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Study of cellulose acetate prepared from spinning combing waste

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Abstract: Acetate Cellulose (CA) is a natural polymer from cellulose used mainly in the manufacture of filters, films, and plastics. Natural polymers have been mainly used in industrial and biological fields due to their safety and low production costs, and biodegradability.

The study focuses on preparing acetate polymer from spinning waste by different methods with acetic acid 80% at acetylation time (15- 30) minutes and 70% acetic acid at a acetylation

time (120- 180) minutes. (Experimental values were obtained based on the speed of forming a network of cellulose acetate fibers prepared on the electrospinning apparatus).

The prepared (CA) was tested with a nuclear magnetic resonance (NMR) test, the thermal behavior was determined by the DSC test.

The research shows that high (DS) was obtained at concentration 70% and high acetylation time, while the (DS) was lower at 80% concentration and low acetylation time. From the DSC test, we find that both the glass transition and melting temperature decrease with increasing the (DS), while the crystallinity increases with decreasing the (DS).

Keywords: polymer, acetate, hydrolysis, acetylation.

دراسة أسيتات السيللوز المحضر من عوادم تمشيط الغزل

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المستخلص: أسيتات السيللوز هو بوليمير طبيعي من السيللوز يستخدم بشكل أساسي في صناعة الفلاتر، الأفلام والبلاستيك. تستخدم البوليميرات الطبيعية بشكل أساسي في الصناعة والمجالات الطبية بسبب سلامتها وتكاليف إنتاجها المنخفضة وقابليتها للتحلل البيولوجي.
يركز البحث على تحضير بوليمير الأسيتات من عوادم تمشيط الغزل بطرق مختلفة وذلك باستخدام حمض الخل بتركيز 80% وزمن حلمهة (15- 30) دقيقة، وحمض الخل بتركيز 70% وزمن حلمهة (120- 180) دقيقة.

(قيم تجريبية تم اعتمادها بناء على سرعة تشكل شبكة من ألياف أسيتات السيللوز المحضر على جهاز الغزل الكهربائي). أسيتات السيللوز المحضرة تم اختبارها بواسطة جهاز الرنين النووي المغناطيسي، الخصائص الفيزيائية تم اختبارها بواسطة جهاز التحليل الحراري التفاضلي. يظهر البحث الحصول على درجة استبدال مرتفعة عند استخدام حمض الخل بتركيز 70% وزمن حلمهة مرتفع بينما تنخفض درجة الأستلة عند تركيز 80% من حمض الخل وزمن حلمهة منخفض. من اختبار التحليل الحراري نلاحظ انخفاض كل من درجة التحول الزجاجي ودرجة الانصهار مع زيادة درجة الاستبدال، بينما تزداد درجة التبلور مع انخفاض درجة الأستلة.

الكلمات المفتاحية: بوليمير، حلمهة، أسيتات، الأستلة.

1. INTRODUCTION.

recent paper focuses on recycling the waste from many industries to avoid environmental pollution and converting it into other useful materials.

Nowadays, natural polymers have an important part in our practical life. They have many important applications such as plastic materials, and raw materials for textile, films, membranes, biomedical applications and cigarette filters etc. [1] [2]

In several studies, we can produced cellulose acetate from avariety of recycled sources, such as bean straw [3], mango seed [4] by reacting cellulose with acids under various conditions. Different degrees of acetylating are obtained due to the process of preparation, we can determine the main fields that we can use this polymer because the properties change due to the value of (DS).

There are two forms of cellulose acetate, depending on the (DS) degree: cellulose diacetate and cellulose triacetate. We get the highest degree of acetylation when all hydroxyl groups are exchanged with acetyl groups, in this case the DS is three [5]. The (DS) degree must be determined because it determines the chemical, physical, mechanical and morphology properties of (CA).

Cellulose diacetate is used widely in industry because of its solubility in acetone, whereas triacetate cellulose is soluble in the chloroform, dichloromethane and all chlorinated solvents.

this work explained the preparation of acetate polymers from spinning combing exhausts.

2. research proplem:

recycling and processing of spinning combing exhaust to optain a polymer that has avariety of uses.

3. Experimental:

3.1. Materials:

Cotton wastes from spinning combing exhausts. The materials were used in the acetylation process acetic anhydride in addition to Glacial Acetic acid and Sulfuric acid which is used as catalyst. Sodium hydroxide and hydrogen peroxide were used in bleaching process.

