

Synthesis and Characteristics of Cellulosic Polymers from Agricultural Environmental Pollutant Wastes

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Abstract: Cellulose esters with saturated fatty acyl substituents (C₁₂ lauroyl to C₁₈ stearoyl) were synthesized in homogenous medium *N,N*-dimethylacetamide solution combined with lithium chloride (DMAc/LiCl) using triethylamine (TEA) as acid scavenger and characterized by means of FTIR and ¹H NMR spectroscopy. The thermal degradation of the esters was studied by thermo gravimetric analysis (TGA) and differential thermogravimetry (DTG). The products possess values of the degree of substitution (DS) between 0.16 and 1.95. Rosin cellulose esters were also prepared and studied for film properties. It was found that these films can be made compatible with conventional film formers such as alkyds, phenolics and epoxy esters and the combinations could be used in various surface coating formulations.

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Key words: Cellulose, cellulose esters, Rosin cellulose esters, DMAc/LiCl, thermal analysis.

1. Introduction

Many agricultural by-products from agricultural activities and agro-based processing litter the environments and constitute waste problems. This research aimed at converting some of these unwanted agricultural wastes or by-products to commercially useful products such as cellulose esters. The principle behind the research is that most by-products are composed of cellulose in the plant cell walls, thus this work has the potential of providing new market and applications for low value and utilized agricultural wastes by converting into fatty cellulose esters.

The multiple hydroxyl groups of cellulose in cellulosic materials (agro-waste) can be partially or wholly modified by reacting with various chemicals to produce a wide range of end products referred to as "cellulosic derivatives." These derivatives have found applications in various fields such as pharmaceuticals, cosmetics, food and packing⁽¹⁻³⁾.

Cellulose esters are produced industrially under heterogeneous conditions, at least at the beginning of the conversion. However homogenous derivatization offers the enormous advantage of good accessibility of the hydroxyl groups. Thus, a better control of the degree of substitution (DS) and a uniform distribution of the functional groups along the polymer chain may occur. The most applied solvent in lab-scale cellulose esterification is *N,N*-dimethyl acetamide (DMAc) combined with LiCl. The conversion of cellulose with carboxylic acids by in-situ activation under homogenous condition is an efficient method of cellulose esterification. Several researches on the esterification of cellulose have been published.⁽⁴⁻¹¹⁾

Esterification of cellulose in heterogeneous system using toluene as a cellulose – swelling medium

has been studied widely by many researchers^(12,13). Esterification of cellulose from waste cotton fabric in DMAc/LiCl solvent system using fatty acid chlorides as an esterifying agent and *N,N*-dimethyl 1-4 amino pyridine as a catalyst was achieved⁽¹⁴⁾. When cotton is ginned, the long staple cotton is removed from the seed and is used in the textile industry to make cloth. Then the seed is further processed in a machine called a "linter" which remove the rest of the seed fabrics, the shorter the fiber are known as cotton linters. Cotton linters are short fibers its value depend directly on its wealth of cellulose, which usually reaches 95-99% of its composition.

In Egypt enormous volumes of agricultural wastes that contain cellulosic fibers especially rice straw are generated annually. These agro-wastes are allowed to rot away utilized. Tons of rice straw are allowed to rot away yearly and eventually polluting the environment. These agricultural wastes can be gainfully utilized in the conversion to cellulose derivatives for manufacture of plastics, photographic films, etc.

Rice straw is an abundant lingo cellulosic agricultural by product from rice production in farming in Egypt. It's a renewable and cheap resource for cellulose fiber. The chemical compositions of rice straw fiber are cellulose (28-36%), hemicellulose (23-28%) lignin (12-14%) and ash (14-20%)⁽¹⁵⁾. Accordingly, cotton linters and rice straw are of interest as a possible resource for cellulose-based film production. This will not only encourage local farmers as new market is developed for materials but will also boost the Egyptian economy. On the other hand, the problem of environmental pollution (the black cloud)

arising from the decay of these materials will be minimized.

The objectives of this work are the synthesis of fatty cellulose esters (CL, CM, CP, Cs & CoL, CoM, CoP, CoS& RL, RM, RP, RS) by esterification. The goal is to use cotton linters cellulose and rice straw cellulose which are a major agriculture waste produced in large quantities from textile industry after removing the long staple cotton from the seed and from rice harvesting for food industry.

In this study, α -cellulose, cotton linters and rice straw cellulose were esterified with fatty acid chlorides (C₁₂-C₁₈) in homogenous system using N, N dimethyl acetamide as a medium and using LiCl as a catalyst, in order to save the solvent cost. The optimum condition for esterification of cellulose was reported. The chemical structure and properties of all the prepared cellulose esters were investigated in terms of solubility and thermal degradation stability. Rosin cellulose esters were also prepared and studied for film properties (Flexibility, scratch hardness and their resistance towards alkali, acid, water and solvents).

2. Experimental

Materials

α -cellulose was obtained from sigma (Saint-Quentin Fallavier, France). Waste cotton linters of short cotton fibre were collected from local cotton processing industry in Egypt and were used as the basic material after degradation. Rice straw was obtained from local rice fields in Egypt. Lauric, myristic, palmitic and stearic acids were reagent grade and used as such. Sodium hydroxide, hydrogen peroxide, hydrochloric acid (37.0%), sulphuric acid are BDH, LR grade. Dimethyl acetamide (DMAc), lithium chloride (LiCl), triethylamine (TEA), Dimethyl sulfoxide (DMSO) and thionyl chloride (SOCl₂) were purchased as analytical grade and used as received. Rosin was of best grade (N). All solvents are of pure grade and were used without further purification.

The code of cellulose, fatty cellulose esters and rosin cellulose esters:

C: α cellulose, Co: Cotton linter cellulose, R: rice straw cellulose; CL: α cellulose laurate.

