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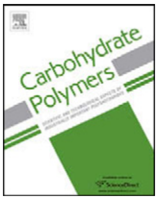

Cellulose esters from waste cotton fabric via conventional and microwave heating

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ABSTRACT

The esterification of cellulose from waste cotton fabric in a *N,N*-dimethylacetamide/lithium chloride solvent system was carried out using different types of fatty acid chloride including butyryl chloride, capryloyl chloride, and lauroyl chloride as esterifying agents, and *N,N*-dimethyl 1-4-aminopyridine as a catalyst under conventional and microwave activation. Microwave esterification was performed under 2.45 GHz with power varying from 90 to 450 W. The optimum conditions for esterification of cotton cellulose with various esterifying agents were investigated in terms of reaction time and temperature to attain appropriate %weight increase and degree of substitution of esterified-cellulose. The degree of substitution, functional group and chemical structure, and thermal stability of cellulose ester powder were characterized by ^{1}H NMR, FTIR, and TGA/SDTA analysis. Morphologies, crystallinity, and solubility of modified cellulose by two different heating methods were compared.

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1. Introduction

Recent concern about the persistence of plastic materials in the environment, either as litter or through landfill disposal of municipal solid wastes, has prompted a rethinking of the use of plastic-based products. Biodegradable plastics are very important as part of the solution to the waste management problem. In several communities, biodegradable plastic has been used in common, short-term applications such as packaging materials. Plastics produced from plant sources could be a good option for replacement of synthetic polymers, if they are biodegradable and have comparable physical properties.

Cellulose is the most common organic polymer, representing about 1.5×10^{12} tons of the total annual biomass production, and is considered as an inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products (Klemm, Heublein, Fink, & Bohn, 2005). Cellulose is a homopolymer consisting of macromolecule of anhydroglucose units. Each unit is joined by β (1-4)-glycosidic linkages. However, cellulose has limitations in its processability. It is neither meltable nor soluble in most common solvents because of the large amount of inter- and intramolecular hydrogen bonding and its high degree of cystallinity in structure. Therefore, the modification or conversion of cellulose to its derivatives renders it processible into various useful forms such as fiber or film. The substitution group can be used to reduce interchain hydrogen bonding and force the chain apart. As a result, cellulose derivatives can be dissolved in common organic solvents and/or melt at relatively low temperatures, making them attractive materials in a wide range of applications (Richardson & Gorton, 2003).

Like simple alcohol, the hydroxyl groups of cellulose can be esterified by reactions with acids or other acylating agents. The esterification of cellulose by fatty acid has been widely studied and used in several industries of food, textile, film, etc. Derivatization of cellulose can be performed under both heterogeneous and homogeneous reaction systems. Normally, cellulose reaction is a heterogeneous reaction in nature, at least initially, due to the two-phase nature of cellulose, which is composed of crystalline and disorder regions. The hydroxyl groups in the disorder region react readily with various reactants, but the crystalline regions, due to their close packing and extensive interchain hydrogen bonding, are not readily accessible, and initial reaction occurs mainly on the surface of crystallites. However, in a homogeneous derivatization process, the cellulose is dissolved in the reaction system. The use of a specific cellulose solvent which disrupts hydrogen bonds results in homogeneous reaction on cellulose (Klemm et al., 2005). The sol-

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vent system consisting of dimethylacetamide and lithium chloride (DMAc/LiCl) seems to be the most promising solvent for a highly suitable media for chemical reaction in which cellulose is dissolved only physically (Klemm et al., 2005). Esterification of cellulose in a DMAc/LiCl solvent system has been studied widely by many researchers (Aburto et al., 1999; Chauvelon et al., 1998, 1999, 2000; Edgar, Arnold, Blount, Lawniczak, & Lowman, 1995; Fang, Sun, Fowler, Tomkinson, & Hill, 1999; Fang, Sun, Tomkinson, & Fowler, 2000; Freire, Silvestre, Pascoal Neto, Belgacem, & Gandini, 2006; Garcia and Vidal, 2000; Gourson et al., 1999b; Grandtner et al., 2005; Hon & Yan, 2001; Luo & Sun, 2006; Marson & El Seoud, 1999; Saikia, Ali, Goswami, & Ghosh, 1995; Sealey, Samaranayake, Todd, & Glasser, 1996; Sealey, Frazier, Samaranayake, & Glasser, 2000; Sun, Fang, & Tomkinson, 2000a, 2000b; Thiebaud & Borredon, 1995; Thiebaud, Borredon, Baziard, & Senocq, 1997; Tosh, Saikia, & Dass, 2000; Vaca-Garcia, Thiebaud, Borredon, & Gozzelino, 1998; Vaca-Garcia & Borredon, 1999; Wang & Tao, 1994; Zhang & McCormick, 1997).

In general, esterification of cellulose given energy by the conventional heating method takes a long time for the reaction to be completed (e.g., 5 h to 1 day or 2 days). In order to minimize energy and control the reaction in view of green chemistry, attempts are being made to make the energy input in chemical systems as efficient as possible. Microwave processing of material has been the focus of attention of numerous researchers in recent years. The effectiveness of using microwaves to promote heating, drying, or melting have been demonstrated in laboratories throughout the world, and some processes have become an industrial reality. In addition, microwave radiation has proved to be a highly effective heating source in chemical reactions. Microwaving can accelerate the reaction rate, provide better yields and uniform and selective heating, achieve greater reproducibility of reactions, and help in developing cleaner synthetic routes. There are several research studies being carrying out on the esterification of cellulose by the microwave heating method (Antova, Vasvasova, & Zlatanov, 2004; Gourson, Benhaddou, Granet, Krausz, Saulnier, & Thibault, 1999a; Joly, Granet, Branland, Verneuil, & Krausz, 2005a; Joly, Granet, & Krausz, 2005b; Loupy, Petit, Ramdani, & Yvanaeff, 1993; Memmi, Granet, Gahbiche, Fekih, Bakhrouf, & Krausz, 2006; Satgé, Granet, Verneuil, Branland, & Krausz, 2004; Satgé, Verneuil, Branland, Granet, Krausz, Rozier, & Petit, 2002;). However, to the authors' knowledge, no work has been performed to investigate the efficiency of the microwave esterification compared with the conventional process. Several factors on the reaction and properties of the cellulose ester, such as reaction time, temperature, and esterifying agent type, are yet to be explored.

Thus, in this work, the synthesis of cellulose ester from waste cotton fabric by conventional and microwave-induced esterification reaction of cellulose was carried out. Before esterification, waste cotton fabric was treated by acid hydrolysis in order to obtain cellulose powder. After that, the esterification reaction of the cellulose powder was carried out by using *N*,*N*-dimethylacetamide/lithium chloride (DMAc/LiCl) as a solvent and *N*,*N*-dimethyl 1-4-aminopyridine as a catalyst. The cellulose solution was esterified by three types of esterifying agent (butyryl chloride, capryloyl chloride, and lauroyl chloride) under conventional heating (hot plate) and microwave heating methods. The optimum conditions for esterification in terms of exposure time, temperature, and microwave power were investigated and evaluated by the percentage weight increase (%WI) and the degree of substitution (DS). The effects of esterification reaction parameters including fatty acid chloride chain length of the esterifying agent and heating method on the properties of the modified cellulose including chemical structure, thermal properties, morphology, crystallinity, and solubility were analyzed.