3.2. Procedure:

3.2.1. preparation of cellulose acetate:

bleaching process: colors, fats and dusts were extracted from spinning combining wastes by washing several times with water and then bleaching procedure with

(3g/l of NaOH and 5% diethylene glycol) and (4ml/l of hydrogen peroxide 35%) in a water bath at 90C°for one hour, followed by washing and drying. Four samples of spinning waste are bleached, each sample weighing 5 g. [6].

dissolving exhaust: The bleached waste was immersed in beaker containing 50ml of Acetic acid and 0.5ml of Sulfuric acid and left for an hour with stirring at room temperature. Then beaker is placed in a water bath at 50C °. 50ml of acetic anhydride and 10ml of acetic acid were added and left for 30 minutes.

Hydrolysis process: The hydrolysis process is done using two different concentrations of acetic acid at different times, where The previous water bath is raised to 60C°, then gradually add to the bath of water with continuous stirring 50ml of Acetic acid 70% and 0.25 ml of concentrated Sulfuric acid then leave in the warm bath with stirring for (3- 4) hours [7]. The other way is by adding 50ml of 80% acetic acid and 0.25ml sulfuric acid and leave it in the warm bath with stirring for 15 minutes and 30 minutes. The resulting solution is then washed with the distilled water by adding 200ml of the distilled water, with stirring, thus obtaining a white polymer filtered and then washed well with warm water at 40C °. Finally, the formed polymers put in the dryer at 70C° for five hours, after that we obtain a white powder that represents to acetate cellulose.

Fig (1) acetate cellulose

Table (1) samples of cellulose acetate.

sample	Concentration of acetic acid	Hydration time
CA1	80%	15 min
CA2	80%	30 min
CA3	70%	120 min
CA4	70%	180 min

3.3. Characterization of cellulose acetate:

3.3.1.1H NMR:

The 1HNMR of cellulose acetate samples were registered in CDCl3 in Fig (2). The peaks at (1.9–2.2) ppm, reffer to the three methyl protons of acetyl groups and the peaks at (3.6–5.2) ppm reffer to the seven an hydro glucose protons [8].

3.3.2. Determination the degree of substitution (DS):

The average number of acetate groups (CH3COO) that substitute hydroxyls in each cycle of glucose gives the (DS). we get this values by spectroscopy of 1HNMR [9].

The (DS) value of CA was calculated as follows: [10].

$$DS = \frac{7 \times I(CH_3, H)}{3 \times I_{(AGU,H)}}$$

I (CH3, H): the integration of the peaks that assigned to the three protons of methyl acetyl group

I (AGU, H): the integration of the peaks that assigned to the seven protons of Glucose ring.

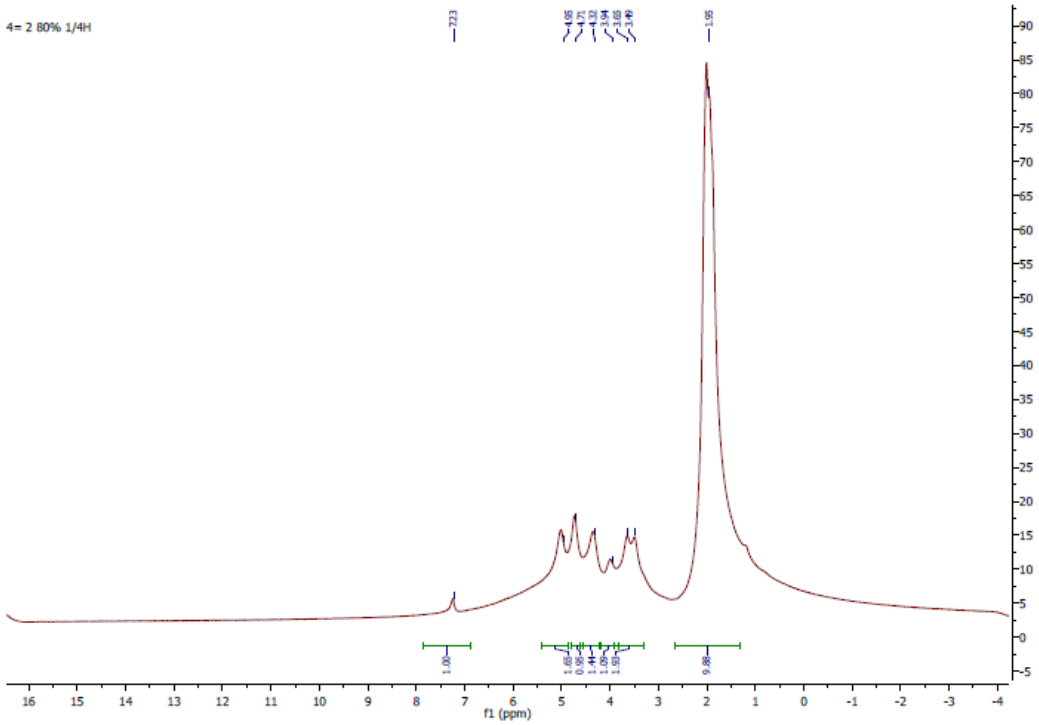
3.3.3. DSC analysis:

