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Elaboration of the new cellulose derivative films (HECA) based on "Stipa Tenacissima" cellulose of Eastern Morocco

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Abstract

Hydroxyethyl cellulose Acetate (HECA) was prepared starting from hydroxyethyl cellulose (HEC), acetic anhydride and perchloric acid which was used as catalyst. The synthesized product was characterized by TFIR, ^{13}C NMR and ^{1}H NMR. Substitution degree (DS) of HECA was determined using FTIR spectra taking a classical titration method and 1H NMR spectra as reference. The DS is substantially affected by the temperature, the time of reaction and especially the equivalent number (eq. nb.) of the acetic anhydride added. The thermal analysis study shows some differences in Tg and thermal degradation between HEC and HECA, moreover these thermal temperatures are influenced by DS values.

Keywords: *Biodegradable; Alfa; plastics; Cellulose; Modification.*

1. Introduction :

Cellulose is the natural most abundant linear polymer. Its isolation and purification represent one of the largest activities **[1]**. Cellulose also is the basis of a large industry **[2, 3]**, and it will be necessary and useful to look for improvements and optimization as well as for environmental safety. Its advantages are that it is renewable, biodegradable and biocompatible and can be derivatized to yield various useful products **[4, 5]**; cellulose will be the main chemical resources of the future, which will still be available when other substances became increasingly scarce. Yet, cellulose is hardly ever used as a chemical raw material because of its difficulty in dissolution resulting mainly from the highly extended hydrogen bonding of its anhydroglucose repeat units. This phenomenon prevents cellulose from being processable by normal melt (or solution) technologies. This processing handicap is conventionally overcome by chemical modification of cellulose, generally accomplished heterogeneously **[6]**.

The non solubility of cellulose in almost all common solvents has been a stumbling block in its appropriate utilization. The dissolution step usually proves to be cumbersome or expensive, or results in extensive degradation of the macromolecular backbone. Some solvents have been reported, but they are seldom useful for a wide range of synthetic reactions **[7, 8]**. For example N, N dimethylacetamide (DMAc) containing lithium chloride is a solvent system used frequently in polysaccharide chemistry and causes a faster dissolution of the material **[9-15]**. However, the solubility gain is not only due to improved activation, swelling or breaking of hydrogen bonds, but also due to a degradation of the high molecular weight distribution of the pulps. All activation treatments accelerate the dissolution rate, cause intra and inter-crystallite swelling, break hydrogen bonds and increase accessibility **[16, 17]**.

A number of cellulose derivatives are currently prepared under heterogeneous conditions. Cellulose esters are generally synthesized employing an anhydride with a catalyst or an acid chloride in the presence of a tertiary base **[18]**. However, problems arise such as poor uniformly of substitution; low yields and extensive by product formation, consequently there is much interest in developing new acetylating methods to provide products with novel characteristics **[19]**. For a maximum conversion of cellulose to its derivatives, it is advisable to carry out the reaction in a homogeneous medium, requiring a suitable solvent system **[20-22]**. The search for new systems and process is important on environmental grounds, because problems tend to be focused around optimization and ecological issues.

Chemical modification has been used as means of improving and enhancing solubility of cellulose and its derivatives by using appropriate chemical entities such as: introducing water-soluble entities, hydrophilic moieties, bulky and hydrocarbon groups, etc **[6]**. The cellulose ether is commonly introduced into industrial formulations in order to improve workability of the fresh material and adherence to the substance. Hydroxyethyl cellulose (HEC) such as one of the cellulose ethers has attracted a considerable attention **[23, 24]** as a retardation of the cement hydration **[25, 26],** , stabilizer and thickener in paint formulation, additive in order to achieve the desired rheological effect, etc.

In the present work, we describe the synthesis of a new cellulose derivative compound (HECA) soluble in most organic solvents such as THF, starting from Hydroxyethyl cellulose (HEC) prepared from "Stipa Tenacissima" cellulose of Eastern Morocco and acetic anhydride27. The resulted product (HECA) will combine, at the same time, the properties of the both most successful industrial biopolymers: Cellulose acetate (CA) and hydroxyethyl cellulose (HEC).