CM: α cellulose myristate, CP: α cellulose palmitate, CS: α cellulose stearate; CoL: cotton linters cellulose laurate; CoM: cotton linters cellulose myristate, CoP: cotton linters cellulose palmitate, CoS: cotton linters cellulose stearate; RL: rice straw cellulose laurate, RM: rice straw cellulose myristate, RP: rice straw cellulose palmitate, RS: rice straw cellulose stearate; RoCL: rosin α cellulose laurate

RoCM: rosin α cellulose myristate, RoCP: rosin α cellulose palmitate, RoCS: rosin α cellulose stearate;

RoCoL: rosin cotton linters cellulose laurate, RoCoM: rosin cotton linters cellulose myristate, RoCoP: rosin cotton linters cellulose palmitate, RoCoS: rosin cotton linters cellulose stearate; RoRL: rosin rice straw cellulose laurate, RoRM: rosin rice straw cellulose myristate, RoRP: rosin rice straw cellulose palmitate, RoRS: rosin rice straw cellulose stearate.

Methods

Degradation of cotton cellulose (cotton linters):

Cellulose was depolymerized with sulphuric acid. 150g cotton linters were taken in two liters beaker, 50 ml of concentrated sulphuric diluted with 1 liter of water was added while stirring. The mixture was heated to 60°C and kept at this temperature for 2 hours with stirring. During this period the cotton linters shortened in length. A further heating of the product gave a powder form of cellulose. The product was washed with hot water in order to remove any trace of acid.

Purification of cotton cellulose (cotton linters):

Degraded cellulose was purified by adding 10% sodium hydroxide solution to the degraded cellulose. The mixture was heated on a water bath at a temperature of 90°C for 10 hours while stirring. Then the product was added to a large volume of water, washed well, and dried at 70°C for 5 hours.

Delignification, Bleaching and Hydrolysis of rice straw cellulose:

The rice straw was boiled in water for 1 hour in order to remove water-soluble hemicellulose. Then it was heated and stirred with 0.5 M NaOH solution at 60°C for 2 hours in order to remove lignin and remaining hemicellulose from the rice straw pulp. After delignification, the rice straw pulp was filtered and washed with distilled water. The delignified pulp was bleached by 10% (V/V) H₂O₂ in 0.5 M NaOH at 60°C for 2 hours. After that, the bleached pulp was washed several times with distilled water until its pH become neutral. The bleached rice straw was hydrolyzed using boiling 2 M HCl for 2 hours then filtered, washed with distilled water, and dried in oven at 60°C for 24 hours where the rice straw cellulose powder was obtained Fig. (1).

Synthesis of fatty acid chlorides⁽¹⁶⁾:

Fatty acid chlorides have been prepared by reacting 1.0g equivalent of fatty acid with 1.5 equivalent of thionyl chloride (SOCl₂) in chloroform (distilled twice). The reaction mixture was initially stirred at 0°C for 30 min and then at room temperature for 6 hours. The excess solvent was evaporated by distillation and the fatty acid chloride was distilled under reduced pressure (Figure 2).

Dissolution of cellulose in *N, N*-dimethyl acetamide (DMAc/LiCl):

Cellulose (1.0g, dried for 6 hours at 110°C under vacuum and KOH) and 40 ml DMAc were stirred for 2 hours at 130°C. LiCl (3.0g, dried at 150°C for 6

hours under vacuum and KOH) was added and the slurry was allowed to cool to room temperature under stirring. After 24 hours a clear cellulose solution was obtained.

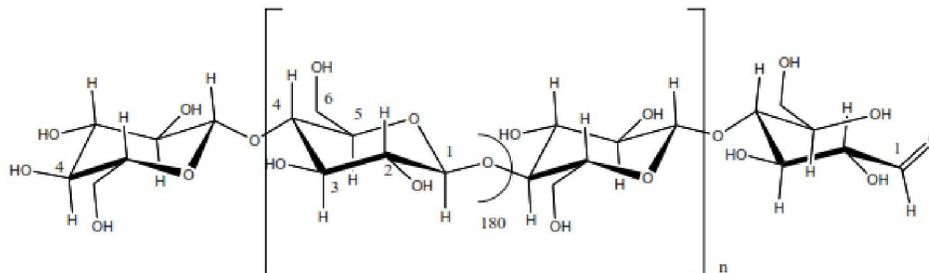
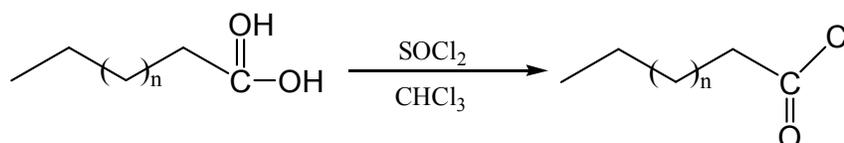


Figure 1. The structure of cellulose



Where n = 8 lauric acid, n = 10 myristic acid, n = 12 palmitic acid, n = 14 stearic acid

Figure 2. Synthesis pathway of fatty acid chloride

Synthesis of cellulose esters:

Twelve different cellulose esters of fatty acids were synthesized using α -cellulose, cotton linters cellulose and rice straw cellulose with saturated fatty acid chlorides (lauroyl, myristoyl, palmitoyl and stearoyl chlorides). Definite amount of TEA in DMAc premixed thoroughly were added slowly in one portion to the cellulose solution. Then definite amounts of

fatty acid chloride in DMAc was added dropwise for 1 h. while stirring was continued for several hours at different temperatures. The product was isolated as white powder by precipitation into large volume of water, purified by soxhlet extraction with methanol for 48 hours and vacuum dried at 50°C for 48 hours (Fig. 3).