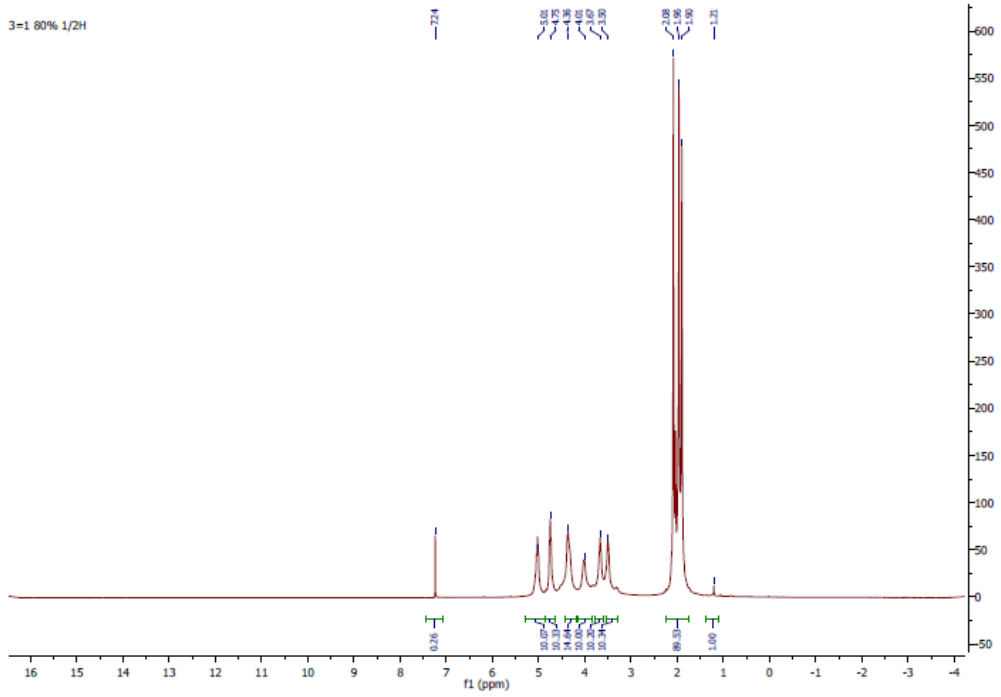
thermal properties of CA were determined by The differential scanning calorimeter in a range of temperature (25–400 °C). In this test (10 mg) of the CA were used. pierced lid in the N2 atmosphere (flow rate of 100 ml/min) at a heating ratio of 10 °C/min. The results were analyzed and recorded.

4. Results and discussion.

4.1. 4.1. Determination of (DS):

Some properties of CA chains determined by the amount of (OH) groups such as density and strength of the Hydrogen bonds. this bonds are strongly due to the number of (OH).


4= 2 80% 1/4H
f1 (ppm)


3=1 80% 1/2H
f1 (ppm)