2. Experimental procedure

2.1. Materials

Cellulose used in this work was waste bleached plain woven cotton fabric provided by a local textile factory. *N*,*N*-dimethylacetamide (DMAc, 98%, Fluka) and anhydrous lithium chloride (LiCl, ≥98%, Fluka) were used as the solvent, while *N*,*N*-dimethyl 1-4-aminopyridine (DMAP, 98%, Fluka) was applied as a catalyst. The esterifying agents were butyryl chloride (≥98%, Fluka), capryloyl chloride (99%, Aldrich), and lauroyl chloride (≥97.5%, Fluka). Hydrochloric acid (HCl, J.T.Baker) was used for hydrolysis and ethanol (99.7–100%, V/V%, BDH AnalaR) was used as the precipitating agent. These chemicals were used without further purification.

2.2. Preparation of cellulose powder

Cotton powder was prepared from waste cotton fabric by acid hydrolysis. First, the waste cotton fabric was cut into approximately 2 cm × 2 cm and then heated and stirred in boiling 2.5 N HCl for 2 h. At the end of the hydrolysis period, the cotton powder was filtered and washed with distilled water until the filtrate was neutral. The obtained cellulose powder was dried in an oven at 60 °C overnight.

2.3. Esterification of cellulose powder

Preparation of cellulose solution was carried out by adding 2 g of cellulose powder into 50 ml of 8% (w/v) LiCl/DMAc solvent system and stirred at 60 °C until completely dissolved. The esterifying agent (10 equiv) and DMAP (0.9 equiv) as a catalyst were added into the cellulose solution (Satgé et al., 2002). The mixture was esterified under two heating methods: conventional heating and microwave heating. For conventional heating, the temperature and reaction time were varied in the ranges of 30–100 °C and 2–24 h, respectively. For microwave treatment, the mixture was activated in a domestic microwave oven (LG Intellowave MS-2643C) under microwave power and irradiation time of 90–450 W and 1–3 min, respectively. Finally, the esterified cellulose was isolated from solution as powder by precipitation, and washed several times with ethanol before further characterization.

2.4. Cellulose ester characterization

Determination of the percentage of weight increase (%WI) was calculated as follows:

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

where W_i is the weight of dried initial cellulose sample (g); W_f is the weight of modified cellulose sample (g). The degree of substitution (DS) of esterified cotton was evaluated by ^{1}H NMR investigation of aliphatic chain protons and cellulosic sugar protons (Satgé et al., 2004). The functional group and chemical structure were examined by FTIR spectroscopy using a Perkin Elmer Spectrum One. Thermogravimetic analysis was performed with Mettler Toledo TGA/SDTA 851^e at a heating rate of 10 °C/min from 30 °C to 800 °C under nitrogen atmosphere. The morphologies of cotton cellulose and cotton ester were investigated using a scanning electron microscope (JEOL: JSM-6400). The solubility test of modified cellulose was determined at 4% (w/v) concentration of different solvents including acetone, toluene, chloroform, *N*,*N*-dimethyl 1–4 acetamide (DMAc), and tetrahydrofurane (THF). X-ray diffraction (XRD) was carried out using a PW 3710 Philips diffractometer with CuKα radiation (λ = 0.1542 nm) in a sealed tube operated at

40 kV and 30 mA. The diffraction patterns were obtained between $2\theta = 10–50^\circ$, in steps of 0.01°, with a scanning speed of 5.0 s/step.

3. Results and discussion

3.1. Chemical structure by FTIR technique

The esterification reaction of cellulose carried out under homogeneous condition in DMAc/LiCl solvent system using DMAP as a catalyst is presented in Fig. 1(a). The functional group and chemical structure of esterified-cellulose were examined by FTIR. The comparison of FTIR spectra of cotton cellulose before and after esterification and the effect of fatty acid chloride chain length on the chemical structure of modified cellulose are presented in Fig. 1(b). The spectrum of raw cellulose (spectrum NC) exhibited the principle strong broad band centered at 3304 cm^{-1} which is attributed to O–H stretching vibration and with a peak at 1647 cm^{-1} which is related to the water hydration (H–O–H bending of adsorbed water). The IR spectra of cellulose ester show different bands from unesterified cellulose one. These spectra (spectra CB, CC, and CL) provide an evidence of esterification by the existence of the ester carbonyl group (C=O) at 1740 cm^{-1}. The occurrence of strong intensity peak at around 2800–2900 cm^{-1} in the spectra is attributed to methyl and methylene C–H stretching associated with acyl substitution, while the intensity of the characteristic band at about 3300 cm^{-1} as assigned to the cellulose O–H vibration decreased. These similar spectroscopic profiles reveal a similar structure of esterified celluloses, all of them containing an intense ester carbonyl band at 1740 cm^{-1}. However, there are some differences among them. As the carbon chain length of the acyl group increases from a four-carbon chain (spectrum CB) to a twelve-carbon chain (spectrum CL), the signals of the methyl and methylene C–H band around 2800–2900 cm^{-1} become more intense with increasing carbon chain length. The band around 710 cm^{-1} attributed to the CH_2 vibrations in the sample bearing carbon chains with more than four CH_2 groups is additional proof of the successful esterification for cotton caprylate (spectrum CC) and cotton laurate (spectrum CL). This band emerged in the spectrum of cotton caprylate and cotton laurate but disappeared in the spectrum of cotton butyrate (spectrum CB).

In this study, two types of heating source were applied to conduct esterification reactions, namely conventional heating from a hotplate and microwave energy. The influence of the heating method on the chemical structure of esterified cellulose was also characterized. Both heating sources revealed similar FTIR profiles for each modified cellulose. There was no difference in the chemical structure of the esterified cellulose between conventional and microwave heating. This means that microwave energy can activate the esterification reaction and, similar to conventional heating method, it does not change the chemical structure of the esterified cellulose. A report has described that the energy in the microwave photon (0.037 kcal/mol) is very low, compared to the typical energy required to break a molecular bond (80–120 kcal/mol). Therefore, microwave excitation of molecules does not affect the structure of an organic molecule, and interaction is purely kinetic (Taylor, Atri, & Minhas, 2005).

3.2. Optimum condition for esterification reaction of cotton cellulose powder under conventional and microwave heating

The optimum condition for the esterification reaction of cellulose powder from waste cotton fabric with various esterifying agents including butyryl chloride, capryloyl chloride, and lauroyl chloride was investigated in terms of irradiation time and temperature to attain appropriate %weight increase (%WI) and degree of substitution (DS) of cellulose ester after esterification.