We studied also the effect of the temperature (T), the time of reaction (t) and equivalent numbers (eq. nb.) of acetic anhydride added on DS variations

2. Experimental and methods

2.1. Material

Hydroxyethyl cellulose (HEC DS=1.5) was prepared in NaOH/Urea aqueous solution **[23]** starting from cellulose extracted in basic medium as mentioned by *A. El Idrissi et al.* **[27]** using “Stipa Tenacissima” of Eastern Morocco. Acetic anhydride and perchloric acid were purchased from Aldrich Chemical Company. All other chemicals were of analytical grade and are used without further purification and purchased also from Aldrich.

2.2. Hydroxyethyl cellulose acetylating

2 g of HEC (8, 83 mmol) were dried at 40 °C during 24 h and were introduced in a three-necked bottle. Various acetic anhydride equivalent numbers were added respectively to the mixture 1 (8, 83 mmol); 1.5; 2; 3; 6; 9; 12 and 15 eq.nb. The temperature and time of reaction have been varied respectively between (0; 25; 50; 60; 90 °C) and (15; 30; 45; 60 and 90 min). The mixture was stirring for 15 min before adding perchloric acid as catalyst at room temperature and a homogenize medium is obtained. The product was precipitated in water or in diethyl ether. After the filtration under vacuum, the product was washed three times with cold water (or cold ether) and dried firstly at 60 °C for 24 h and secondly in desiccators for one week with P_2O_5. The HECA samples resulted were purified a second time by the dissolution-precipitation method in different solvents. The samples recovered were characterized and studied using different techniques.

2.3. HECA characterization

3.3.1 Casting

The plastic films were obtained by the casting method, 1g of the HECA samples were dissolved in 30 ml of (DMF for DS≤ 1.5, THF for DS ≥1.5 or water for DS=0). Each solvent was eliminated by evaporation process under vacuum.

3.3.2 DS determination

Volumetric method:

HECA (sample 8) prepared by adding 15 equivalent number of acetic anhydride at 60 °C for 1 h, was reacted with 0.15 M (KOH/ethanol) solution for 24 h at 25 °C. The resulted solution was titrated with 0.1 M acetic acid solution. The DS value calculated is named DS_{ref} .

$$DS_{ref} = \frac{M_{HEC} \cdot \Delta n_{KOH}}{m_{sampl} - \Delta n_{KOH} \cdot M_{acl}} = 2.6 \quad (1)$$

In which:

DS_{ref} = degree of substitution of the reference sample (sample 8)

M_{HEC} = HEC monomer molar weight = 228.22 g mol^{-1}

Δn_{KOH} = molar number variation of KOH before and after saponification

M_{acl} = acetic liberated group molar weight = 42.04 g mol^{-1}

Equation 1 was used to determine the DS of a sample which had been chosen as a reference. The DS value of other HECA samples were calculated by taking into account the absorption band surfaces of the functions existing in their structure (C= O and O–H), using FTIR spectra.

$$DS_{sampl} = DS_{ref} \frac{\left(S(CO) / S(OH) \right)_{sampl}}{\left(S(CO) / S(OH) \right)_{ref}} \quad (2)$$

S (OH) and S (CO) are area of the absorption bands of the function hydroxyl and carboxyl respectively.

NMR method:

The NMR spectra were performed on esters dissolved in DMSO-d6. The different signals can be classified in three parts: 15 HEC main chain protons are located between 3.2 ppm and 5.6 ppm and H_4 HEC proton hidden by water protons at 3 ppm (fig.3), and methyl protons appeared at 2 ppm. ^{1}H NMR method can also be used as tool to calculate the DS of cellulose derivatives based on protons integrations of different functions. The equation 3 obtained from this NMR investigation may be used to deduct the DS value of HECA samples in this case:

$$\frac{I_{HEC}}{I_{CH_3}} = \frac{(16-H_4)-DS}{3DS} = \frac{15-DS}{3DS}$$

$$\Rightarrow DS = \frac{15 I_{CH_3}}{3 I_{HEC} + I_{CH_3}} \quad (3)$$

In witch:

I_{CH_3} = methyl protons integration

I_{HEC} = 15 HEC protons integration

2.4. Spectroscopic measurements

The chemical structure of HECA samples were evaluated by FTIR, ^{13}C NMR and ^{1}H NMR spectroscopy techniques. FTIR spectra were obtained on a Shimadzu Fourier transform infrared spectrometer FTIR- 8400S using a KBr disc containing 2% finely ground samples. Twenty scans were taken of each sample recorded from 4000 to 400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a *Bruker 200 MHz* spectrometer at 360 °K by Technical scientific research national centre at Rabat-Morocco, using TMS as internal standard and DMSO-d_6 as solvent respectively.