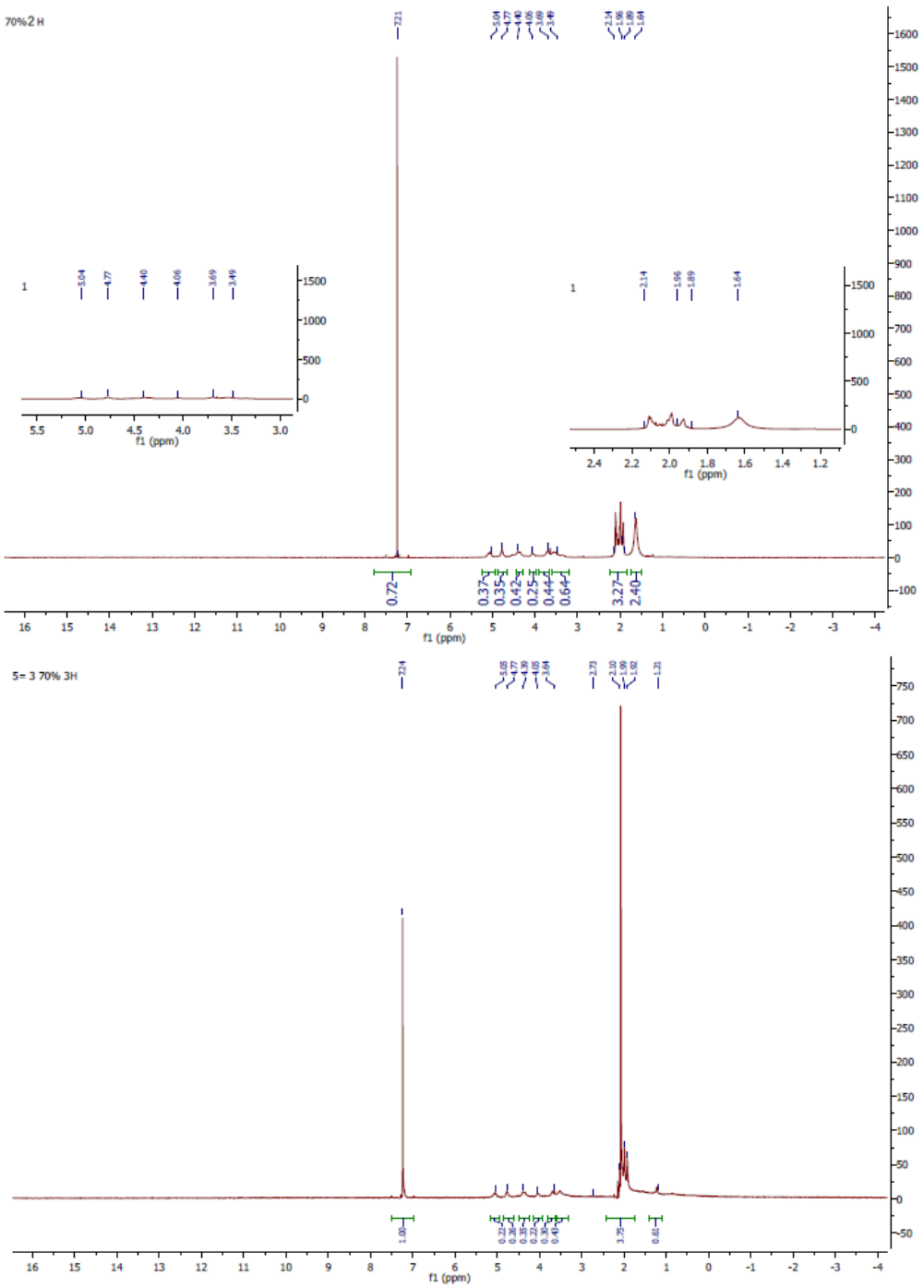


Fig (2)1H NMR spectra of the CA samples

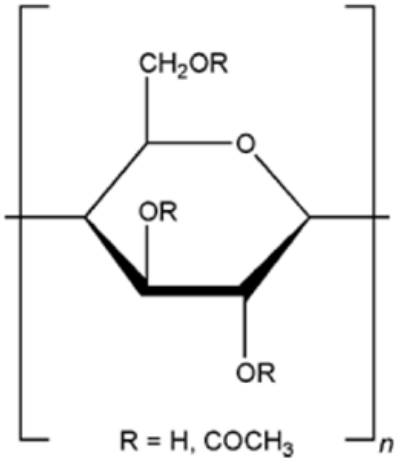
fig (2) shows an increase in the degree of substitution by increasing the acetylation time in a hot water bath, and we note that the use of lower concentrations of acetic acid and more time acetylation in CA3, CA4 gave higher substitution degrees.

Table (2) DS of cellulose acetate.

samples	DS
CA1	1.68
CA2	2.03

samples	DS
CA3	2.54
CA4	2.91

We note that the acetylation reaction happened from the NMR spectrum through the peaks that are between 1.6- 2.5ppm refers to the acytele groups while the peaks that are between 3.6- 5.2ppm refers to the protons of the glucose ring.



Acetate cellulose

4.2. Thermal analysis:

The glass transition and melting temperature were determined by DSC. Fig (3) and Fig (4) shows the curves by DSC of cellulose and acetate samples. [11]

The crystallinity degree of acetate is evaluated by the rate between the enthalpy of melting of the prepared sample (ΔHm) and respective enthalpy for the completely crystalline material (ΔHm^0). [12].

$$X_C\ (\%) = (\Delta H_m / \Delta H_m^0) \times 100$$

Where (ΔHm^0) = 58.8 J/g [13].