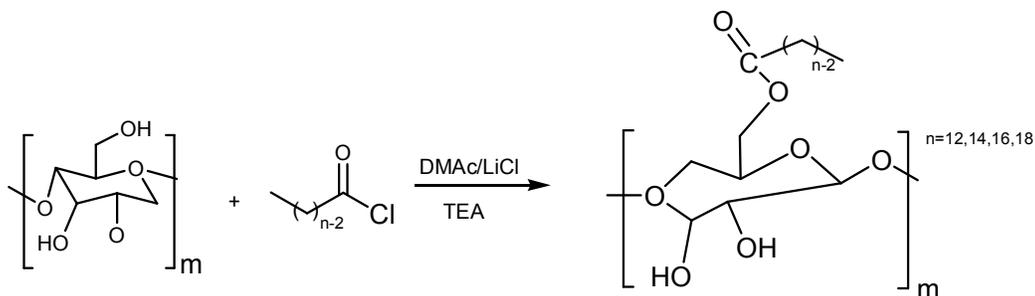


Figure 3. Synthesis pathway of cellulose esters

Synthesis of cellulose esters modified with rosin

Cellulose ester was heated with equal part of rosin at 150°C for 2 hours. The mixture was cooled and dissolved in DMSO. The solutions of fatty cellulose esters modified with rosin were of yellow to brown colour and had a fair clarity.

Characterization and testing **FTIR analysis**

IR spectra of cellulose and cellulose esters samples were recorded on a Perkin Elmer spectrophotometer (Spectrum RX1, Perkin Elmer, Singapore) using KBr pellet technique, in the range 4000-400 cm^{-1} , with a resolution of 2 cm^{-1} , using 4 scans per sample.

NMR analysis

The ^1H NMR spectra of cellulose and cellulose esters were collected on a Bruker WM -400 spectrometer, opening at 300 MHz for proton. All the

chemical shifts were reported in parts per million (ppm) using tetramethylsilane (TMS) as the internal standard and DMSO- d_6 as the solvent for the samples.

Dispersability and solubility

The dispersability of fatty cellulose esters was checked as follows: 10 mg product was dispersed in 1 ml solvent selected at room temperature, the solubility was recorded as shown in Table 1. The solvents used are dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), *N, N*-dimethyl acetamide (DMAc), pyridine, and chloroform ($CHCl_3$).

Thermal analysis

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) of cellulose and cellulose esters were carried out using a Perkin Elmer simultaneous thermal analyzer (STA 6000), in the temperature range 50-600°C at a heating rate of 10°C min^{-1} , under the nitrogen atmosphere.

Determination of degree of substitution DS:

In order to determine the degree of substitution of the cellulose esters, free hydroxyl groups in the cellulose were determined by the method used by **Bayantet *al.***⁽¹⁷⁾ by acetylating the samples with mixture of acetic anhydride and pyridine following by titration with standard alkali. The drop in hydroxyl value of cellulose esters indicated the degree of substitution (DS).

Drying of rosin cellulose esters:

The solutions of rosin cellulose esters were applied on glass and tin panels and backed under 100°C for 3 hours and were tested for flexibility and scratch hardness as well as their alkali, acid, water and solvents resistance.

Flexibility⁽¹⁸⁾: Two percent by weight of dibutyl phthalate plasticizer was thoroughly mixed with all the samples before performing this test. Flexibility of the dried film was tested on tin panels with 1/4" mandrel. (Table 3).

Scratch hardness⁽¹⁹⁾: scratch hardness was carried out at a load of 1kg. Table 3, includes the results of scratch hardness.

Alkali resistance: Table 4 shows the alkali resistance of all rosin cellulose esters in 10% NaOH for 7 days.

Acid resistance: Table 4 gives a clear picture of the acid resistance in 20% HCl and 20% H_2SO_4 solutions after 30 days.

Water resistance: water resistance of all rosin cellulose esters are summarized in Table 4. The water resistance was tested at 30°C for 7 days and in boiling water for 24 hours.

Solvents resistance: The resistance of rosin cellulose esters to toluene/xylene (50/50), white spirit and petrol have been carried out and summarized in Table 4.

3. Results and Discussion

Cellulose is a poly-dispersed polymer of high molecular weight comprised of long chain of D-glucose units joined together by β -1,4-glycosidic bonds. The possibility exists that a very small percentage of the linkages may be there other than β -1,4.

Cotton linters are short fibers found wrapped in cotton seed after its recovery (removal of the plume). Its value depends on its wealth of cellulose which usually reaches 95-99% of its composition.

On the other hand, rice straw is a major agricultural waste produced in large quantities from rice harvesting for food industry. Rice straw is rich in cellulose content (28-36%). Thus because of their high cellulose content cotton linters and rice straw are of interest as a possible resource for cellulose-based film production. Esters of α -cellulose (commercial cellulose) was used for comparison.

Cotton linter cellulose esters and rice straw cellulose esters with different fatty acid chlorides (lauroyl, myristoyl, palmitoyl and stearoyl) were prepared and then the prepared cellulose esters were modified with rosin. Rosin has been incorporated in order to reduce the cost of the products and to make them soluble in hydrocarbon solvents by reaction typical of the compounds containing hydroxyl groups. Most of the technical problems of cellulose reactions are centered around the availability of the hydroxyl groups for reaction. The multiplicate hydrogen bonding between the hydroxyl groups in the 2,3 and 6 positions of each glucose unit sometimes make intrusion of the other chemical species to cellulose molecule difficult. To overcome this drawback, cellulose is converted into useful derivatives by esterification. Production of cellulose esters is carried out by reacting the free hydroxyl groups in the anhydroglucose unit with various chemical substitution groups (fatty acid chlorides) the introduction of the substituent disturbs the inter- and intramolecular hydrogen bonds in cellulose, which lead to liberation of the hydrophilic characters of the numerous OH groups and restriction of the chains to closely associate.

Esterification of α -cellulose, cotton linter cellulose and rice straw cellulose were carried out by dissolving cellulose first in a non-degrading non-aqueous organic solvent and then reacting the dissolved cellulose with different fatty acid chlorides (lauroyl, myristoyl, palmitoyl and stearoyl).