For conventional heating, Fig. 2(a) illustrates the influences of reaction time and temperature on (a) %WI and (b) DS of cotton butyrate (C_4), respectively. In general, %WI of cellulose butyrate gradually increased with increasing reaction time and temperature, then tapered and decreased after reaching the maximum value. From Fig. 2(a), at the reaction temperature of 30 °C, %WI of cotton butyrate increased continually with increasing reaction time, while at higher reaction temperatures of 60–100 °C, after reaching its optimum value, the %WI of cotton butyrate started to fall off with increasing reaction time. The DS value displayed a similar trend as shown in Fig. 2(b). At low reaction temperatures of 30–80 °C, the DS of cotton butyrate increased in the early period of reaction time, thereafter, the degree of substitution decreased. However, at 100 °C, the DS of cotton butyrate started to fall off from the beginning as reaction time increased. The reason for this enhancement of the esterification reaction by increasing temperature and time was probably because high temperatures can cause swelling of cellulose and also increase the diffusion rate of acid chloride significantly. In addition, a long reaction time could allow the esterifying agent to react and substitute with the free hydroxyl group of cellulose, resulting in the higher DS value. On the contrary, the decrement in %WI and the DS at the excess temperature and reaction time could be because of cellulose degradation. The decrement of DS also could be explained by the possible competition between the esterification reaction and the partial hydrolysis of the ester group formed, i.e., by the presence of moisture in the reaction medium. From the result, the esterification of cotton cellulose with butyryl chloride under conventional heating should be conducted at 100 °C for 2 h to achieve an appropriate %WI (84.8) and the maximum DS (2.94) of cotton butyrate without the degradation of cellulose, along with the reasonable energy and time used. The optimum conditions for esterification of cotton cellulose with different esterifying agents under conventional heating were varied case by case as summarized in Table 1.

Fig. 2(c and d) shows the influences of microwave power and irradiation time on (c) %WI and (d) DS of cotton laurate (C_{12}) esterified under microwave energy. The percent weight increase (%WI) of cotton laurate increased with increment of microwave power and reaction time until it reached the optimum value and then dropped. For example, at the microwave power of 180 W, %WI of cotton laurate increased from 40.5% (at 60 s) to 66.5% (at 90 s) and up to 112.0% (at 180 s) and then dropped to 20.0% at the reaction time of 210 s, respectively. It was also observed that when the higher microwave power was applied, a shorter reaction time was required to obtain maximum %WI. The optimum reaction time for samples esterified at 180, 270, 360, and 450 W were 180, 150, 120, and 60 s, respectively. A similar trend of the DS was observed as shown in Fig. 2(d). The DS of cotton laurate increased with the increment of microwave power and reaction time. At a low microwave power level, DS was improved up to critical reaction time and then decreased afterwards. Whereas at a higher microwave power level, reaction times longer than 60 s seemed to yield less DS value. The drop of the DS and %WI could be explained by the observation that the surplus reaction time and microwave power absorbed can cause high temperature, leading to the cellulose degradation which was confirmed by a brown color of cotton laurate. In general, the data showed that the condition that gave the maximum DS was not the same as the one that yielded the highest %WI. However, in this study, the optimum condition selected was mainly based on the highest DS. Therefore, when considering energy and time saving together with the reasonable %WI (60%) and the maximum DS (2.69), the esterification reaction of cotton cellulose with lauroyl chloride under microwave heating should be performed under 180 W for 150 s. The optimum conditions for esterification cotton cellulose

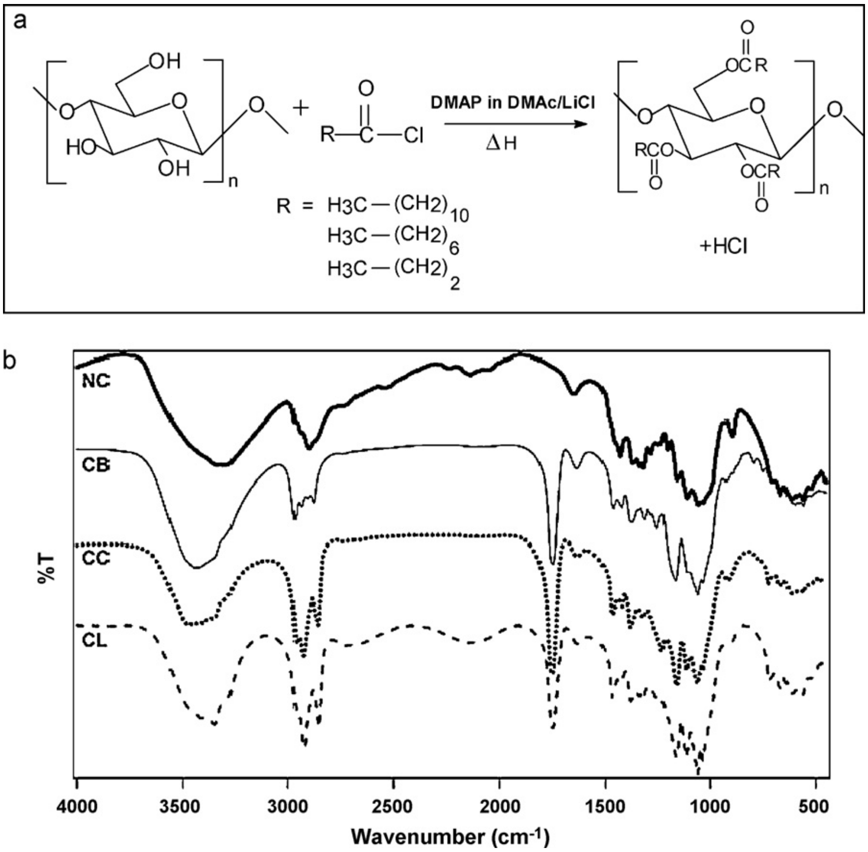

Fig. 1. (a) An overview of cellulose esterification with fatty acid chloride and (b) FTIR spectra of native cotton cellulose (NC), cotton butyrate (CB), cotton caprylate (CC) and cotton laurate (CL).