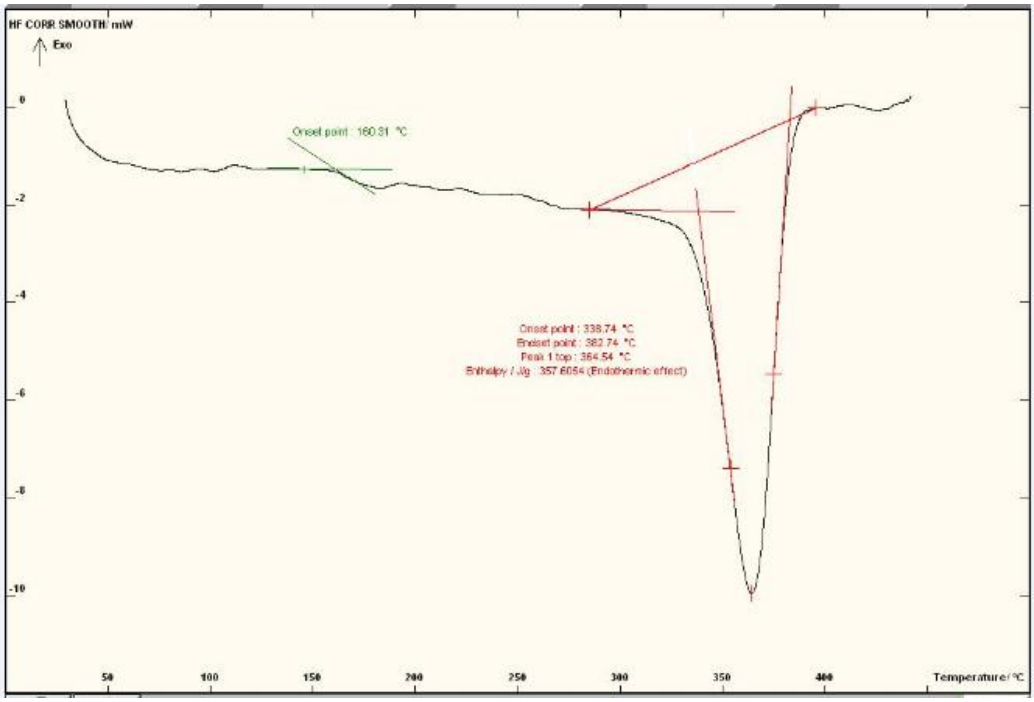
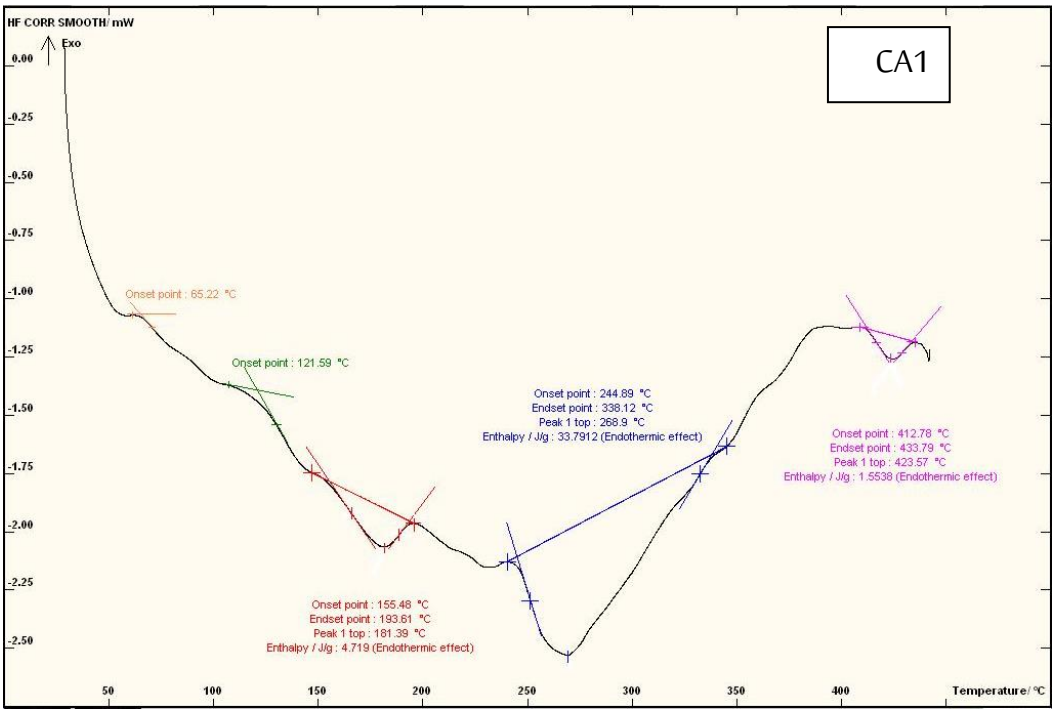