In order to study variation of yield with time, the reaction was conducted at 80°C. Samples were taken from the start of reaction. Figure (4) which was taken as an example shows that the degree of substitution of cotton laurate (CoL) ester increased but did not reach the maximum possible 3.0 even at long reaction time

which confirm that no extensive degradation of the polymer took place in the course of esterification. Figure 5 shows that esterifying Co cellulose is very difficult at lower temperature. The DS of Co cellulose greatly increased with increasing reaction temperature, and the yield of cotton linters cellulose ester (CoL) increased when reaction temperature rise from 60 to 80°C, and the yield decreased when the temperature increased from 100 to 140°C. this may have been due to HCl production during esterification. Since our reaction produce large amount of HCl. The lower DS than the maximum possible 3.0 obtained even at long reaction times suggested that hydroxyls were not easily available for reaction. This is possible as the three hydroxyls on an anhydroglucose unit of cellulose are not equally accessible. The primary hydroxyl is more reactive than the two secondary hydroxyls, by virtue of less stereochemical hindrance. An alternative explanation for incomplete reaction could be that the acid chloride was unable to reach the hydroxyls due to mass – transfer limitations. The swollen cellulose, upon some reaction, might undergo structural alterations and not allow more acid chloride to enter into itself. High temperature led to acid degradation of cellulose and to minimize cellulose degradation, reaction temperatures below 100°C are recommended. It was concluded that the suitable condition given the greatest DS of cellulose esters (1.95) was 80°C of reaction temperature for 8 hours of reaction time.

Chemical structure of cellulose esters was investigated by FTIR and ¹H NMR spectroscopy. The FTIR spectra of α cellulose (C), cotton linters cellulose (CO) and rice straw cellulose (R) (Fig. 6-8) and those of α cellulose palmitate (CP) (Fig. 9), cotton linters cellulose stearate (CoS) (Fig. 10) and rice straw cellulose stearate (RS) (Fig. 11) provide an evidence of esterification by showing a decrease in the intensity of the characteristic band of hydroxyl group in cellulose around 3360 cm⁻¹, that arising from the hydroxyl group of cellulose which was substituted by alkyl group of fatty acid chlorides. This decrease in the intensity occurred concurrently with the presence of the important ester carbonyl band at 1706 cm⁻¹ (C=O) and an increase in the intensity of the methyl band (C–H) stretching due to CH₂ and (CH₃) around 2857 cm⁻¹ and 2924 cm⁻¹, respectively.

¹H NMR analyses of fatty cellulose esters of CP, CoS and RS (Fig. 12-14) show signals between 0.835-0.877 ppm corresponds to the alkyl group of fatty acid chain and the peaks observed in the range of 1.1-4.8 ppm were related to the anhydroglucose unit protons. Both FTIR and ¹H NMR results confirm and accomplishment in the formation of fatty cellulose esters.

The dispersability of the cellulose esters was tested in aprotic polar solvents such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), N, N-dimethyl acetamide (DMAc), pyridine, and chloroform (Table 1). The solubility of cellulose esters depends on their DS and the length of the carboxylic acid. All cellulose esters with DS between 0.94 and 1.95 are investigated and the results are shown in Table (1). It was clear that DS decreased as the chain length of the fatty acid increased from CL to CS, from CoL to CoS and from RL to RS.

Thermogravimetric analysis shows the thermal behavior of cellulose (αC, Co, R) (Fig. 15) and cellulose esters (CL, CoL, RL) (Fig. 16) as a function of % weight loss with temperature. All samples showed three different zones. An initial zone of slight loss in weight is due to the evaporation of water. Then the break in each thermogram indicates the onset of the decomposition process involving a rapid loss in weight. At the end of this break a slight curvature is formed, which might be due to the formation and evaporation of some volatile compounds. Finally, the decomposition rate decrease gradually to a constant weight representing carbonization

The percentage weight loss with temperature are given in (Tables 2, 3). The initial decomposition temperature for cotton linters cellulose (Co) started at 289°C and for rice straw cellulose (R) started at 146°C, which are lower than the initial decomposition temperature of commercial cellulose (C) (327°C). The DTG curves show the active decomposition temperature (ADT) for commercial cellulose (C) which is 366°C and goes on increasing to 374°C for cotton linters cellulose (Co), but goes on decreasing to 308°C for rice straw cellulose (R). this means that the thermal stability of Co is higher than that of R (Table 2)..

On the other hand the initial decomposition temperature of commercial cellulose ester (CL) started at 100°C, and for cotton cellulose ester (CoL) started at 241°C and for rice straw cellulose ester (RL) started at 121°C as indicated in Table (3). The DTG curves (Fig. 16) show the active decomposition temperature (ADT) of cellulose esters CL, CoL and RL which indicate that the thermal stability of RL (310°C) is higher than those of CL and CoL (246°C and 259°C) respectively.

The prepared derivatives are not soluble in common solvents and do not lend themselves to useful application. Therefore, the prepared esters were modified with rosin. Rosin has been incorporated in order to reduce the cost of the products and to make them soluble in hydrocarbon solvents. The samples of rosin cellulose esters are yellow to red colours. Solutions of almost all the samples were clear.

The samples were evaluated for drying characteristics, flexibility, scratch hardness and resistance to alkali, acids, water and solvents.

Drying characteristics: The solutions of rosin cellulose esters were applied on glass and tin panels and baked. It was found that the films of rosin cellulose esters dry at 100°C in 3hours without showing any appreciable tackiness or change in colour.

Flexibility: Two percent by weight of dibutyl phthalate plasticizer was thoroughly mixed with all the samples before performing this test. Flexibility of the dried film was tested on tin panels with 1/4" mandrel. Rosin cellulose esters of CL & CM passed the flexibility test, but these of CP & CS failed (Table 4). The possible explanation for this behavior is that the higher fatty acid chain cause cleavage of cellulose chain which lead to embrittlement of the film and loss in flexibility.

ScratchHardness: Table 4 includes the results of scratch hardness test. All rosin cellulose esters showed satisfactory results with respect to scratch hardness

because the large number of cyclic rings present in these derivatives contribute towards the hardness.