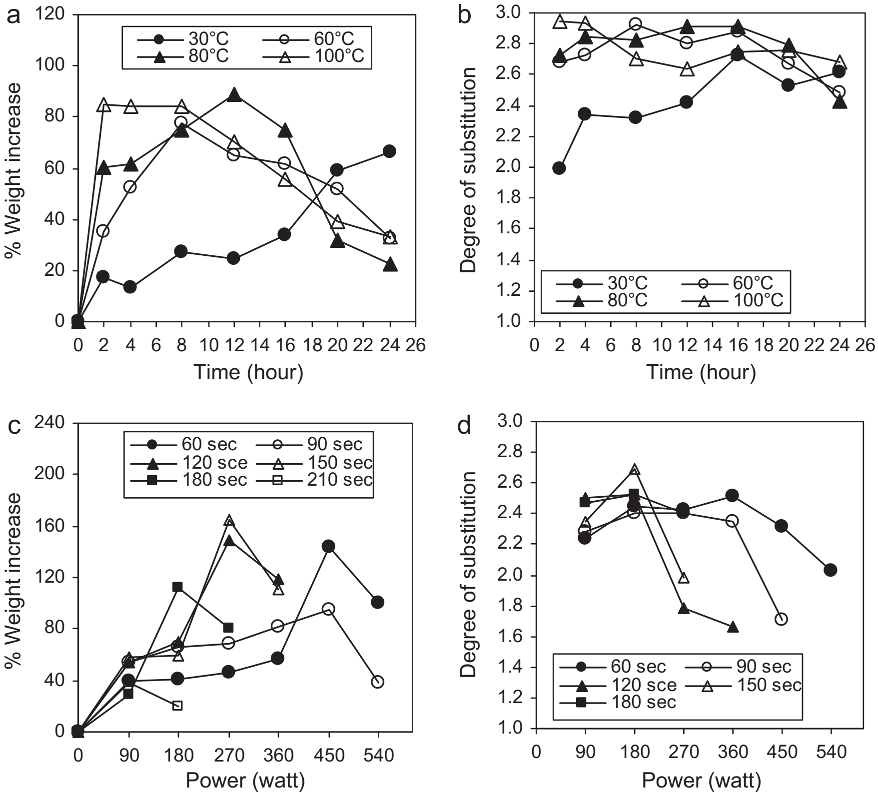

Fig. 2. The effects of reaction time and temperature on (a) %WI and (b) DS of cotton butyrate (C4) under conventional heating and the effects of microwave power and irradiation time on (c) %WI and (d) DS of cotton laurate (C12) under microwave heating.

Table 1
The optimum conditions for esterification of cotton cellulose with butyryl chloride (C_4), capryloyl chloride (C_8), and lauroyl chloride (C_{12}) under conventional heating and microwave heating and final temperatures in the microwave heating method.

Sample	Conventional heating				Microwave heating				
	T (°C)	Time (h)	%WI	DS	Power (W)	Time (s)	%WI	DS	T_{final} (°C)
Cotton+C4	100	2	84.8	2.94	360	60	65	2.41	122
Cotton+C8	80	12	183.5	2.74	270	60	81.5	2.44	120
Cotton+C12	60	12	175	3.00	180	150	60	2.69	115

with other esterifying agents under microwave energy are listed in Table 1.

3.3. Effect of fatty acid chloride chain length on %WI and DS

Fig. 3 presents the influence of the fatty acid chloride chain length on %WI and DS values of esterified cotton, under conventional heating. As seen, higher %WI of cellulose ester was obtained with an increase in the number of carbon atoms in the acyl group of esterifying agent (%WI $C_{12} > C_8 > C_4$). The increment of %WI for each cellulose ester sample with an increase of fatty acid chain length was due to the grafting of acyl substituents. The longer fatty acid represented the higher molecular weight of acyl group which can cause the higher %WI of cellulose ester samples. Therefore, when using lauroyl chloride which has higher molecular weight (218.77 g/mol) than the other two acid chlorides (the molecular weight of capryloyl chloride and butyryl chloride are 162.5 g/mol and 106.5 g/mol, respectively) as an esterifying agent, the higher %WI of esterified product was obtained. For the DS of cellulose ester, the result revealed that the DS values of cellulose butyrate, cellulose caprylate, and cellulose laurate were nearly equal. Generally, the fatty acid chain length had no significant effect on the DS of esterified cellulose, although cellulose laurate gave a slighly higher value. This means that the reactivity of butyryl chloride, capryloyl chloride, and lauroyl chloride as the esterifying agent was comparable. The effect of fatty acid chloride chain length on %WI and DS values of modified cotton under microwave heating is displayed in Fig. 4. The results were consistent with the results from conventional heating. The %WI of esterified cellulose increased with the fatty acid chain length whereas the DS values were not affected much.

The results are in good agreement with the conventional esterification of various cellulose reported by several research groups (Gourson et al., 1999b; Sun et al., 2000a; Vaca-Garcia et al., 1998). Gourson et al. reported that %WI and DS were increased with the increasing fatty acid chain length in the maize brane cellulose esterified with hexanoyl chloride (C_6), octanoyl chloride (C_8) and lauroyl chloride (C_{12}), respectively. Vaca-Garcia et al. studied esterification of cellulose from various agricultural wastes with saturated fatty acids including *n*-octanoic to *n*-octadecanoic (C_8 to C_{18}). They reported that, when passing from $n = 8$ to $n = 12$, the %WI values increased slightly because the molecular weight of the substituent increased while the DS values were relatively constant. However, with the longer fatty acid ($n > 12$), particularly with stearic acid ($n = 18$), the DS values fell so abruptly that %WI diminished even if the fatty substituent was heavier. Sun et al. found that percent yield of esterified hemicellulose from rye straw increased from 70.2% to 87.8% and DS rose from 1.15 to 1.65 when the carbon atoms of fatty acid chloride increased from 10 to 18, and then diminished when the carbon atom increased from 18 to 20.

Nevertheless, these results were different to the esterification of oak wood sawdust with fatty acid chlorides (C_8, C_{10}, C_{12}, C_{14}, C_{16}, and C_{18}) in the absence of organic solvents investigated by Thiebaud & Borredon (1995) and Thiebaud et al. (1997). Less weight increase was obtained with an increase of carbon atoms in the corresponding acyl group. This contrast phenomenon can be explained by two factors: (1) the diffusion of acid chloride into the cellulose sample is more difficult with an increase in the molecular volume of the acyl group; (2) when carbon chains are longer, the acyl group inductive effect becomes greater; therefore reactivity decreases. Recently in 2006, Freire et al. (2006) also reported the contrary results to the data in this study such that the extent of esterification of Eucalyptus fiber in heterogeneous system decreased considerably with the fatty acid chain length (C_6, C_{12}, C_{18}, and C_{22}) because reactivity of fatty acyl chlorides decreased with the increasing of chain length. The contradictory result may be due to the use of fatty acid chloride as an esterifying agent and also from the esterification solvent system. The addition of longer chain length (carbon atoms > 12) as compared to this work (C_4, C_8, C_{12}) as an esterifying agent leads to a greater size of substituent and, consequently, a pronounced steric hindrance that subdues an increase in the esterification reaction. As a result, the decrement of %WI and DS of esterified cellulose occurred. The esterification solvent system may be another synergetic effect that caused the discrepant result. In those cases, the esterification reaction was conducted in a heterogeneous (solvent-free) system whereas, in the case of this study, DMAc/LiCl was used as a solvent with the assistance of DMAP as a catalyst. The use of an effective solvent system and catalyst promoted the swelling of cellulose, and hence increased the number of hydroxyl groups available for esterification, reduced the steric hindrance, and increased the diffusion and adsorption of reactants onto the cellulose molecule. Consequently, the higher esterified cellulose products with a high DS were obtained.