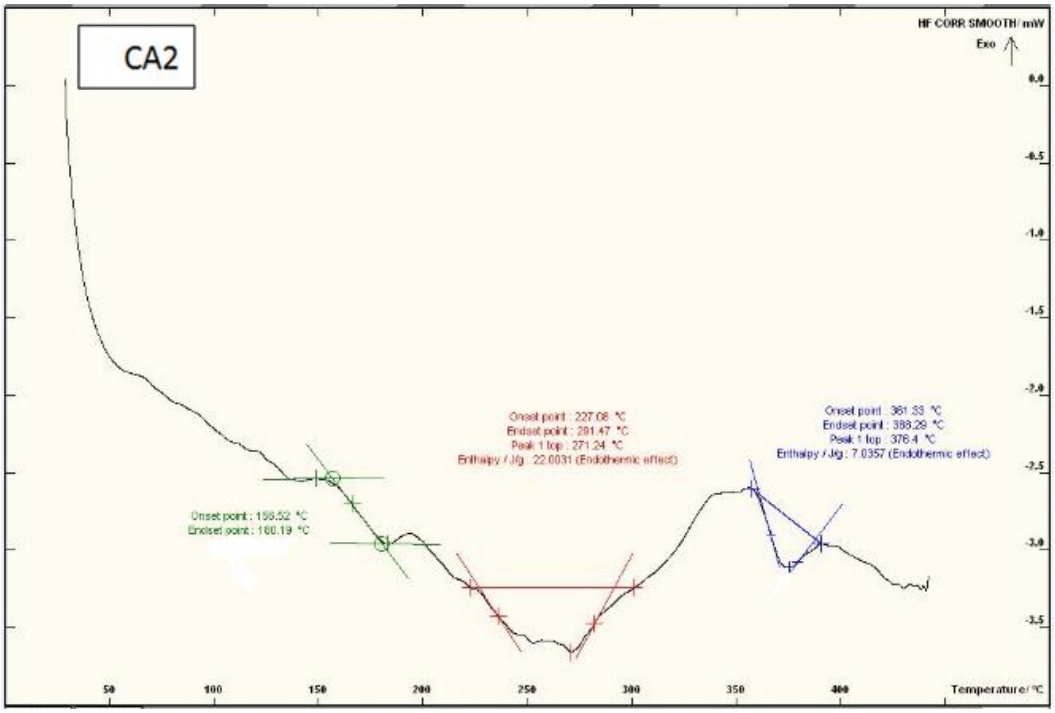
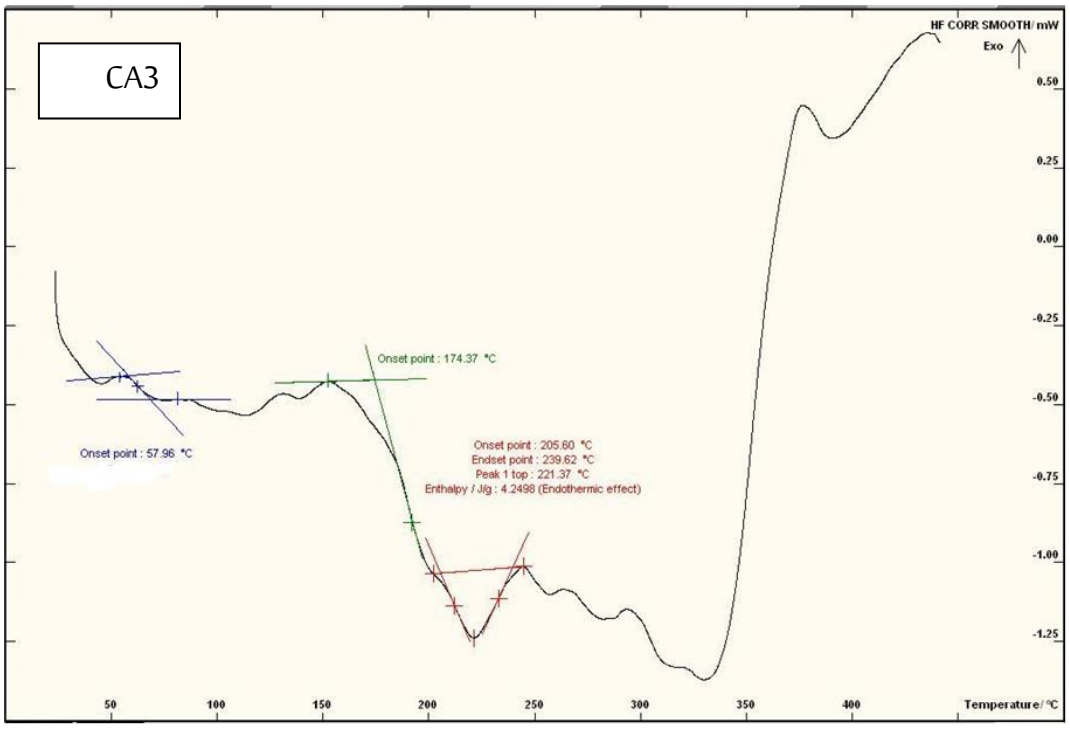