2.5. Thermal analysis

Thermal study of HECA samples with various DS was performed using thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) on a Shimadzu DTG-60 simultaneous DTA-TG apparatus. The weight sample was between 8 and 12 mg. Two scans were run from room temperature to 500 °C at a rate of 10 °C/min under nitrogen flow.

2.6. Solubility:

The experimental results for the description of the solubility have been obtained by test solvents, where; the spatula point of the HECA samples was added to ~3ml of each solvent. HECA samples have been used in the granular form (as prepared).

3. Results and discussion

The HEC modification

Figure (1) presents the acetylating reaction of HEC using acetic anhydride as reagent. The most important aspects to be considered when developing methods for the chemical modification of natural products are their simplicity and the time required for this process.

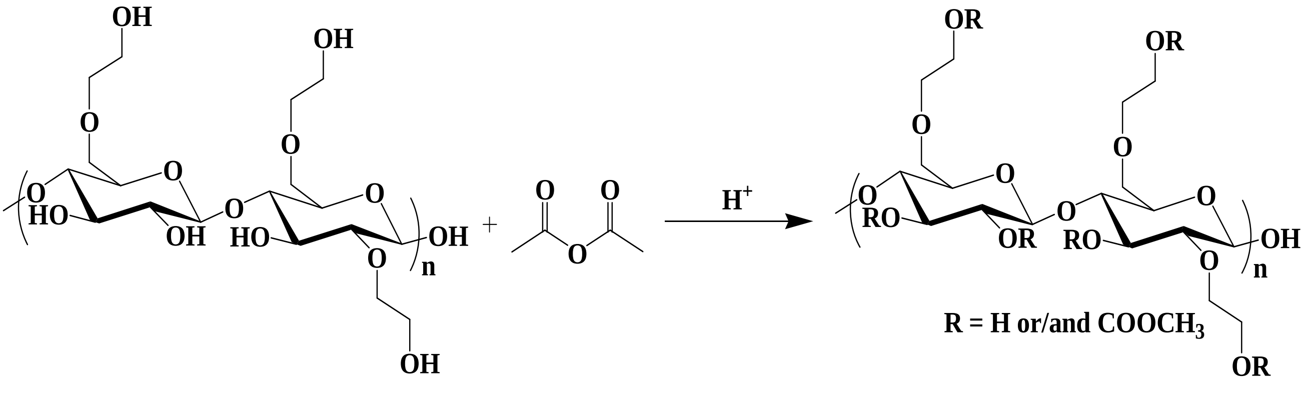

Fig. 1. HEC acylation reaction.

This reaction was conducted at various molar ratio of HEC to acetic anhydride for different times and temperatures, the results obtained are grouped in table 1.

Table 1. Results and conditions of the HEC acetylation. a: acetylation without catalyst; X: non soluble ; O: soluble;

						Solvent			
Spl.	t (min)	T (°C)	Eq. nb.^{b}	DS. IR-TF	DS.^{1}H NMR	EtOH	THF	DMSO	H_2O
1	60	60	1	0.41	-	O	x	O	x
2	60	60	1.5	0.57	-	O	x	O	x
3	60	60	2	0.7	0.72	O	x	O	x
4	60	60	3	1.07	1.27	O	x	O	x
5	60	60	6	1.4	-	O	O	O	x
6	60	60	9	1.61	-	O	O	O	x
7	60	60	12	2.24	2.4	x	O	O	x
8	60	60	15	2.6^c	-	x	O	O	x
9	15	25	6	0.26	-	O	x	O	O
10	30	25	6	0.34	-	O	x	O	O
11	45	25	6	0.45	-	O	x	O	x
12	60	25	6	0.6	-	O	x	O	x
13	90	25	6	0.81	-	O	x	O	x
14	60	0	6	0.35	-	O	x	O	O
15	60	25	6	0.6	-	O	x	O	x
16	60	50	6	1.14	-	O	x	O	x
17	60	60	6	1.4	-	O	O	O	x
18	60	85	6	3.2	-	O	O	O	x
S.c^a	60	25	6	0.26	-	O	x	O	O

b: 1 eq; a mount to acetylat one hydroxyl group; c: determined by volumetric method (ref).