3.4. Effect of heating method on %WI and DS

Table 1 summarizes optimum %WI and DS values of cotton cellulose esterified with butyryl, capryloyl, and lauruyl chloride from both heating methods. It can be seen that microwave activation led to considerably lower values of %WI than those from conventional heating, or approximately 1.5–3 times. Nevertheless this result did not reflect significantly on the substitution of fatty acid chloride on hydroxyl group of cellulose. The DS values of cellulose esterified under microwave heating were 10–20% slightly lower than those obtained from conventional heating. In contrast to the results published by Memmi et al. (2006), microwave-assisted acylation of olive pomace and barley bran gave better yields than classical heating but a comparable degree of substitution value. They mentioned that the higher yields could be explained by the microwave stabilization of a transition state that has more polarity than ground state reactants.

The lower % WI value (product yield) of microwave-assisted cellulose esterification in this study may be because microwave radiation induced volumetric heating that led to overabundant heat occurring in the esterification system and caused cellulose degradation. As seen in Table 1, cellulose solutions in the microwave esterification systems experienced higher temperatures than those in the system using a hotplate as a heating source, even though the shorter time was used. However, when considering energy and time savings along with the acceptable product yield (%WI) of 60–82% with DS values of 2.41–2.69, it can be concluded that microwave is another effective heating source to assist cellulose

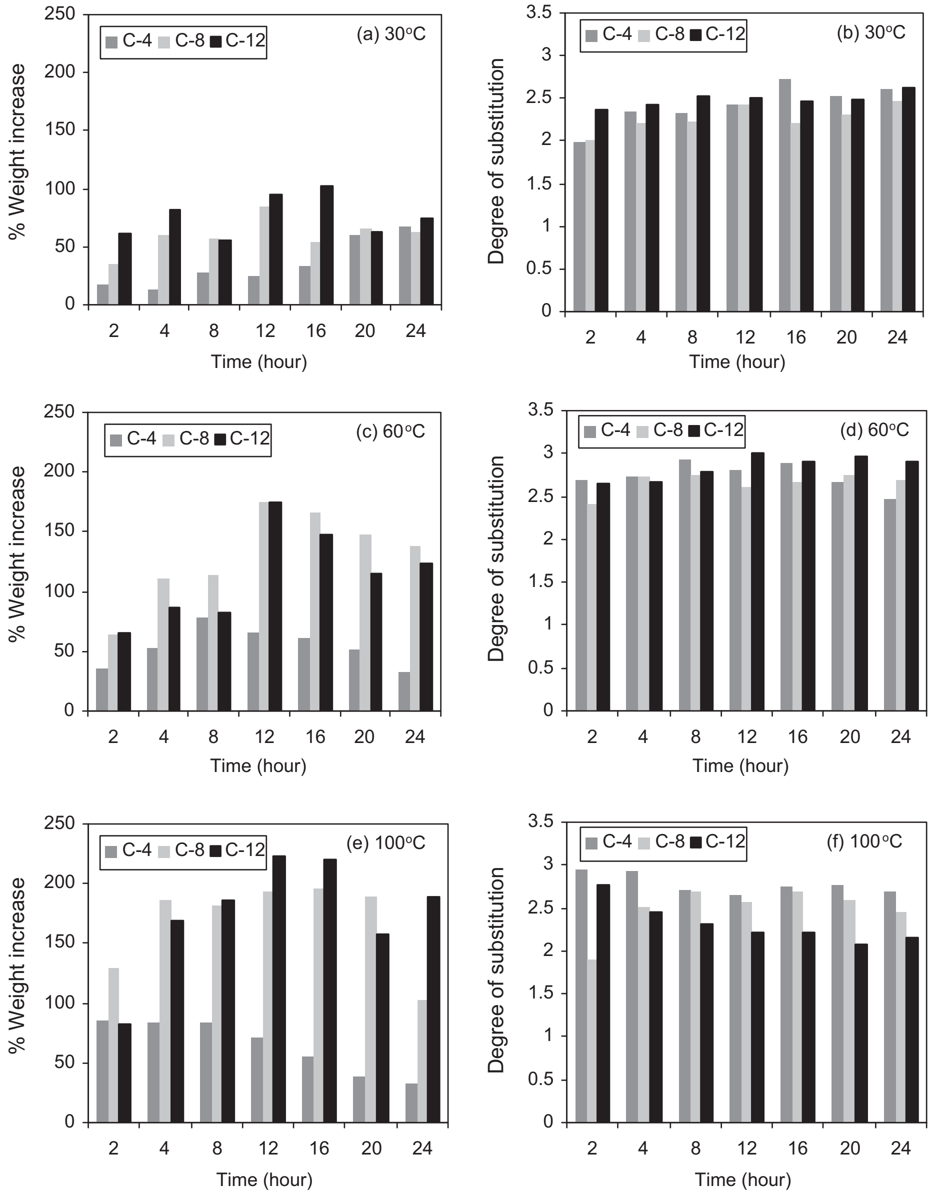

Fig. 3. The effect of fatty acid chloride chain length on %WI and DS of modified cotton under conventional heating at (a and b) 30 °C, (c and d) 60 °C, and (e and f) 100 °C.

esterification. By using microwave irradiation, the reaction time is significantly diminished from 2 to 12 h to less than 3 min, and consequently the energy consumed for the reaction is greatly reduced.

3.5. Thermal properties

The effect of fatty acid chloride chain length as an esterifying agent on thermal stability of cellulose ester is demonstrated in Fig. 5(a). The TGA curve of unesterified cotton cellulose presents two decomposition stages. The first one around 70–90 °C with a total weight loss of approximately 3.4% is due to the absorbed water in cellulose structure. The second stage appearing at a higher temperature of around 328 °C is due to the decomposition of cellulose with the 72% of total weight loss. After esterification under conventional heating, all esterified cellulose started to decompose at a temperature substantially lower than native cellulose. This behavior is attributed to the decrease in crystallinity associated with the substitution of the fatty acid chloride chain in the cellulose structure. Similar results were reported by Jandura, Riedl, and Kokta (2000) and Freire et al. (2006) for long chain organic acid cellulose ester of 11 and 18 carbon atoms and in the range of 6–22 carbon atoms, respectively. They stated that the thermal stability of cellulose fibers was affected by crystalline order, which decreased after substitution of hydroxyls groups with fatty acid chain. Therefore, the thermal stability of cellulose ester is lower than that of original cellulose. TGA curves of cotton butyrate, cotton capryrate, and cotton laurate exhibited a significant single weight loss stage due to the degradation of cellulose itself. No decomposition stage of absorbed water was observed, confirming that the esterified cotton was more hydrophobic than the microcrystalline cotton cellulose before esterification. The thermal degradation of cellulose ester was influenced by the fatty acid chain length such that it decreased with increasing chain length of fatty acid chloride. As shown in Fig. 5(a), the Td onset of cotton butyrate (C_4) was about 293 °C whereas the cotton capryrate (C_8) and cotton laurate (C_{12}) revealed the Td onset around 287 °C and 270 °C, respectively. The shifting of Td onset towards lower temperature indicated the decrease in thermal stability of cellulose ester due to the decrease in crystallinity associated with the substitution of longer length of acyl group. Lauroyl chloride which has the longest chain of carbon atoms (12 carbon