Fig (3) DSC of spinning combing exhausts




CA2
HF CORR SMOOTH / mW
Exo
Onset point : 227.08 °C
Endset point : 281.47 °C
Peak 1 top : 271.24 °C
Enthalpy / J/g : 22.0031 (Endothermic effect)
Onset point : 361.33 °C
Endset point : 388.29 °C
Peak 1 top : 376.4 °C
Enthalpy / J/g : 7.0357 (Endothermic effect)
Onset point : 156.52 °C
Endset point : 180.19 °C
Temperature / °C


CA3
HF CORR SMOOTH / mW
Exo
Onset point : 174.37 °C
Onset point : 57.96 °C
Onset point : 205.60 °C
Endset point : 239.62 °C
Peak 1 top : 221.37 °C
Enthalpy / J/g : 4.2498 (Endothermic effect)
Temperature / °C

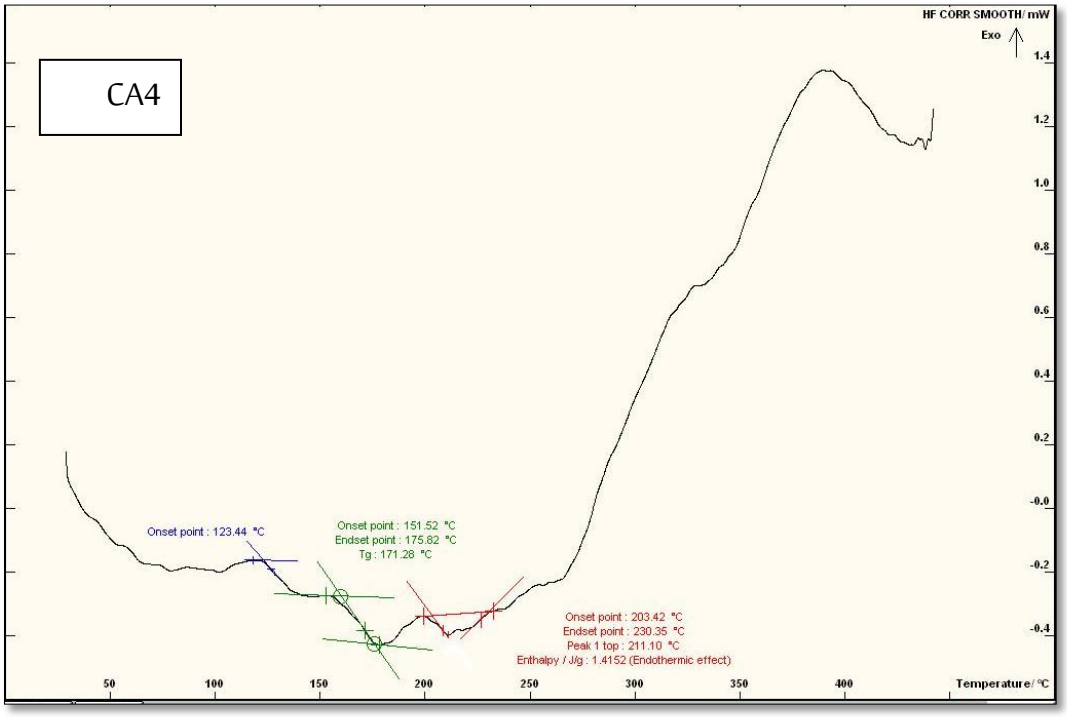


Fig (4) DSC of CA prepared in different conditions

Table (3) Thermal analysis of cellulose acetate samples.

Sample	Glass Transition (Tg)	Melting (°C)	Degradation (°C)	ΔH_m Melting (J.g- 1)	Xc %
CA1	181.39	268.9	423.57	33.79	57.46
CA2	180.19	271.24	376.4	22.0031	37.42
CA3	174.37	221.37	340	4.249	7.22
CA4	171.82	211.10	390	1.415	2.40

- we note that combing waste given an endothermic result evidenced in 160.31°C which refers to the (Tg). Tm is not present in Cellulose, that is a physical thermosetting natural polymer as shown in Fig 3 [14].
- desorption of the humidity is The first endothermic event apparent in all samples. depending on the (Ds) degree, this event happens at various temperatures. This event vary between 57.98C° and 123C° as show in Fig. 4.the presence of residual moisture causes Desorption.
- the glass transition is represented by the graph's second endothermic peak, we note samples (CA1, CA2) have greater (Tg) than (CA3, CA4), this is due to that acetyl groups reduce the intensity of hydrogen bonds formation, requiring lower temperatures to begin the (Tg). As a result, samples with a higher substitution degree have a lower glass transition temperature than samples with a lower substitution degree.
- The melting temperatures of the CA at the same concentration were very similar. The melting point of the acetate samples decreased as the (Ds) increased because the increased amount of acetyl groups

inhibits hydrogen bonds. so, the melting temperature of the acetate samples decreased with increasing acetylation time.