Alkali resistance: The rosin cellulose esters showed satisfactory resistance to 10 percent sodium hydroxide solution for 7 days. (Table 5)

Acid resistance: Table (5) gives a picture of the acid resistance of all the samples, it is clear that acid resistance of all samples was superior.

Water resistance: Water resistance of various rosin cellulose esters are summarized in Table (5). From the results obtained it can be concluded that the water resistance at 30°C of all samples was good. However, when immersed in boiling water for 24 hours, the films were cracked and partially removed.

Solvent resistance: The resistance of rosin cellulose esters to toluene/xylene (50/50), white spirit and petrol have been summarized in Table (5). From the results obtained it has been found that the films were partially and completely removed by the solvents. This could be due to the presence of a linear chain, where no crosslinking could take place.

Table 1. The solubility of α -cellulose esters, cotton linters cellulose esters and rice straw cellulose esters in selected solvents.

Code sample	DS	Solubility				
		DMSO	DMF	DMAc	Pyridine	CHCl ₃
CL	1.86	+	○	●	↓	○
CM	1.44	+	○	●	↓	○
CP	1.15	+	○	●	↓	○
CS	0.96	+	○	●	↓	○
CoL	1.87	+	○	●	↓	○
CoM	1.53	+	○	●	↓	○
CoP	1.35	+	○	●	↓	○
CoS	0.94	+	○	●	↓	○
RL	1.95	+	○	●	↓	○
RM	1.67	+	○	●	↓	○
RP	1.42	+	○	●	↓	○
RS	0.97	+	○	●	↓	○

DMSO: Dimethyl sulphoxide, DMF: Dimethyl formamide, DMAc: Dimethyl acetamide

+: soluble and small particle precipitate, ↓: Insoluble particle precipitate

●: Big swollen particle, ○: Small swollen particle

Table 2. Thermal stability of C, Co and R cellulose in nitrogen atmosphere at a heating rate of 10°C. min⁻¹

Sample code	IDT ^a (°C)	ADT ^b (°C)	wt. loss (%)						
			100°C	200°C	300°C	400°C	500°C	600°C	700°C
C	327	366	4.3	5.5	6.7	87.5	93.2	99.7	99.9
Co	289	374	5.1	6.8	11.3	75.4	84.1	93.1	99.4
R	146	308	7.6	11.3	35.0	57.7	64.1	69.7	74.2

^aIDT: the initial decomposition temperature.

^bADT: the active decomposition temperature.

Table 3. Thermal stability of CL, CoL and RL cellulose esters in nitrogen atmosphere at a heating rate of 10°C. min⁻¹

Sample code	IDT ^a (°C)	ADT ^b (°C)	wt. loss (%)							
			100°C	200°C	300°C	400°C	500°C	600°C	700°C	800°C
CL	100	246	10.1	24.6	71.0	87.5	99.9	--	--	--
CoL	241	259	2.6	5.2	38.1	48.6	56.8	67.8	75.1	75.4
RL	121	310	8.5	19.5	41.0	57.9	62.3	63.6	64.4	66.1

^aIDT: the initial decomposition temperature.^bADT: the active decomposition temperature.**Table 4.** Mechanical properties of rosin cellulose esters.

Sample code	Flexibility test (1/4" mandrel) with 2% dibutyl phthalate at 100° for 50 minutes	Scratch hardness test (at 1kg load)
RoCL	P	P
RoCM	P	P
RoCP	F	P
RoCS	F	P
RoCoL	P	P
RoCoM	P	P
RoCoP	F	P
RoCoS	F	P
RoRL	P	P
RoRM	P	P
RoRP	F	P
RoRS	F	P

P: passed

F: Failed

Table 5. Alkali, acids, water and solvents resistance of rosin cellulose ester films

Code sample	Alkali solution at 30°C for 7 days 10% NaOH	Acid solution at 30°C for 30 days		Water		Solvents		
		20% HCl	20 % H ₂ SO ₄	30°C for 7 days	Boiling for 24hours.	Toluene/xylene (50/50)	White spirit	petrol
CL	5	5	5	5	3	1	1	1
CM	4	5	5	5	3	1	1	1
CP	3	5	5	5	1	1	1	1
CS	2	5	5	5	0	0	0	0
CoL	4	5	5	5	3	1	1	1
CoM	3	5	5	5	3	1	1	1
CoP	3	5	5	5	1	1	1	1
CoS	1	5	5	5	0	0	0	0
RL	3	5	5	5	3	1	1	1
RM	2	5	5	5	3	1	1	1
RP	3	5	5	5	1	1	1	1
RS	0	5	5	5	0	0	0	0

5: Unaffected, 4: Slight loss in gloss, 3: loss in gloss, 2: swelling of the film,

1: film partially removed, 0: film completely dissolved

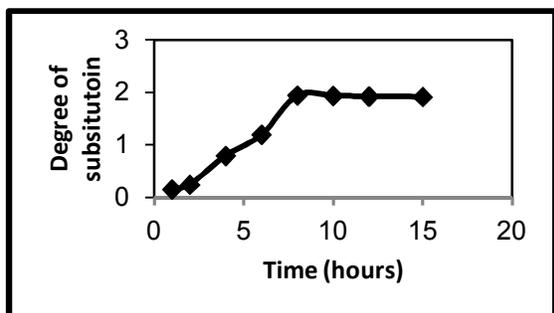


Figure (4) Change in degree of substitution (DS) VS time at 80° for CoL

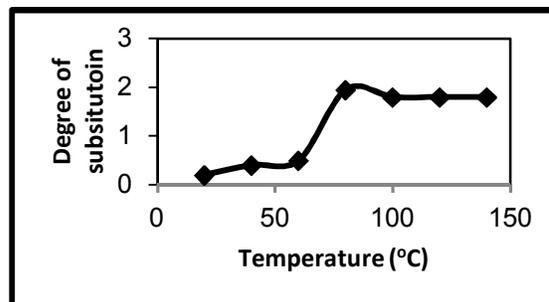


Figure (5) Change in degree of substitution. (DS) VS reaction temperature of CoL

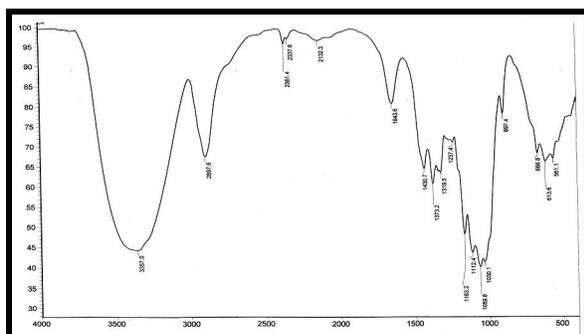


Fig. (6) FTIR of α -cellulose (C)