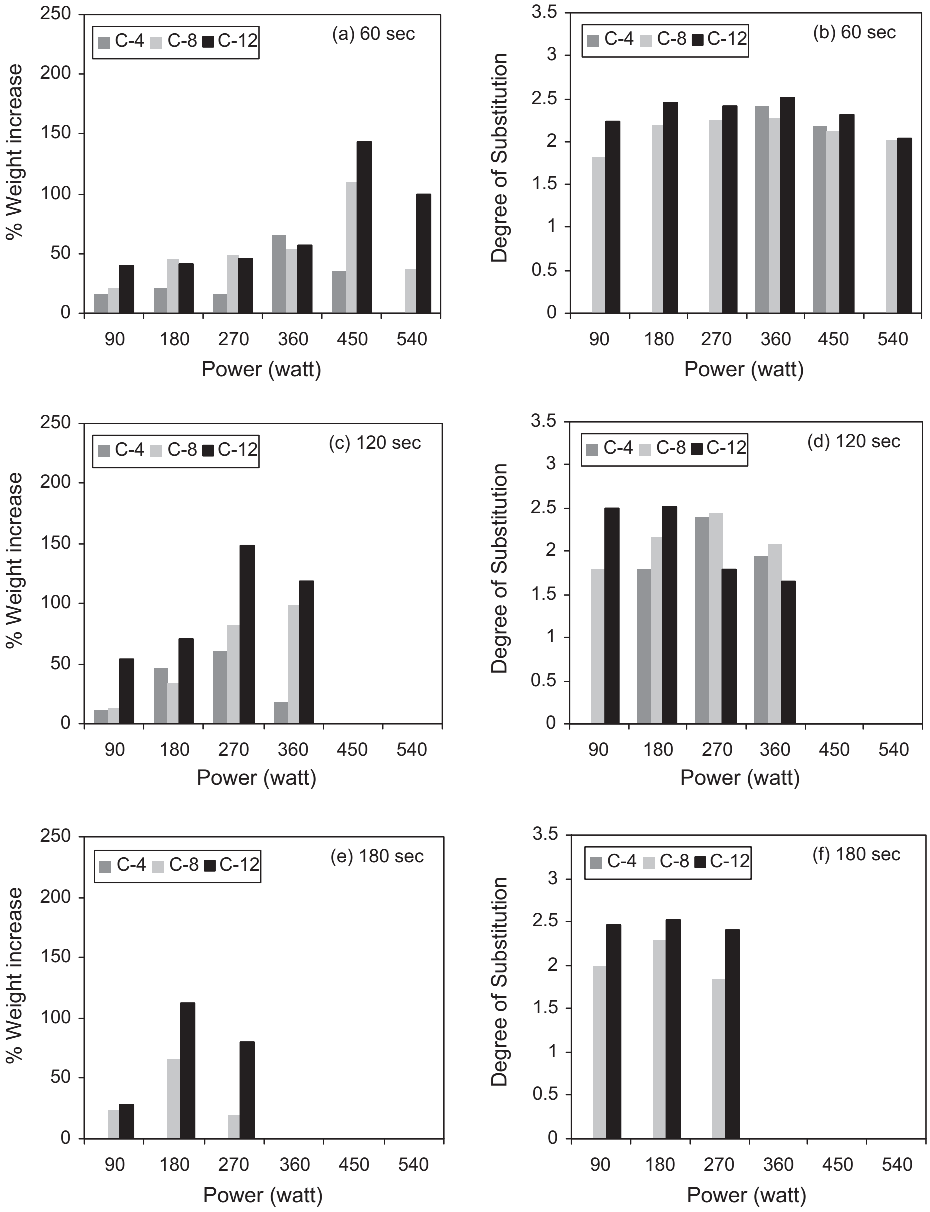

Fig. 4. The effect of fatty acid chloride chain length on %WI and DS of modified cotton under microwave heating for (a and b) 60 s, (c and d) 120 s, and (e and f) 180 s.

atoms) can reduce the crystallinity of cellulose structure more than capryloyl and butyryl chloride; as a result, lesser thermal stability was obtained. These results are in good agreement with work reported by Freire et al. (2006). Their results disclosed that the thermal stability of esterified cellulose decreased with the increasing of fatty acid chain length from 6 to 12 carbon atoms. Nevertheless, when the length of fatty acid was extended to 18 carbon atoms, a small increase in the degradation temperature was found. This behavior was explained by the formation of a new order region associated with the crystallization of the long aliphatic side chains.

Degradation temperature profiles of conventional and microwave esterified cellulose, cotton laurate (C_{12}), with the comparable DS value are characterized (not shown). The result exhibited that both cellulose ester displayed a similar step change of %weight loss as temperature increased. A little higher Td onset of conventional esterified cellulose (270–320 °C) as compared to that of microwave processed one (260–290 °C) was found. A total weight loss of 80.5–81.6% was observed at these temperatures. This result implied the lower thermal stability of the microwave esterified products. This was probably due to a shorter esterification time during the microwave process that led to a lesser crystallinity.

3.6. *Morphological studies*

After acid hydrolysis of waste cotton fabric, the fabric became a white powder as observed by the naked eye. The appearance in microscopic scale revealed a different structure as illustrated in Fig. 5(b–d). Morphology of unesterified cotton revealed short fiber shapes with a smooth surface of approximately 10 μm in diameter (Fig. 5(b)). After esterified with lauroyl chloride, the rough surface and larger structure were obtained for both cotton esterified under conventional and microwave heating (Fig. 5(c and d)). These results indicated that the acyl substitution of lauroyl chloride as an esterifying agent led to an aggregation of acyl substituent groups on the cotton surface. It was noted that the deposition of acyl groups on microwave esterified cotton was less than conventional case.

