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**Research Article**

# Esterification of Shambat Cotton Cellulose using weth acyl chlorides: Myristoyl (C14), palmitoyl (C16), using N,N-Dimethyl Acetamide/Lithium Chloride Solvent System

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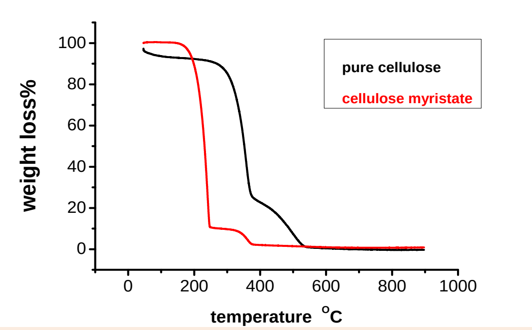
## Abstract

Shambat cotton contains about 96 % cellulose with a high degree of crystallinity. Cellulose is an important source in textile industry. The aim of this work is to solublize and esterify the Shambat cotton cellulose, and to study the properties of product esters and their application in the polymer industry. First Shambat cotton cellulose was mercerized via pretreatment in 30% NaOH to help solubilize cellulose. The mercerized cotton was then solubilized using N,N-dimethylacetamide/lithium chloride (DMAc/LiCl) solvent system. Cellulose esters are then synthesized by reacting the solubilized Shambat cotton with the acyl chlorides: myristoyl ($C_{14}$), palmitoyl ($C_{16}$), in the presence of pyridine to convert the hydroxyl groups of cellulose into ester groups. The optimum conditions for esterification of cotton cellulose with various esterifying agents were investigated in terms of reaction time and temperature. The degree of substitution, functional group and chemical structure, and thermal stability of cellulose esters were characterized by elemental analysis, FT-IR, and TGA\DSC analysis Cellulose esters possess different solubilities in different organic solvents. The solubility depends on their DS and the chain length of the acyl group.



**Keywords:** Shambat cotton, cellulose, esterification, FT-IR, and TGA\DSC analysis

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## Introduction

Cellulose is the main structural component of plant cell walls and, as such, the most abundant polymer on earth. Today, cotton and bleached wood pulp form the basis for a large number of products routinely used in our daily lives (Roman, 2010). Cellulose is a polydisperse polymer with a degree of polymerization (DP) that ranges from 8000 to 10000 [1].Cotton contains the purest form of cellulose.

Cellulose is often largely a linear polymer, and is not soluble in water because of the presence of strong intra and intermolecular hydrogen bonds, and sometimes the presence of a small amount of cross- linking. Cellulose is a linear homopolymer composed of D-glucopyranose units linked by β-1,4-glycosidic bonds [8]. 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. Cellulose esters are the second major class of commercially important cellulose derivatives. Cellulose esters can be further classified by the acid used for esterification to inorganic and organic esters. Cellulose esters of organic acids are produced by the reaction of cellulose with anhydrides of acetic, propanoic, and butyric acids in the presence of sulfuric acid as a catalyst. It is difficult to synthesize cellulose esters with long chain carboxylic acids via this method, due to the slow reaction rate and competitive cellulose chain cleave. The first method to prepare long chain cellulose esters was the so-called (impeller) method employed by Clarke and Malm in 1932[4]. The second method for preparation of long-chain cellulose esters was described by Malm and coworkers. They found that acylation of cellulose with acid chloride in 1,4-dioxane in the presence of pyridine as an acid acceptor and catalyst produced cellulose triesters ranging from acetate to hexanoate to palmitate.

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. 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[5].

## Materials and Methods

### Materials

### Cellulose sample

The cotton linters (Shambat cotton linters) were obtained from the Cotton Breeding Section, Agricultural Research Corp, Wad Medani, Sudan.

### Cellulose mercerization

The cellulose from cotton linters used in this study with polymer chain do not dissolve easily in DMA /LiCl unless the linters are first mercerized with an alkaline solution.Cotton linters cellulose was mercerized in 30% NaOH solution (0.25 g of cotton linters in 12.5 ml of NaOH at 0°C for 1 h. The alkali-swollen material was washed with distilled water until base-free. The mercerized cellulose was dried at room temperature for 24-48 h then was dried in an oven before dissolution.

