average gloss values.

Tensile properties such as tensile strength, tensile modulus and percent elongation at break of film samples with dimensions of 10 mm wide, 150 mm long and approximately 250-300 μm thick were carried out by universal testing machine (LR100k, LLOYD, Fareham, UK). Tensile tests were performed according to the ASTM D882 standard method, using a crosshead speed of 10 mm/min, a gauge length of 100 mm and load cell of 50 N.

RESULTS AND DISCUSSION

The esterification reaction of modified cellulose:

Cellulose powder from corn husk was modified in LiCl/DMAc solvent system with DMAP as a catalyst and lauroyl chloride as an esterifying agent under microwave energy at various microwave power and reaction time. The effect of microwave power and reaction time on %weight increase (%WI) of modified cellulose is shown in Fig. 1. The result revealed that %WI of modified cellulose enhanced with increasing microwave power and reaction time until it reached an optimum value and then decreased owing to the degradation of cellulose structure as evidenced by brown color of modified cellulose. Obviously, at 160 W of microwave power, %WI of modified cellulose was increased from 14.0% (at 30 sec) to 50.5% (at 60 sec), 74.0% (at 90 sec), 87.5% (at 120 sec) and 89.5% (at 150 sec) and then it was dropped to 37.0% at 180 sec. Similarly, at 60 sec, %WI was enhanced from 17.5% (at 80 W) to 90.5% (at 240 W), further increased in the microwave power resulted in a decrease in %WI to 71% (at 320-400 W). This result indicated that the excess microwave power and reaction time caused an increase in the reaction temperature resulting in the cellulose degradation.

In addition, microwave power and reaction time also affected on the difference in DS values as displayed in Fig. 2. As seen at 60 sec, the DS values of modified cellulose were increased when increasing microwave power from 80-240 W. After that, when higher microwave power of 320 W and 400 W was applied, the DS values were decreased. As mentioned earlier, the decrease in the DS values were due to the degradation of cellulose structure after it was exposed to the excess microwave power and reaction time. To investigate the effect of DS values on the properties of modified cellulose, three different levels of DS representing low (DS 1.99), medium (DS 2.44) and high (DS 2.73) DS values with appropriate %WI of 67.5, 89.5 and 90.5% were selected. These values were obtained at 90 sec 320 W, 150 sec 160 W and 60 sec 240 W, respectively.

Table 1: Mechanical and physical properties of modified

| Variables | High DS (2.73) | Medium DS (2.44) | Low DS (1.99) |
|-------------------------|----------------|------------------|---------------|
| Tensile strength (MPa) | 8.87±0.26 | 6.35±0.13 | 0.98±0.18 |
| Tensile modulus (MPa) | 670.40±50.39 | 537.91±16.71 | 486.26±151.67 |
| Elongation at break (%) | 4.70±0.42 | 3.62±0.16 | 0.72±0.09 |
| Contact angle (degree) | 121.20±3.72 | 93.97±7.80 | 92.43±9.29 |
| Water absorption (%) | 20.25±4.17 | 22.95±1.89 | 63.70±4.95 |
| Gloss* | 23.14±1.66 | 16.56±3.22 | 6.72±1.47 |

Gloss of standard black calibration = 95.1

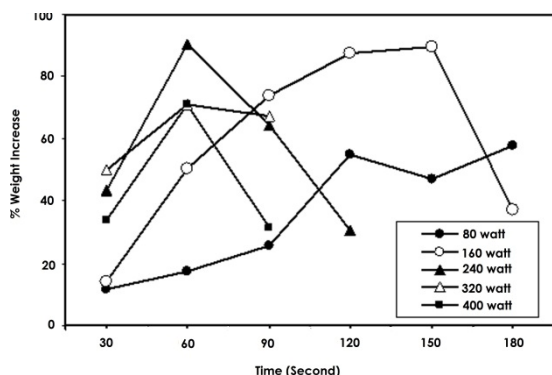


Fig. 1: The relationship between %weight increase and reaction time at different microwave power

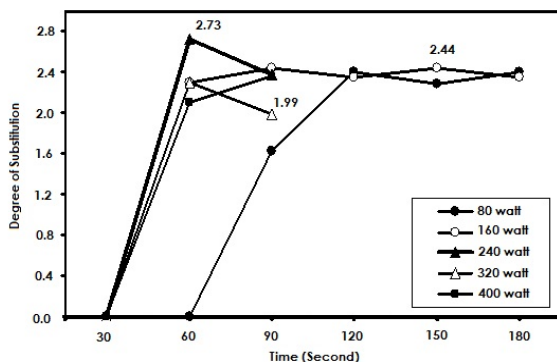


Fig. 2: The relationship between degree of substitution and reaction time at different microwave power