FT-IR spetra

Fig. 2, shows the FTIR spectra of unmodified HEC (1) and Hydroxyethyl cellulose acetate samples (HECA) with different substitution degree [DS=0.72; 1.27 and 2.4]. When the acetylating reaction takes place between acetic anhydride and HEC, the modification may be proved by the carbonyl ester band apparition at 1739 cm^{-1} and the decrease of OH broad band intensity assigned to alcohol group at 3480 cm^{-1}.

The peaks located at ~ 2948 cm^{-1}and ~ 2885 cm^{-1}are attributed to ν(C-H) and ν($C\text{-}H_2$) groups respectively **[28]**. The band located also at 1647 cm^{-1} corresponds to the bending mode of the naturally absorbed water **[29]**. The absorbance at 1375 cm^{-1} arises from the $C\text{-}CH_3$ vibration, moreover the peak at 1242 cm^{-1} is originated from ν(C-O)$_{\text{ester}}$ vibration.

The effect of acetic anhydride equivalent numbers added to the solution mixture is illustrated by comparing the FTIR spectra (2), (3) and (4) presented in figure 2. Using the experimental data, we have noted that with increasing fraction of acetic anhydride in the mixture, the absorption band surface change, and the ratio between ν(C=O) and ν (O-H) surfaces increases. The experiments based on FTIR spectra show that the DS increases with increasing acetic anhydride amounts added. The equation 1 was proposed to determine the (DS) values and the results obtained are grouped in table 1.

NMR Study

First, it must be noted that the sample must be purified. The spectra represented on figure 3 shows the peak attributed to the water at ~3 ppm. The HEC methylene proton signals between ~3.5 ppm and ~3.6 ppm were overlapped with the broad ring proton signals (2.8~5.6 ppm) of the cellulose skeleton. HECA synthesis was successfully proved by the presence of a novel signals at 2.0 ppm and at 4.11 ppm which are attributed respectively to the acetyl protons and to the methylene in α to the ester.

The DS values of HECA samples were also estimated using ^{1}H NMR technique from the acetyl protons to the total HEC proton integrations as mentioned in section 3.3.2 (eq.3), and the results are summarized in table 1.

Figure 4, presents the ring carbon of HECA DS = 2.4 (sample 7), in DMSO-d_6 at 360°K. The signals at 21 ppm and ~170 ppm in the ^{13}C NMR spectra indicate the presence of the acetyl group carbon and the carbonyl ester respectively. The assignments of the other peaks are, according to *Qi Zhou et al.* **[23]** and *Juli et al.* **[24]**, attributed to the HEC carbon region (60 – 105 ppm).