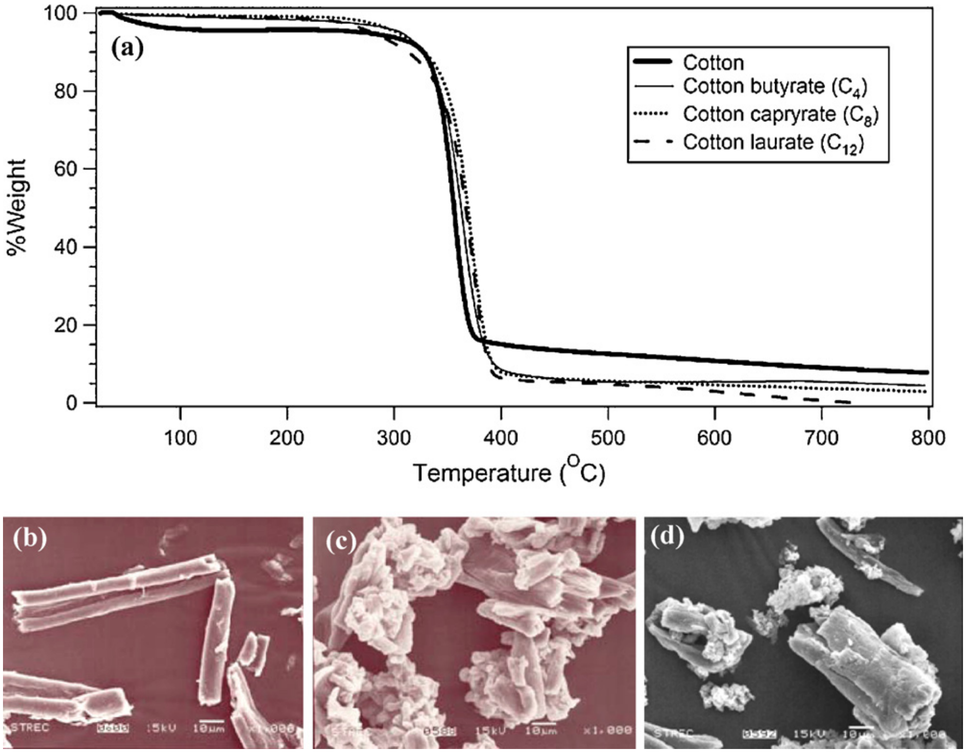

Fig. 5. (a) TGA curves of unesterified cotton, cotton butyrate, cotton capryrate, and cotton laurate and SEM micrographs of (b) cotton cellulose before esterification, (c) cotton esterified with lauroyl chloride using conventional heating, and (d) cotton esterified with lauroyl chloride using microwave-heating, respectively.

This reflected well with the lower %WI value of microwave-assisted cellulose esterification in this study.

3.7. Solubility test

The solubility of esterified cotton in various organic solvents was investigated with a concentration of 4% (w/v) and results are summarized in Table 2. It was found that the native cellulose was insoluble in either organic solvents or water. However, due to the abundance of the hydroxyl group along the cellulose chain, it can absorb moisture reversibly and has the tendency to form intra- and intermolecular hydrogen bonds with the adjacent cellulose chain, resulting in the formation of crystals. These crystals or crystallites make cellulose insoluble in normal aqueous solutions as well as in common organic solvents. In general, the introduction of hydrophobic acyl groups into the molecular structure of cellulose leads to the destruction of highly organized hydrogen-bonding of cellulose structures and, thus, was expected to alter its solubility

Table 2
Solubility of cotton cellulose and esterified cotton at different DS values.

Heating method	Sample	DS value	Solvent				
			A	To	C	D	T
–	Cotton	DS = 0	–	–	–	–	–
Conventional heating	Cotton butyrate	High (DS = 2.94)	++	++	++	++	++
		Medium (DS = 2.48)	++	++	++	++	++
		Low (DS = 1.99)	+	+	+	+	+
	Cotton capryrate	High (DS = 2.75)	–	+	++	+	+
		Medium (DS = 2.31)	–	+	++	+	+
		Low (DS = 1.89)	–	++	++	++	++
	Cotton laurate	High (DS = 3.0)	–	+	++	+	+
		Medium (DS = 2.53)	–	+	++	+	+
		Low (DS = 2.15)	–	++	++	++	++
Microwave heating	Cotton butyrate	High (DS = 2.41)	+	++	++	++	++
		Medium (DS = 1.79)	+	+	+	+	+
		Low (DS = 0.94)	–	–	–	–	–
	Cotton capryrate	High (DS = 2.44)	–	++	++	++	+
		Medium (DS = 1.90)	–	+	+	+	+
		Low (DS = 1.45)	–	+	+	+	+
	Cotton laurate	High (DS = 2.69)	–	+	++	+	+
		Medium (DS = 2.24)	–	+	++	+	+
		Low (DS = 1.66)	–	++	++	++	++

A: acetone, To: toluene, C: chloroform, D: *N*, *N*-dimethyacetamide, T: tetrahydrofuran.
(– insoluble, (+) partially soluble, (++) soluble.

properties. As listed in Table 2, the esterified cotton was dissolved in each solvent differently depending on fatty acid chloride chain length and degree of substitution. Cotton butyrate (C_4) is highly soluble in both polar (acetone) and non-polar (toluene, chloroform *N*,*N*-dimethyacetamide (DMAc), and tetrahydrofuran (THF)) solvents; while cotton capryrate (C_8) and cotton laurate (C_{12}) are moderately to highly soluble in those non-polar solvents. This is probably due to the increase in hydrophobicity or decrease in its polarity caused by acyl substituent of those esterified cotton (C_8 and C_{12}) resulting in the decrease in solubility under polar solvents as acetone. The solubility of esterified-cellulose prepared from both conventional and microwave heating methods were similar.

For the degree of substitution, as expected, it was found that the solubility of cotton butyrate (C_4) increased with increasing degree of substitution; unlike the solubility of cotton capryrate (C_8) and cotton laurate (C_{12}) that decreased with increasing degree of substitution. This may be attributed to the partial crystallization and overlapping of C_8 and C_{12} side chains. Even though the substitution of acyl group reduced the crystallinity in cellulose structure and improved their solubility; the greater substitution with the long-chain acyl group can cause the crystallization of the long-side chains or the so-called side-chain crystallization, resulting in the decrease in solubility of cotton capryrate (C_8) and cotton laurate (C_{12}).

3.8. *X-ray diffraction pattern*

X-ray diffraction measurements were carried out to prove if chemical modification altered the crystallinity of cellulose. X-ray diffraction patterns for unmodified and modified cotton cellulose are shown in Fig. 6(a). The unmodified cotton cellulose powder exhibited main crystal planes of the crystalline cellulose I structure with the main characteristic peaks at around $2\theta = 14.5^\circ$, 16.0°, 22.5°, and 33.5°. These signals were assigned to the diffraction planes 101, 101, 002, and 040, respectively (Matsumura, Sugiyama, & Glasser, 2000). After modification by using either microwave or conventional heating methods, the X-ray diffraction patterns of the modified cotton cellulose showed a decrease and broadening in the intensities of the peaks referred to 101, 101, and 002 planes ($2\theta = 14.5^\circ$, 16.0°, and 22.5°) while the intensity of the corresponding signal of the 040 plane was decreased for the microwave modified cellulose and disappeared in the case of conventional modified cellulose ($2\theta = 33.5^\circ$). In addition, the XRD patterns noticeably revealed the new diffraction peak at around $2\theta = 20.0^\circ$, which was commonly assigned to the less ordered or amorphous region of the cellulose chains (Freire et al., 2006). These results are in agreement with the thermal stability and solubility results that the crystallinity of modified cotton cellulose was decreased by the substitution of fatty acid chloride chain in cellulose structure via the esterification reaction.