### Reagents

Lithium chloride ( LiCl ) was obtained from BDH. Anhydrous lithium chloride was dried at 130°C for 2 hours. Petroleum ether and triethylamine were obtained from LOBA Chemise – India, myristoyl chloride and oleoy chloride was obtained from Aldrich. Palmitoyl chloride was obtained from Fluka. All reagents were used without further purification and treatment.

Dimethylacetamide (DMA) for solubilization was obtained from Acoros Organic and Fine-Chem, Mumbai, India; and was dried by distilling off water by heating at 100-110 °C.

Ethanol and acetone were obtained from Lab Tech-chemicals. Pyridine was obtained from BDH, and was purified and dried by heating under reflux over potassium hydroxide.

### Methods

### Dissolution of Cellulose in DMA/LiCl Solvent

0.25 g of mercerized cellulose was placed in a 250 ml conical flask and 25 ml of DMA were added, the mixture was heated at 160°C with stirring for 2 h, then the temperature was adjusted to 100°C and 2 grams of LiCl were added under stirring for one hour. The mixture was allowed to cool to 60°C. The mixture was left with stirring at room temperature for several hours until dissolution was completed

**Preparation of Cellulose myristate ($C_{14}$) and cellulose palmitate ($C_{16}$)**

**Table 1** Reaction conditions for acylation of cellulose (Cellulose myristate, palmitate)

| Experiment | Carbon chain | Pure cellulose(g) | Acid chloride (ml) | Pyridine(ml) | Temp (ºC) | Reaction time (h) | Product (%) |
|---|---|---|---|---|---|---|---|
| Cellulose myristate | $C_{14}$ | 0.25 | 2.00 | 2.00 | 8 | 48 | 88.55 |
| Cellulose palmitate | $C_{16}$ | 0.25 | 2.00 | 2.00 | 8 | 48 | 92.60 |

The reaction conditions for preparing cellulose esters having $C_{14}$, $C_{16}$, carbon atoms is summarized in Table (1). Chemical modification method of cellulose esters was described by[3]. The conical flask of the cellulose solution was placed in an ice water bath, and 2 ml of pyridine were added (for acid capture), then 2 ml of myristoyl and palmitoyl chlorides dissolved in 2 ml of DMA were added dropwise under stirring for 15 minutes. The mixture was stored for 48 hours at 8°C. The product ester was precipitated into 500 ml ice water, filtered and then was washed with ethanol and distilled water, then again washed with acetone and distilled water, then the produced ester was dried at room temperature for 2-3 days. The cellulose ester after that was dried in oven at 50° C for several hours.