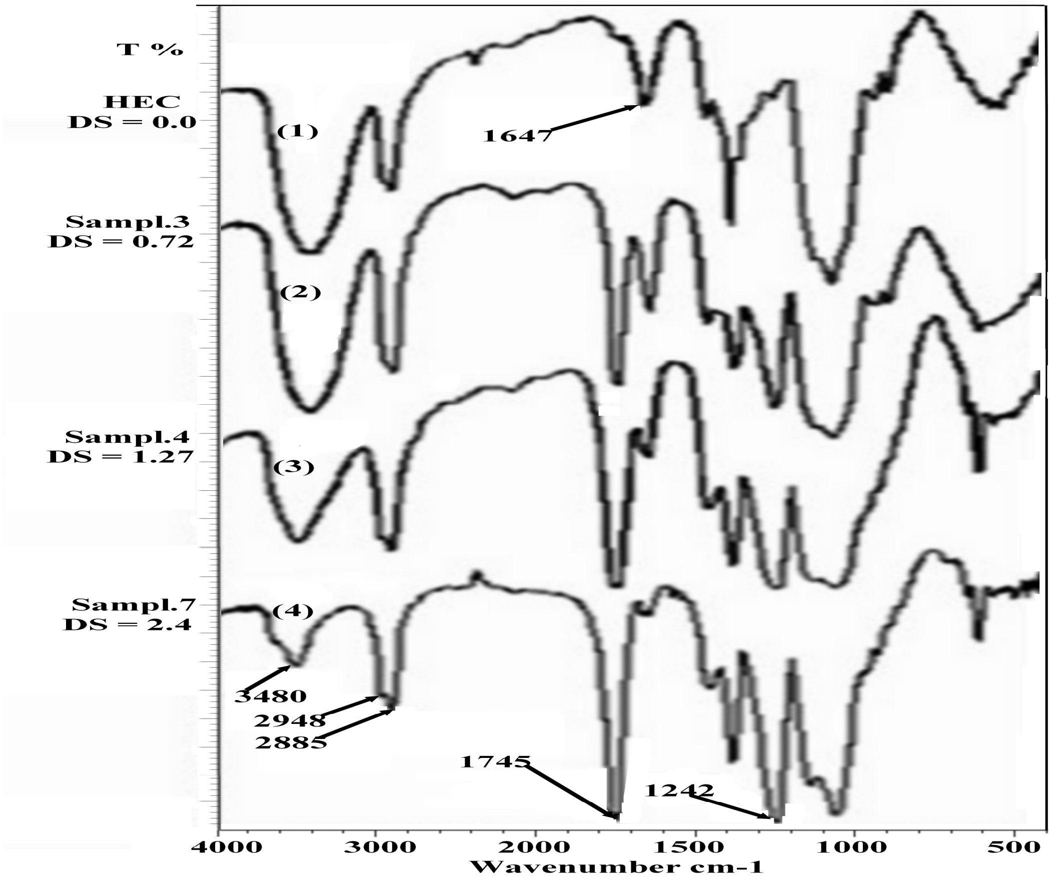

Fig. 2. FT-IR spectra of unmodified HEC (1) and HECA with DS=0.72 (2), DS=1.27(3) and DS=2.4 (4)