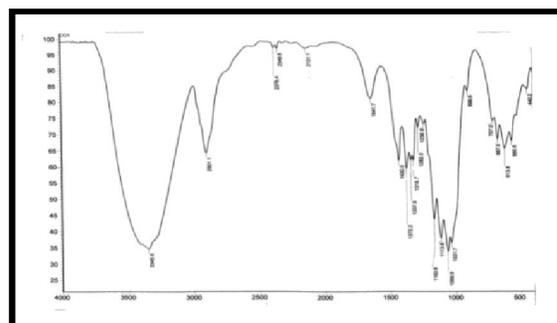


Fig. (7) FTIR of cotton linter cellulose (Co)

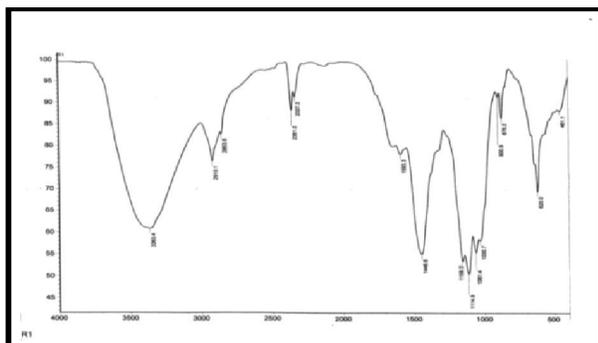


Fig. (8) FTIR of rice straw cellulose (R)

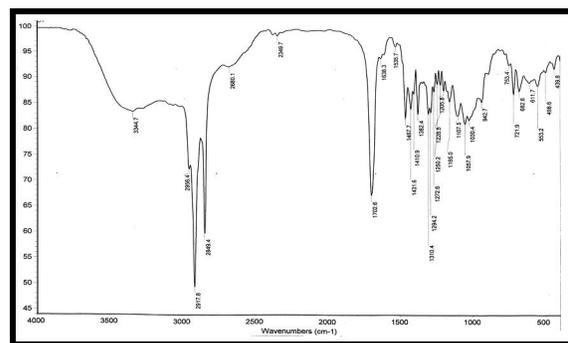


Fig. (9) FTIR of α cellulose palmitate (CP)

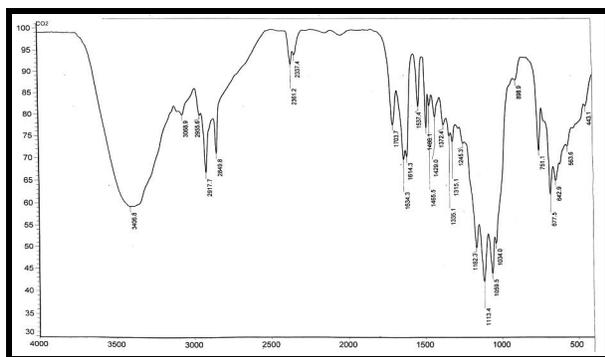


Fig. (10) FTIR of cotton linter cellulose stearate (CoS)

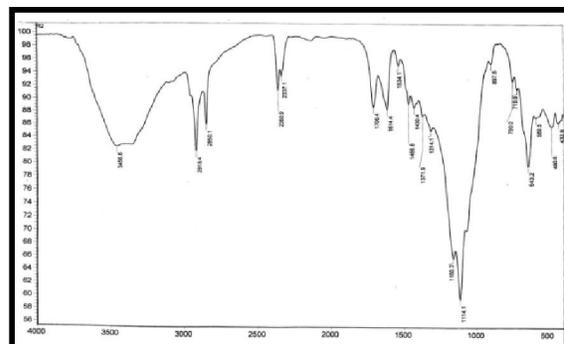


Fig. (11) FTIR of rice straw cellulose stearate (RS)

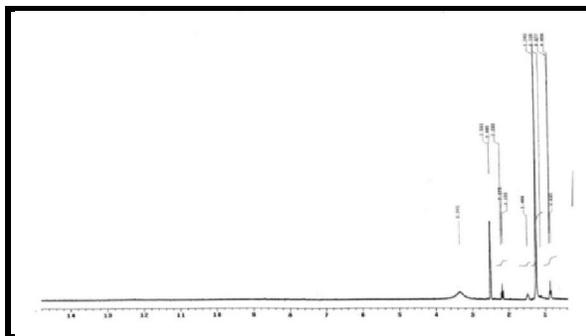


Fig. (12) ¹H NMR spectra of α cellulose palmitate (CP)

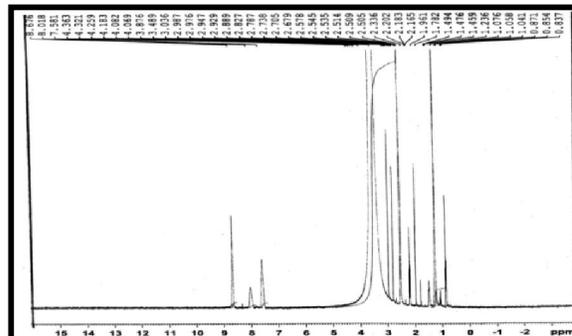


Fig. (13) ¹H NMR spectra of Cotton linter cellulose stearate (CoS)