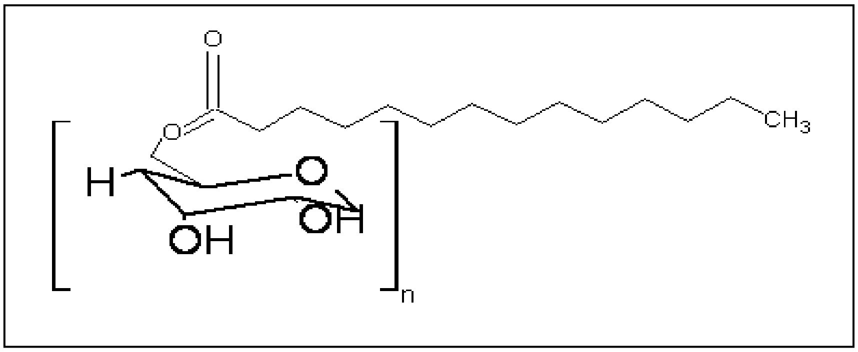

**Figure 1** Structure of Cellulose myristate ( $C_{14}$ )

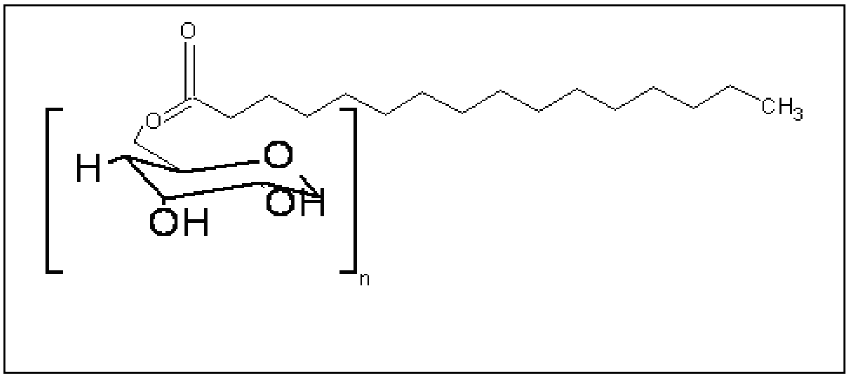

**Figure 2** Structure of Cellulose palmitate ($C_{16}$)

### Chemical characterization

### FT-IR spectroscopy

Pure cellulose and synthesized cellulose esters has been characterized by fourier transformed infra red (FT-IR) spectroscopy, using a Shimadzu FT-IR 8400 S.CE instrument using potassium bromide (KBr) discs prepared from the powdered sample mixed with dry KBr in the ratio 1:100. FT-IR spectra were performed in Central Research Laboratories, University of Khartoum.

### Elemental analysis

Elemental analysis was performed on dry finely ground samples using LECO CHNS-932 element analyzer. Elemental analysis of the samples was carried out in the laboratories of the Department of Chemical Engineering, University Technologi Petronas, Bandar Seri Iskandar Tronoh, Malaysia.

### Thermal analysis

### Thermogravimetric analysis

TGA was performed in a TGA Perkin Elmer STA 6000 Simultaneous Thermal Analyzer. Measurements were carried out at ramp 2.00 °C/min. to 600 °C using a platinum pan. The sample gas was oxygen flow was 60 ml /min, and the balance gas flow was nitrogen 50ml/min. All samples were in the powdered from. Thermogravimetric analysis of the samples was carried out in the laboratories of the Department of Chemical Engineering, University Teknologi Petronas, Bandar Seri Iskandar Tronoh, Malaysia.

### Differential scanning calorimetry

DSC measurements were carried out on Perkin Elmer Pyres 1 DSC. Each sample (5-10 mg) was first heated to 200 °C under protection of nitrogen at a flow rate of 20 ml/min, then immediately cooled with liquid nitrogen to -50°C. The sample is then scanned at a heating rate of 10 °C/min. The results were recorded from -50 °C to 300 °C. All samples were in the powdered form. Differential scanning calorimetry analysis of the samples were carried out in the Laboratories of the Department of Chemical Engineering, University Teknologi Petronas, Bandar Seri I skandan Tronoh, Malaysia.

## Results and Discussion

### Degree of substitution by elemental analysis

The DS values of acylated cellulose were calculated on the basis of measured C% from elemental analysis. Results of actual elemental analysis and calculated (theoretical) DS values are shown in Table (3).

The results from Table (2) showed gradual increase of DS from $C_{14}$ to $C_{16}$.

**Table 2** Calculated DS-value based on elemental analysis of modified cellulose esters

| Sample | Carbon (%) from elemental analysis for esters | Theoretical value of C(%) for DS= 3 | DS | Reaction Time (h) |
|---|---|---|---|---|
| Cellulose Myristate($C_{14}$) | 69.33 | 72.72 | 2.86 | 48 |
| Cellulose Palmitate($C_{16}$) | 70.71 | 73.97 | 2.90 | 48 |

## Fourier Transform (FT-IR) Spectroscopy results

The functional groups and chemical structure of unmodified pure cellulose was examined by FT-IR. The effect of FT-IR spectra of pure 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 **Figure 3, Figure 4, and Figure 5**.

The FT-IR of cellulose esters show different bands from unesterified pure cellulose, adcrease in the intensity and a shift of the hydroxyl group characteristic band (OH stretching) were observed compared to the native cellulose, this difference indicates a large amount of –OH groups were substituted. These spectra of cellulose esters provide an evidence of esterification by the existence of the ester carbonyl group (C=O) at 1700-1750 cem$^{-1}$. The occurrence of peaks at around 2800-2900 cm$^{-1}$ in the spectra of cellulose esters is attributed to methyl and methylene C-H stretching associated with acyl substitution. These similar spectroscopic profiles indicate a similar structure of esterified cellulose, all of them containing an intense ester carbonyl band at 1700-1740cm$^{-1}$, this band is indicative of absorption by the carbonyl group in carboxylate esters. In general the absorption by the carbonyl bond in esters gives a peak at 1750cm$^{-1}$ and the one in carboxylic acids exhibits a band at 1700 cm$^{-1}$ (Liu et al., 2007). The band around at 721cm$^{-1}$ in cellulose palmitate is characteristic for at least four linearly concentrated $CH_2$ groups ($(-CH_2)_4$) rocking.