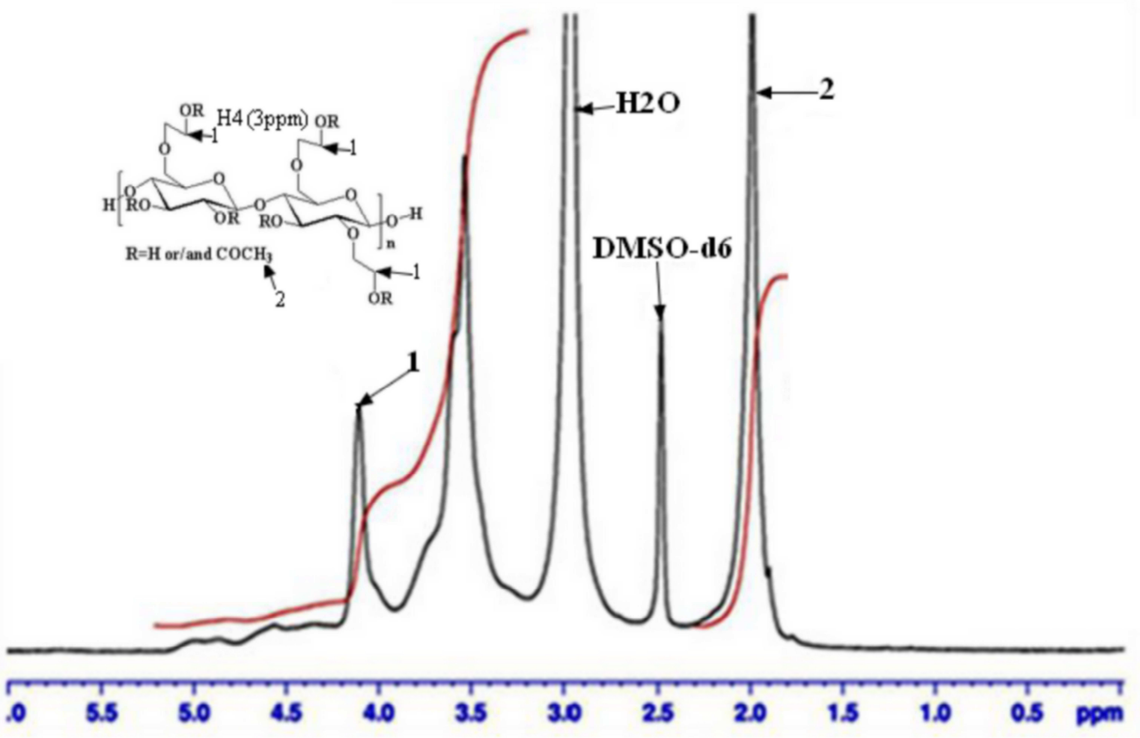

Fig. 3. ^{1}H NMR Spectra of HECA DS = 2.4

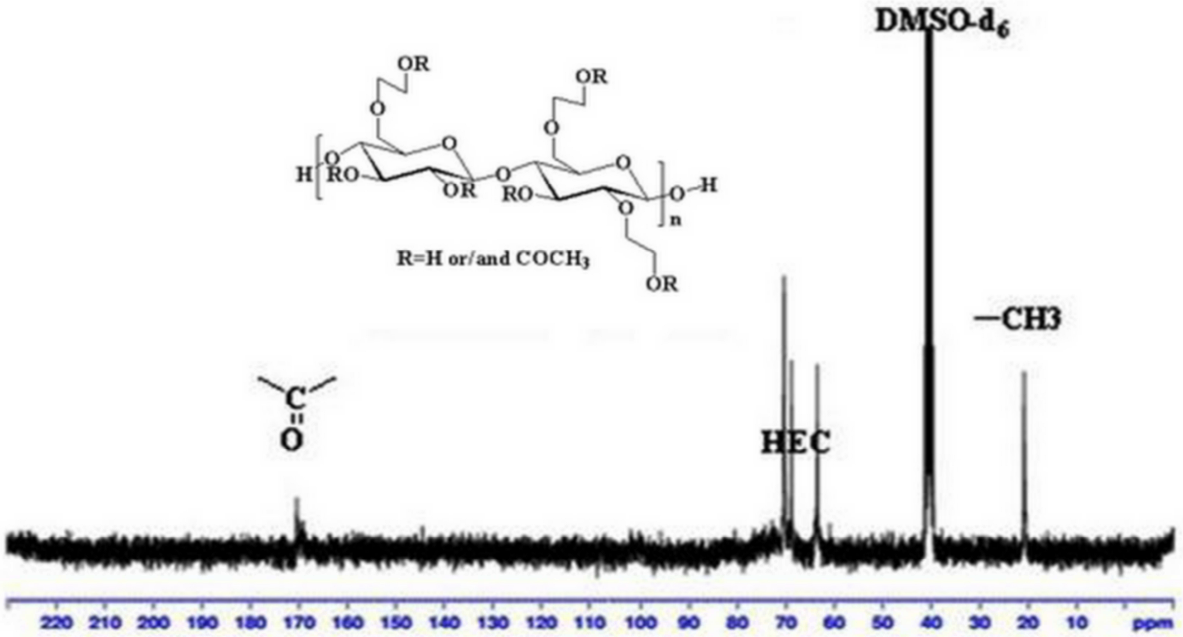

Fig. 4. ^{13}C NMR Spectra of HECA DS = 2.4 (sample 7)

The substitution degree (DS) in the HECA samples increases with increasing respectively the acetic anhydride equivalent numbers, and the reaction time as shown in the figure 5 (a) and (b).

At 80 °C, the process runs at a higher rate and the HECA obtained have a higher degree of substitution than the samples obtained at room temperature (c). From above experiments, the non variation of the degree of substitution at low temperature from 0 to 20 °C (figure 5. c) was noted. The DS values increase exponentially with an increase in the reaction temperature.