Chemical structure of modified cellulose: The chemical structure of cellulose powder before and after esterification was characterized by FTIR and $^1\text{H-NMR}$ techniques. The FTIR spectra of unmodified and modified cellulose powder are shown in Fig. 3. Before modification, the FTIR spectrum of unmodified cellulose displayed strong broad band centered at 3304 cm^{-1} owing to O-H stretching vibration and a small peak at 1647 cm^{-1} associated with water hydration (O-H-O bending of absorbed water). After modification, the spectra of modified cellulose (spectra B, C and D) show a clear-cut confirmation of esterification by presenting the new ester band at $1735\text{--}1750\text{ cm}^{-1}$ ($\text{C}=\text{O}$ stretching of ester) as well as the increasing in the intensity of methyl band

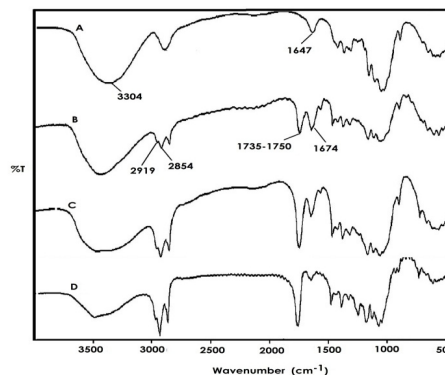


Fig. 3: FTIR spectra of (A) unmodified corn husk (DS = 0) and modified corn husk with (B) low (DS = 1.99), (C) medium (DS = 2.44) and (D) high (DS = 2.73) DS values

(C-H Stretching) at 2854 and 2919 cm^{-1} . The appearance of carbonyl and methyl bands was due to the substitution of long chain aliphatic of lauroyl group at the hydroxyl group of cellulose molecules. Furthermore, the FTIR analysis also indicated the slight decrease in the intensity of the characteristic band at about 3300 cm^{-1} assigned to the cellulose O-H vibration and the enhancement of the hydrophobic character of the modified cellulose as evidenced by the decreasing of the intensity of the band at 1647 cm^{-1} which was assigned to the absorbed water molecule. As the DS value was higher, the intensity of ester band was more intense. In case of the relatively high DS value (spectrum D), the signal for ester band at 1740 cm^{-1} was as strong as the band at $2800\text{--}2900\text{ cm}^{-1}$ for C-H stretching associated with the lauroyl substituents while the reverse trend appeared in the case of a lower DS value (spectrum C) and particularly in the sample with the lowest DS value (spectrum B). The chemical structure of esterified cellulose was also characterized by $^1\text{H-NMR}$ spectroscopy as shown in Fig. 4. Modified cellulose with different degree of substitution values revealed similar proton signals. The peak observed in modified cellulose within $3.46\text{--}4.91\text{ ppm}$ indicated the presence of the cellulose skeleton or anhydroglucose unit protons. The signals between $0.91\text{--}2.34\text{ ppm}$ were attributed to methyl protons of acyl substituent proton groups. These signals were used to evaluate the DS values by an

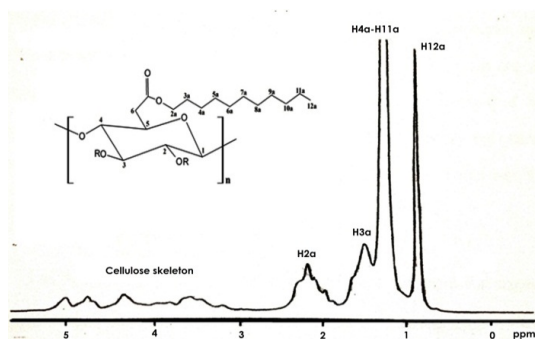


Fig. 4: ^1H -NMR spectrum of esterified cellulose from corn husk with lauroyl chloride as an esterifying agent

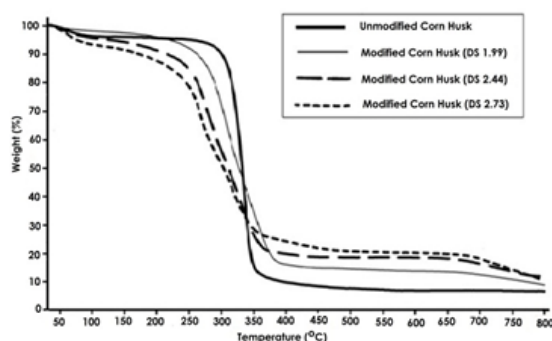


Fig. 5: TGA curves of unmodified and modified cellulose with different DS value

integration of aliphatic chain protons and cellulosic sugar protons. Figure 3 FTIR spectra of (A) unmodified corn husk (DS = 0) and modified corn husk with (B) low (DS = 1.99), © medium (DS = 2.44) and (D) high (DS = 2.73) DS values Fig. 5 ^1H -NMR spectrum of esterified cellulose from corn husk with lauroyl chloride as an esterifying agent

Thermal properties of modified cellulose: Thermal stability of unmodified and modified cellulose was analyzed by TGA. As seen in Fig. 5, the TGA curves of unmodified and modified cellulose appeared two steps of weight loss. The first step occurred around 70°C was attributed to the moisture decomposition in cellulose structure while the second step of weight loss displayed at higher temperature was due to the decomposition of cellulose structure itself. For the unmodified cellulose, this second step appeared around 313°C whereas the modified cellulose exhibited the second step of weight loss at lower temperature around 275, 250 and 192°C for samples having low, medium and high DS values, respectively. Obviously, the modified cellulose had lower thermal

stability than the unmodified one and its thermal stability was also significantly decreased with increasing of the DS values. This result was attributed to the decrease in crystallinity associated with the esterification with lauroyl chloride (Ratanakamnuan *et al.*, 2012; Jandura *et al.*, 2000).