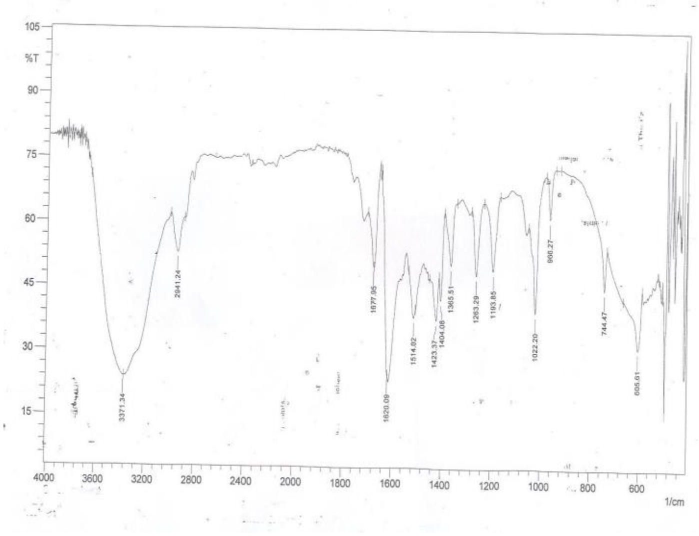

**Figure 3** FT-IR curve of pure unmodified cellulose

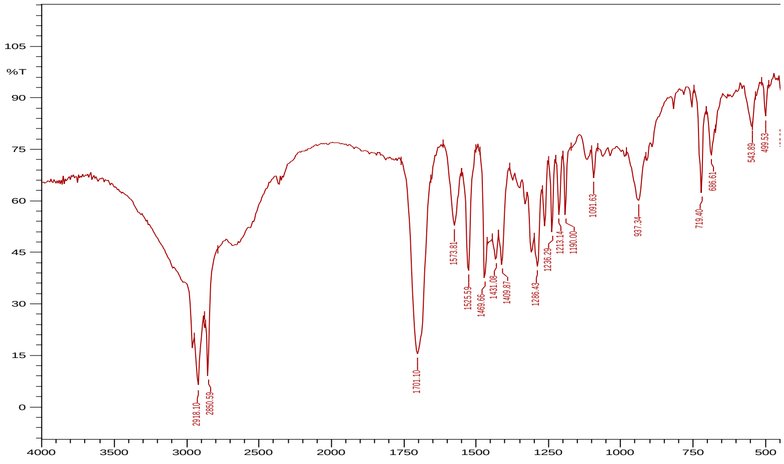

**Figure 4** FT-IR curve of cellulose myristate

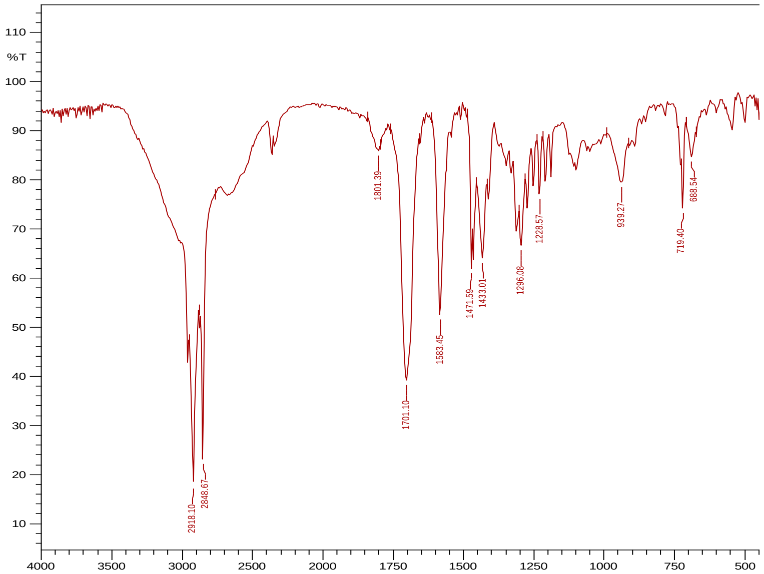

**Figure 5** FT-IR curve of cellulose palmitate

### Thermogravimetric analysis (TGA)

Figure 6, Figure 7, and Figure 8 show the TGA charts for pure unmodified mercerized cotton cellulose and the synthesized cellulose esters. In the TGA of pure unmodified cellulose (mercerized cotton linters) and cellulose derivatives (cellulose esters) the thermal decomposition of pure cellulose and cellulose esters occurs by three or four steps: the first thermogravimetry step at 20-150ºC, water desorption and dehydration processes; the second step at 150-400ºC, deacylation and cross linking with formation of levoglucosan; and the last step at 400-600ºC, decomposition and charring of the products.

From TGA results of pure unmodified mercerized cellulose and cellulose derivatives (esters), the thermal stability of cellulose (mercerized cotton linters) is affected by the crystalline order, which decrease after substitution of cellulose hydroxyls with acyl groups. This behaviour is attributed to the decrease in crystallinity associated with the substitution of the fatty acid chain in the cellulose structure [10].

The thermal degradation of cellulose esters was influenced by the fatty acid chain length of fatty acid chloride. As shown in Figure 6, Figure 7, and Figure 8, and Table (3) the thermal stability of cellulose myristate ($C_{14}$) was 245 ºC, and cellulose palmitate ($C_{16}$), was 375 ºC. The shifting of the thermal degradation