- The crystallinity degree of acetate decreases with the increase in the degree of substitution in the samples (CA3, CA4) because the increase in the number of acetyl groups separating the polymeric chains from each other due to the decrease the hydrogen bonds. [15].

5. Conclusions.

(CA) was prepared by changing the concentration of acetic acid and the acetylation time. We obtained higher substitution degrees at 70% of acetic acid and a greater acetylation time, and lower glass transition and melting temperature. We also note a decrease in the crystalline degree with an increase the acetylation time due to the acetyl groups that reduce the density of the hydrogen bonds formed between the polymeric chains of acetate.

6. Acknowledgements.

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References.

1- Law, R. C., (2004) Cellulose acetate in textile application in "Cellulose Acetates: Properties and Applications", Macromolecular Symposia 208, Rustemeyer, P., Ed., WILEYVCH Verlag GmbH & Co. KGaA, Weinheim, Germany, pp. 255- 266.

2- Law, P. W., Longdon, A. ve Willins, G. G., (2004) Solvent Cast Cellulose Diacetate Film in "Cellulose Acetates: Properties and Applications", Macromolecular Symposia 208, Rustemeyer, P., Ed., WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, pp. 293- 322.

3- Brum, S.S., Oliveira, L.C.A., de Bianchi, M.L., Guerreiro, M.C., Oliveira, L.K., de Carvalho, K.T.G., 2012. Synthesis of cellulose acetate from the bean straw using N- bromosuccinimide (NBS) as catalyst. Polímeros 22 447–445.

4- Cruz, A.C., Meireles, C.S., Ribeiro, S.D., Rodrigues Filho, G., Assunção, R.M.N., de Cerqueira, D.A., Zeni, M., Poletto, P., 2011. Utilization of cellulose acetate produced from mango seed cellulose as matrix for production of microparticles systems. Quím. Nova 34, 385–389.

5- Roberta R.M. de Freitas, André M. Senna, Vagner R. Botaro., Influence of degree of substitution on thermal dynamic mechanical and physicochemical properties of cellulose acetate. Industrial Crops & Products 109 (2017)

6- N.A. Mostafa, Awatef A. Farag Hala M. Abo- dief, Aghareed M. Tayeb, (2015), Production of biodegradable plastic from agricultural wastes, Arabian Journal of Chemistry.

7- A.U. ISRAEL, I.B. OBOT, S. A. UMOREN, V. MKPENIE and J.E. ASUQUO, (2007), Production of Cellulosic Polymers from Agricultural Wastes, E- Journal of Chemistry, Vol. 5, No. 1, pp. 81- 85, January 2008.

8- Basta, A. H., & Hosny, W. M. (1998). Dioxouranium (VI) complexes with celluloseacetate. Polymer Degradation and Stability, 60, 239–245

9- Archana M. Das, Abdul A. Ali, Manash P. Hazarika, Synthesis and characterization of cellulose acetate from rice husk:Eco- friendly condition, A.M. Das et al. / Carbohydrate Polymers 112 (2014) 342–349

10- Ass, B. A. P., Ciacco, G. T., & Frollini, E. (2006). Cellulose acetates from linters andsisal: Correlation between synthesis conditions in DMAc/LiCl and product properties. Bioresource Technology, 97 (14), 1696–1702.

11- Antal, M. J., & Varhegyi, G. (1995). Cellulose pyrolysis kinetics: The current state ofknowledge. Industrial and Engineering Chemistry Research, 34, 703–717.

12- Congyu Bao. (2015). "Cellulose acetate / plasticizer systems: structure, morphology and dynamics" Université Claude Bernard.

13- Cerqueira, D. A., Filho, G. R., & Assuncao, R. M. N. (2006). A new value for the heat of fusion of a perfect crystal of cellulose acetate. POLYMER BULLETIN, 56, 475- 484.

14- Wan Daud, W.R., Djuned, F.M., 2015. Cellulose acetate from oil palm empty fruit bunch via a one step heterogeneous acetylation. Carbohydr. Polym. 132, 252–260.

15- Kendouli, S., khalfallah, O., Sobti, N., Bensouissi, A., Avci, A., Eskizeybek, V., Achour, S., 2014. Modification of cellulose acetate nanofibers with PVP/Ag addition. Materials Science in Semiconductor Processing. Int. Semicond. Sci. Technol. Conf. ISSTC- 2014