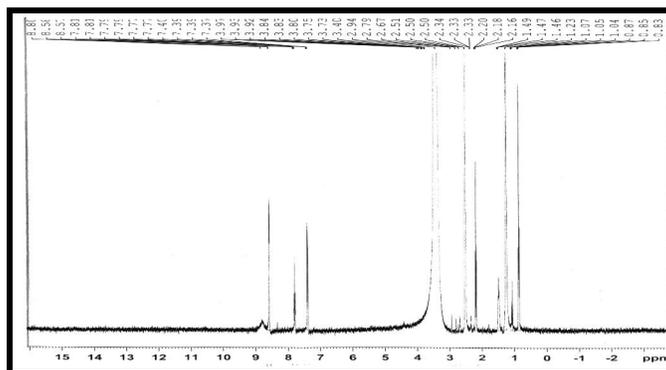


Fig. (14) ¹H NMR spectra of Rice straw cellulose stearate (RS)

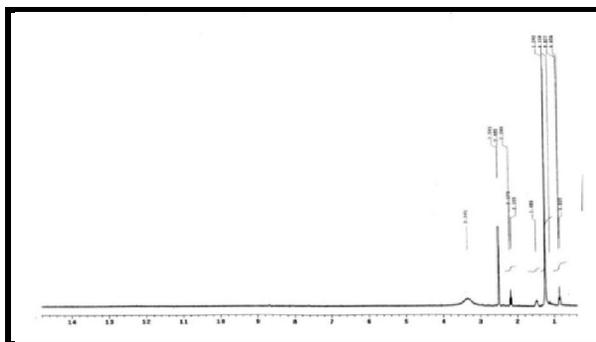


Fig. (12) ¹H NMR spectra of α cellulose palmitate (CP)

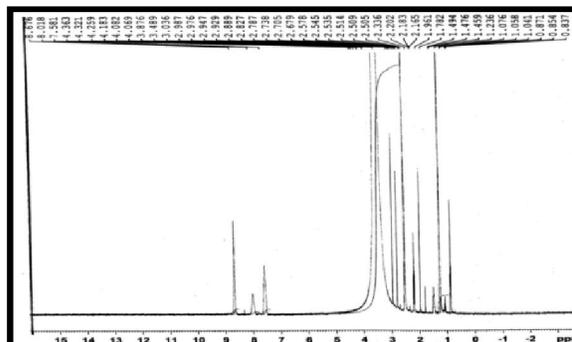


Fig. (13) ¹H NMR spectra of Cotton linter cellulose stearate (CoS)

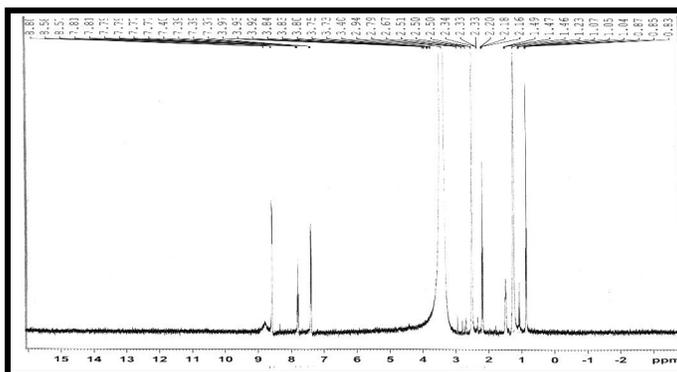


Fig. (14) ¹H NMR spectra of Rice straw cellulose stearate (RS)