towards lower temperature indicates the decrease in thermal stability of cellulose ester due to the decrease in crystallinity associated with substitution of longer lengths of the acyl group. Cellulose palmitate has higher thermal stability than that of pure unmodified cellulose. The increase in the thermal stability of cellulose palmitate was attributed to an increase in side chain length because the effect of the overlapped side chains became larger with increasing DS. Cellulose palmitate has a higher DS value of 2.90. A similar case was reported by Kun [6].

According to TGA analysis thermal stability also depends on the molecular weight and crystallinity of the polymer. Generally, the lower the molecular weight and crystallinity the easier the degradation of the polymers [2].Therefore, the thermal stability of cellulose esters is lower than that of pure unmodified cellulose (mercerized cotton linters). In addition, with increasing DS the decomposition temperature of cellulose esters increases[7]. This increase in thermal stability of cellulose esters may be explained by the formation of new-ordered structures in the substituted regions.

**Table 3** TGA result of pure cellulose and cellulose esters

| Sample | DS | T<sub>Onset</sub> of decomposition | Weight residue at onset decomposition | T<sub>decomposition</sub> | Weight residue percent after decomposition | Final temp of decomposition |
|---|---|---|---|---|---|---|
| Pure umodified cell cellulose | 0.00 | 225 ℃ | 92% | 377 ℃ | 25% | 530 ℃ |
| Cellulose Myristate(14) | 2.86 | 150 ℃ | 99% | 245 ℃ | 2% | *360* ℃ |
| Cellulose palmitate(16) | 2.90 | 180 ℃ | 90% | 392 ℃ | 15% | *570* ℃ |