The effect of fatty acid chain length on the crystallinity of cellulose structure is exhibited in Fig. 6(b). The decrystallization of cellulose structure by the esterification reaction was dependent on fatty acid chain length. As the fatty acid chain length increased from C_4 to C_8, the intensities of four crystalline peaks of cellulose I structure decreased, while the intensity of the peak around $2\theta = 20.0^\circ$ attributed to the amorphous region gradually increased. However, as the length of fatty acid chain increased up to C_{12}, the signals represented the crystalline cellulose I structure became prominent. This phenomenon could be described by the formation of new-ordered structure associated with the crystallization of aliphatic chain as described in Section 3.5. Even though the substitution of acyl group reduced the crystallinity in cellulose structure, however, the greater substitution with long chain acyl group can make the crystallization of the long side chains (C_{12}) or the so-called side-chain crystallization, as attested by the solubility results previously discussed. Similar result can also be observed in the work of Sealey et al. (1996) and Jandura et al. (2000). They found the existence of side-chain crystallization in fully esterified cellulose fatty esters when the substituent size reached a length of C_{10} or C_{12}.

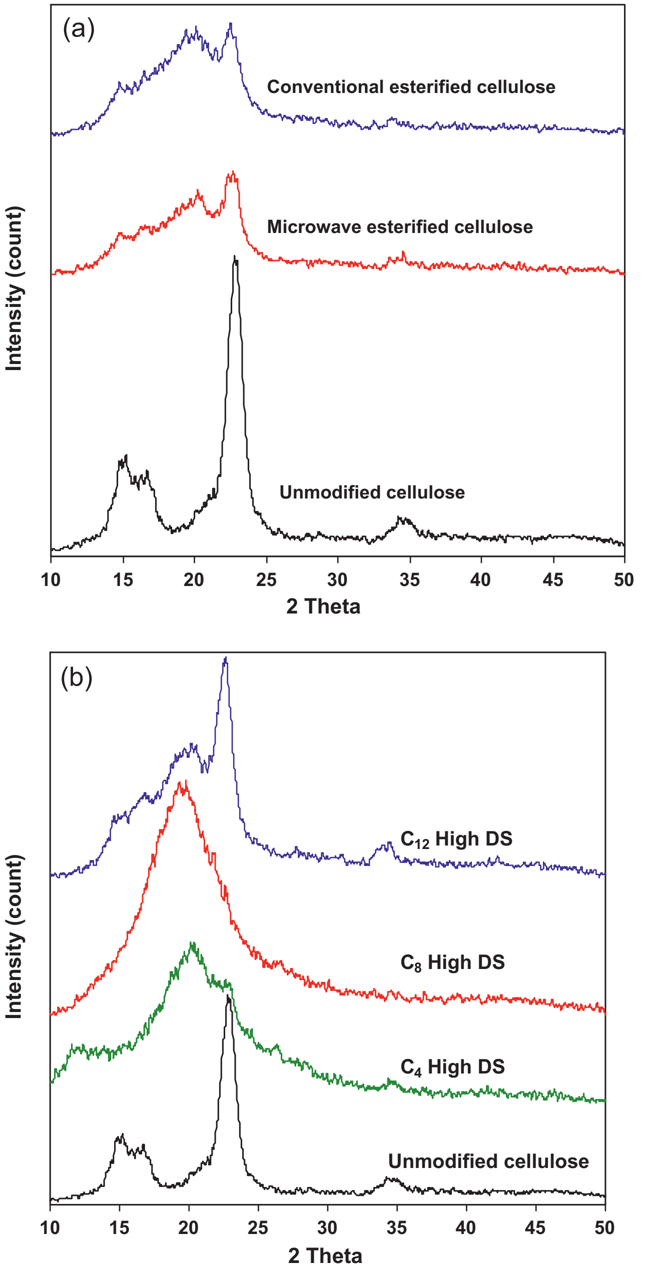

Fig. 6. XRD patterns of (a) unmodified cellulose compared to microwave and conventional esterified cellulose and (b) conventional esterified cellulose at various chain lengths.

4. Conclusion

Waste cotton fabric was successfully transformed into modified cellulose by esterification using different types of fatty acid chloride including butyryl chloride (C_4), capryloyl chloride (C_8), and lauroyl chloride (C_{12}) as esterifying agents in *N*,*N*-dimethylacetamide/lithium chloride solvents system using *N*,*N*-dimethyl 1-4-aminopyridine as a catalyst under a conventional heating method and microwave irradiation. Microwave can activate the esterification reaction similar to conventional heating where it does not change the chemical structure of the esterified cellulose. The optimum conditions were investigated by %weight increase (%WI) and degree of substitution (DS) in terms of reaction time, temperature, and microwave power. The results showed that %WI and DS of cellulose ester gradually increased with increasing reaction time and temperature and then decreased after it reached maximum value, probably attributable to cellulose degradation. The optimum conditions for esterification of cotton cellulose with C_4, C_8, and C_{12} under conventional heating were at 100 °C for 2 h, 80 °C for 12 h, and 60 °C for 12 h, respectively. Whereas the optimum conditions under microwave heating were at 360 W for 60 s, 270 W for 60 s, and 180 W for 150 s when esterified with C_4, C_8, and C_{12}, respectively. The increase of fatty acid chloride chain length led to the higher %WI while having no significant effect on the DS of esterified cellulose under both heating methods. In addition, microwave activation led to considerably lower values of %WI than with conventional heating (i.e., approximately 1.5–3 times) but slightly lower DS values (10–20%). The %WI and DS values of conventional esterified cellulose were 85–184% and 2.74–2.97, while those processed with microwaves were 60–82% and 2.41–2.69, respectively. However, when considering energy and time savings along with the acceptable product yield (%WI) and DS values, it seemed that microwave is another effective heating source to assist cellulose esterification. By using microwave irradiation, the reaction time is significantly diminished from 2 to 12 h under conventional heating to less than 3 min. The morphology of cellulose ester showed an aggregation of the acyl group on the surface of esterified cellulose powder. Lesser thermal stability exhibited in cellulose products esterified with a longer chain length of fatty acid and in products esterified with microwaves. After esterification, cellulose ester can dissolve in toluene, chloroform, DMAc, and tetrahydrofulan due to the destruction of hydrogen-bonding of the cellulose structure. The decrease in crystallinity associated with the acyl substitution in cellulose structure resulted in lower thermal stability and greater solubility property of esterified cellulose was verified by the XRD patterns. For future work, the modified cellulose will be casted into film and assessed for its physical, mechanical, and biodegradability properties.

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