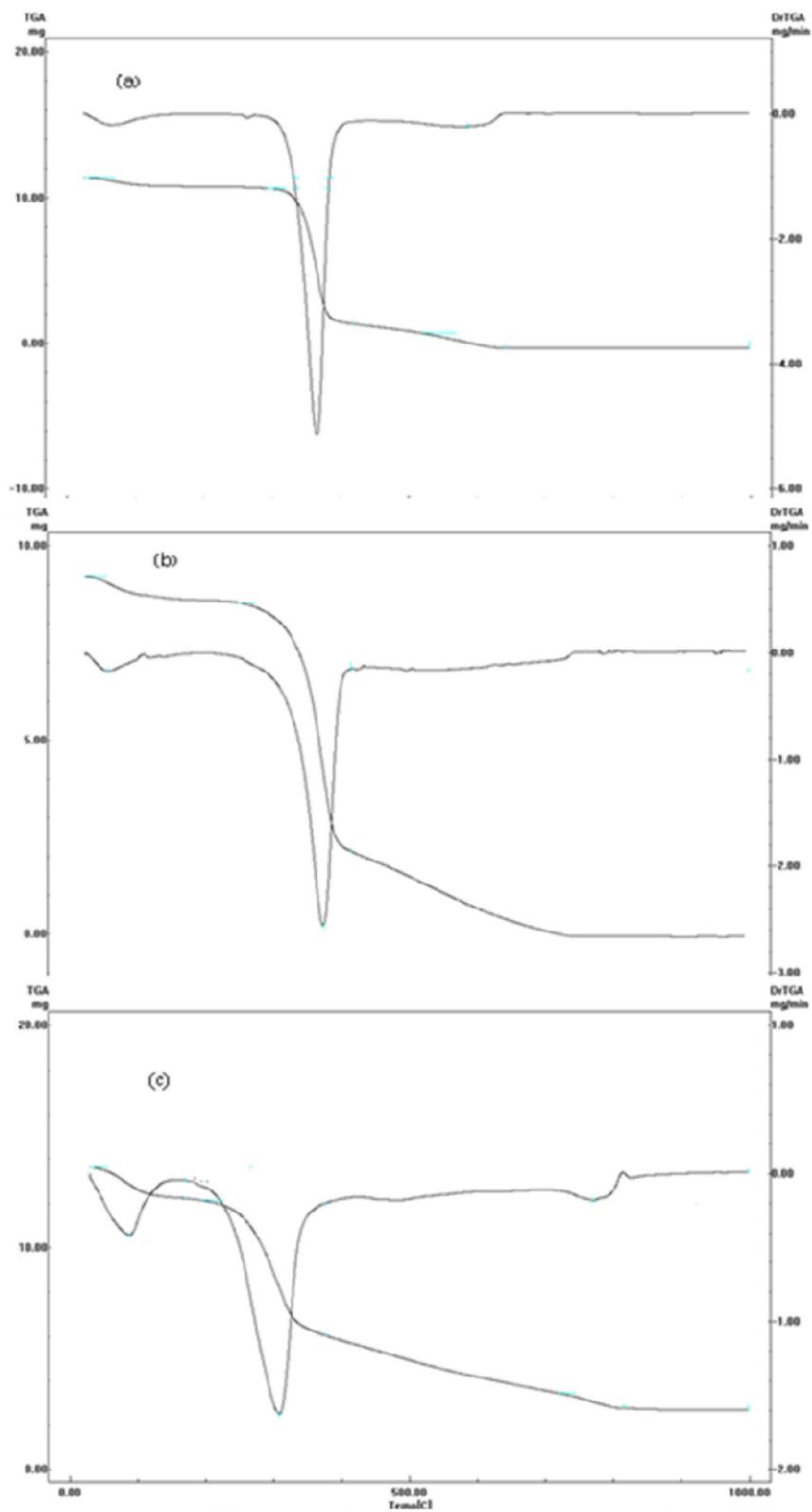


Fig. (15) Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) of (a) C, (b) Co and (c) R

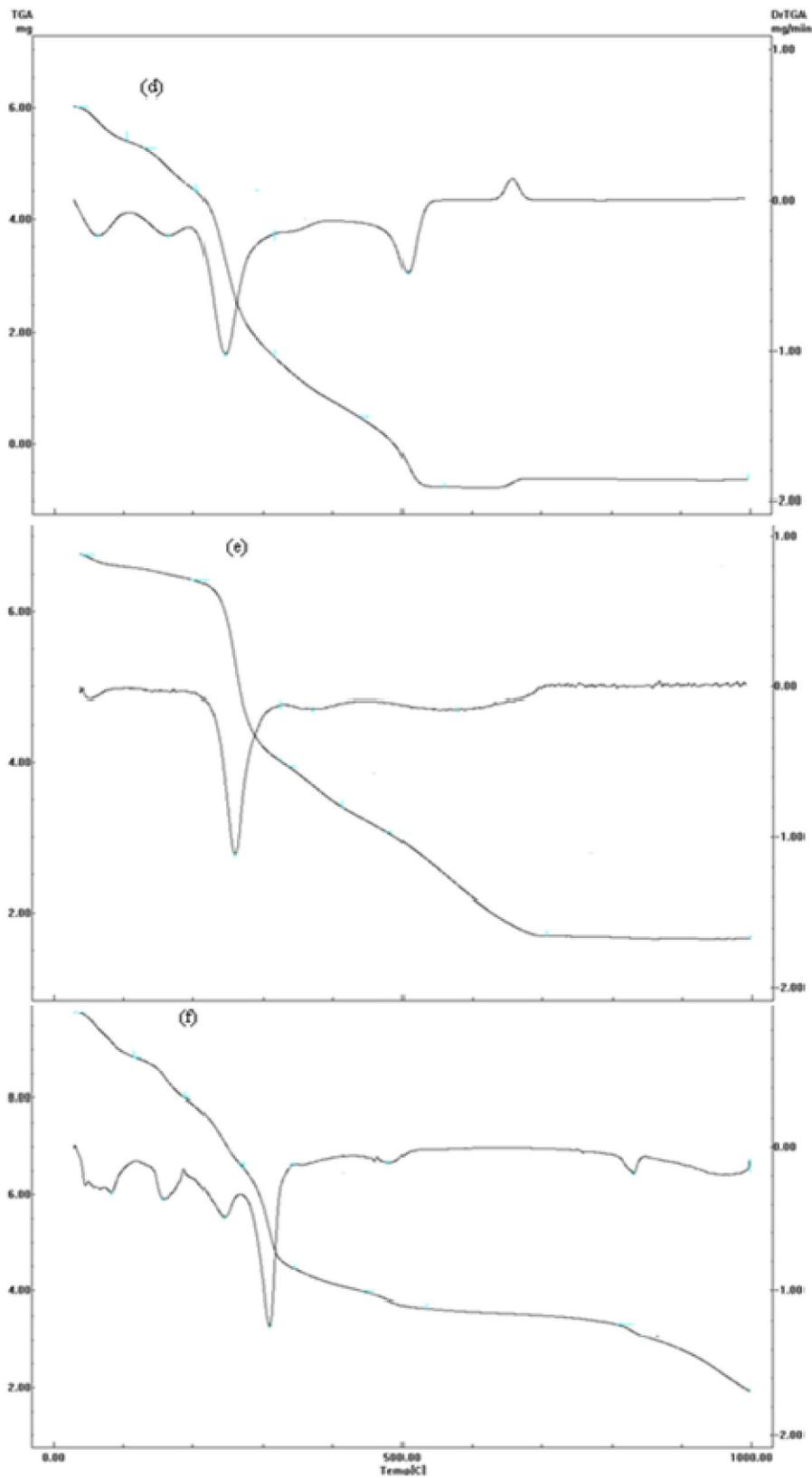


Fig. 16. TGA and DTG of (d) CL, (e) CoL and (f) RL

Conclusion

From the results obtained, it was found that cellulose esters showed high temperature of active decomposition and the active decomposition temperature (ADT) for cotton linters cellulose (Co) is higher than those of α cellulose (C) and rice straw cellulose (R) while that of RL is higher than those of CL and CoL. All rosin cellulose esters showed excellent physico-chemical properties and it can be suggested that these derivatives can be made compatible with conventional film forms such as alkyds, phenolics and epoxy esters and the combinations could be used in various surface coating formulations.

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