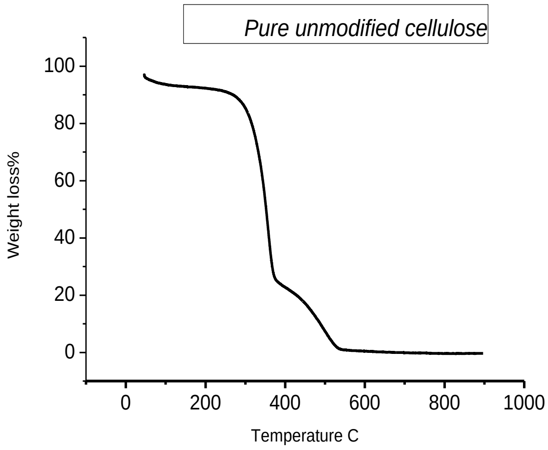

**Figure 6** TGA curve of pure unmodified cellulose

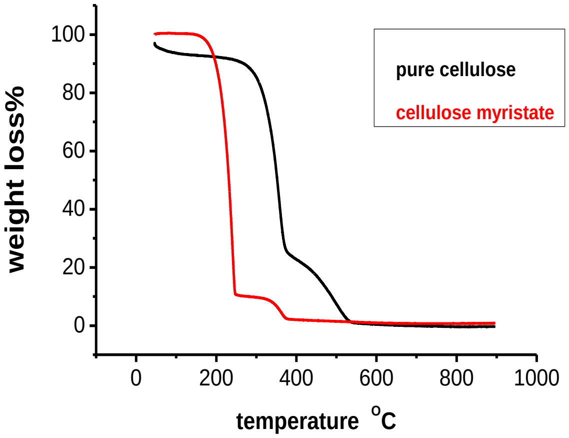

**Figure 7** TGA curve of cellulose myristate

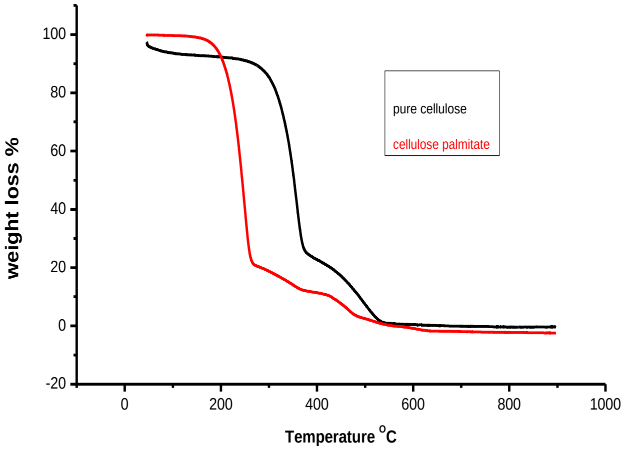

**Figure 8** TGA curve of Cellulose hexadecanoate (Palmitmate)

## Differential Scanning Calorimetry (DSC) results

DSC curves are also used to study the thermal behaviour of modified and non-modified cellulose (mercerized cotton linters). DSC analysis and the results are shown in **Figure 9, Figure 10 and Figure 11** and summarized in **Table 4**. Small endothermic peaks can be observed for cellulose and cellulose esters, there is almost no weight loss or endothermic peak associated with the evaporation of moisture in pure cellulose and cellulose esters. Because of massive hydrogen bond association, the glass transition of pure cellulose is higher than synthesized esters; this result was reported by [6].

The DSC themograms show the endothermic peaks of pure cellulose with their maximum at 83 ℃, and for cellulose myristate ($C_{14}$), cellulose palmitate ($C_{16}$), were 69 ℃, 81℃ respectively. For cellulose, the small exothermic peak following endothermic peak is present in cellulose palmitate at 85℃, which is due to the crosslinking reaction occurring during thermal degradation, this was reported by Peter [7]. It is observed that the decomposition temperature (endothermic peak) decreases as a function of the modified condition and this can be explained by the difference introduced by chemical modification. Table (4) shows the DSC curves of the unmodified crude cellulose (mercerized cotton linters) and cellulose esters.

From Table (4) above, the glass transition of pure cellulose and synthesized cellulose esters was influenced by the fatty acid chain length of fatty acid chloride. The shifting of the glass transition towards lower temperature indicated the decrease in thermal stability of cellulose ester due to the decrease in crystallinity associated with substitution of longer acyl groups.

**Table 4** DSC result of pure cellulose and cellulose esters

| Sample | Onset temp ($T_i$) | Melt peak ($T_m$) | Final temp ($T_f$) | DS |
|---|---|---|---|---|
| Pure cellulose | 68 ℃ | 83 ℃ | 99 ℃ | |
| Cellulose myristate($C_{14}$) | 60 ℃ | 69 ℃ | 74 ℃ | 2.86 |
| Cellulose palmitate($C_{16}$) | 76 ℃ | 81 ℃ | 86 ℃ | 2.90 |