Mechanical properties of modified cellulose film:

Modified cellulose powder was transformed into plastic film by casting method and the thickness of film samples was about 250-300 μm . The mechanical properties of modified cellulose film are reported in Table 1. As shown, the mechanical properties of modified cellulose film in terms of tensile strength, tensile modulus and elongation at break were increased with increasing of the DS values. This result is possibly owing to the increasing amount of long-chain substituent from lauroyl chloride upon increasing the DS values which may be attributed to the partial crystallization, overlapping and entanglement of these side chains. As a result, the modified cellulose film sample having high DS value (2.73) had greater mechanical properties than the ones having lower DS values (Sealey *et al.*, 2002).

Physical properties of modified cellulose film:

The physical appearance of modified cellulose film was investigated in terms of gloss, wettability and water absorption as presented in Table 1. Gloss value of modified cellulose film was determined by gloss measurement. The data showed that the gloss values of modified cellulose films were increased with increasing of the DS value. This is because an increase of DS value corresponding to an increment of acyl substitution in the cellulose structure led to an increasing in the solubility of modified cellulose in chloroform (Ratanakamnuan *et al.*, 2012) as a result, the modified cellulose films shown smooth surface without any defects.

Wettability of films surface determined by contact angle measurement revealed the hydrophobicity of the surface as indicated by increasing of contact angle values. As shown, the contact angle values of modified cellulose films were increased when the DS value was increased which means that the wettability of the films surface was reduced with increasing of the DS value. This result can be explained in terms of the change in hydrophobicity of cellulose surface upon esterification reaction. In general, the nature celluloses are less or inconsiderably hydrophobic than the modified celluloses. The decreasing of hydroxyl groups or increasing of acyl groups in cellulose structure upon esterification reaction lead to the enhancement in the hydrophobicity of modified cellulose. As a result, water droplet is more

difficult to be absorbed onto the cellulose surface. Water absorption of modified cellulose films was found to be significantly decreased with an increasing of the DS values. Similar to gloss value and wettability, the obtained result is due to a decreasing of hydroxyl groups and an increasing of hydrophobicity of the modified cellulose. In other words, the increasing of DS value resulted in high acyl substitution of cellulose structure leading to the high hydrophobicity of modified cellulose.

CONCLUSION

Modified cellulose from corn husk was prepared in LiCl/DMAc solvent system by esterification reaction under varying microwave energy and reaction time using lauroyl chloride and DMAP as an esterifying agent and a catalyst, respectively. The optimum conditions for modification of corn husk which yield high, medium and low Degree of Substitution (DS) values with reasonable %weight increase under microwave heating are 60 sec 240 W (DS 2.73, 90.5%), 150 sec 160 W (DS 2.44, 89.5%) and 90 s 320 W (DS 1.99, 67.5%), respectively. The esterification reaction was successfully confirmed by the FTIR and ¹H-NMR techniques. The FTIR analysis showed three important bands: the presence of ester band at 1735-1750 cm⁻¹ (C = O stretching of ester), the increasing in the intensity of alkyl chain absorption (C-H stretching) at 2800-2900 cm⁻¹ and the decreasing in the intensity of O-H band at 3400-3500 cm⁻¹. The ¹H-NMR spectrum showed peaks between 0.85-2.34 ppm, corresponding to alkyl group of fatty acid chain. Thermal stability of esterified cellulose was lower than unmodified cellulose due to the decrease in crystallinity associated with the substitution of acyl side chain in cellulose structure. Moreover, the thermal stability of esterified cellulose was dependent on the DS value which decreased with the increasing of the DS value. Similarly, the tensile properties of esterified cellulose films were also dependent on the degree of substitution. The tensile strength, tensile modulus and elongation at break were improved with an increasing of the DS values. The gloss values of esterified cellulose films were enhanced when the DS values were increased while the wettability and water absorption of the esterified cellulose films were reduced upon increasing of the DS values which means that the films with high DS values are more hydrophobic than the films having low DS values.

ACKNOWLEDGEMENTS

This research was funded by the Ratchadapisek Sompoch Endowment Fund (2015), Chulalongkorn University (CU-58-034-AM). In addition, the researchers

would like to thank the partial financial support from the Ratchadapisek Sompoch Endowment Fund, Chulalongkorn University (Sci-Super 2014-030).

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