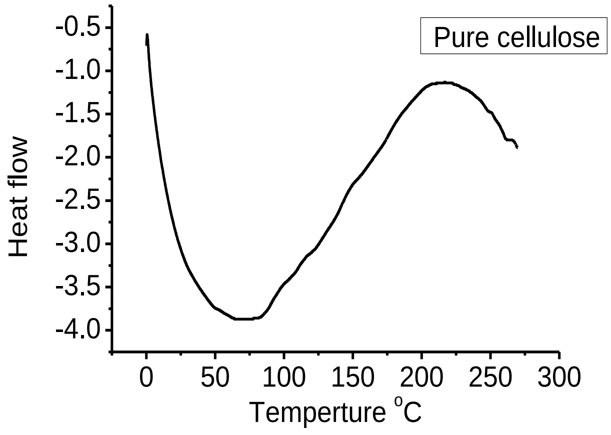

**Figure 9** DSC curve of pure unmodified Cellulose

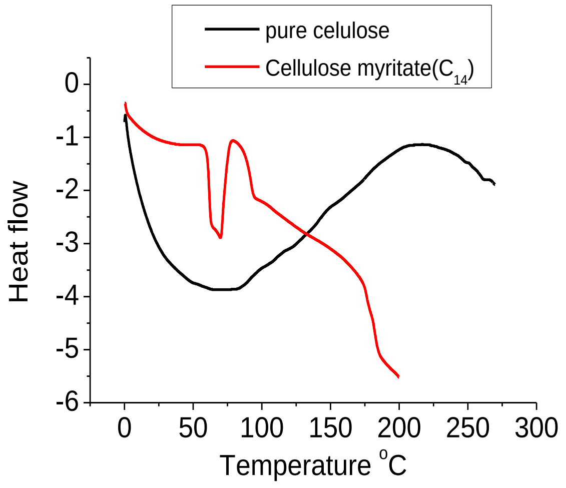

**Figure 10** DSC curve of Cellulose Myristate

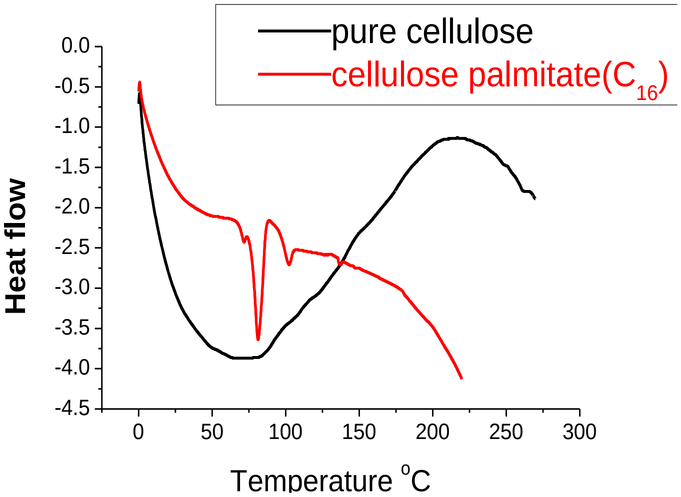

**Figure 11** DSC curve of Cellulose Palmitate

### Solubility

The solubility of esterified cotton cellulose in various organic solvents was investigated, and the results are summarized in Table (5). It was found that cotton cellulose was insoluble in either organic solvents or water [10]. These crystallity make cellulose insoluble in normal aqueous solvents and common organic solvent. In general, the introduction of acyl groups into the molecular structure of cellulose leads to the breaking of highly organized hydrogen bonding of cellulose structure and therefore affects its solubility properties.

Cellulose myristate, cellulose palmitate are insolubl organic solvents (Toluene, dimethylsulfoxide(DMSO), dimethylformamide (DMF), and tetrahydrofuran (THF), and dimethylacetamide (DMAc), this probably due to the increase of fatty acid chain length . For the degree of substitution, as expected it was found that the solubility of cellulose myristate, cellulose palmitate, decreases with increasing degree of substitution. This may be attributed to the partial crystallization and overlapping of long chain cellulose esters side chains.

**Table 5** Solubility of pure cellulose and cellulose esters in different organic solvents 0.0l g/ml at room temperature

| **Sample** | **DS** | **Toluene** | **DMAc** | **DMSO** | **DMF** | **THF** |
|---|---|---|---|---|---|---|
| Pure cellulose | 0.00 | – | – | – | – | – |
| Cellulose Myristate($C_{14}$) | 2.86 | – | – | – | – | – |
| Cellulose Palmitate($C_{16}$) | 2.90 | – | – | – | – | – |

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