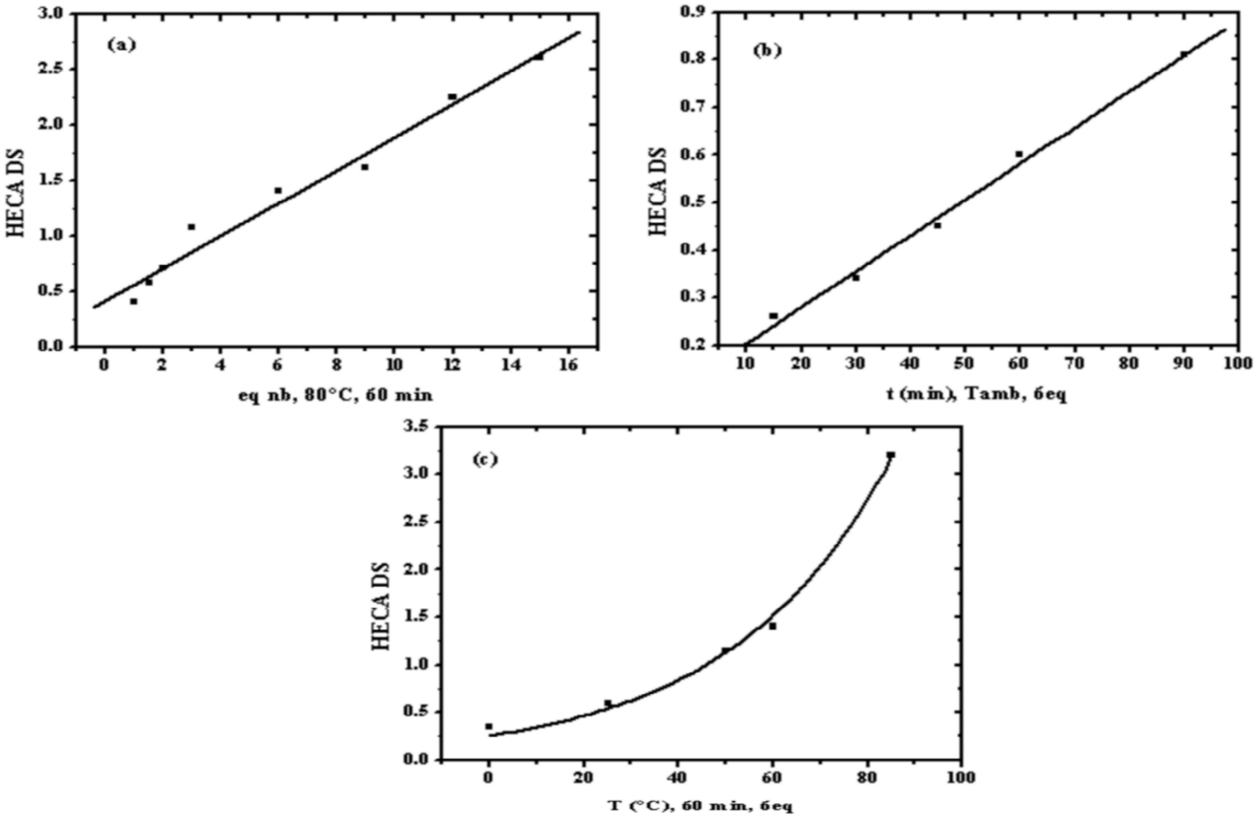

Fig. 5. (a) Acetic anhydride equivalent number, (b) time and (c) temperature reaction controlled acetylation of HEC

Thermal study

The effect of the acetylating on the thermal behavior of HEC was also studied by TGA and TDA in the temperature range from 35 °C to 500 °C. Figure 6 Shows the TGA and TDA Thermograms of unmodified HEC (a), HECA with DS=0.72 (b) and HECA with DS= 2.4 (c). From the above figure, it can be seen that the thermal degradation temperature of HECA increases with increasing DS values. The HEC starts to decompose at 280 °C, while the acetylated HEC DS = 0.72 (b) and DS = 2.4 begin to decompose respectively at 312 °C and 327 °C. At 50% weight loss, the decomposition temperature occurs at 330 °C for unmodified HEC and 345 °C for HECA (DS = 0.72) and at 355 °C for HECA (DS = 2.4). This increasing in the decomposition temperature implied that the thermal stability of HECA is more important than that of HEC, and increases with the DS values. Similar results were also observed in the case of cellulose and cellulose acetate **[30]**.

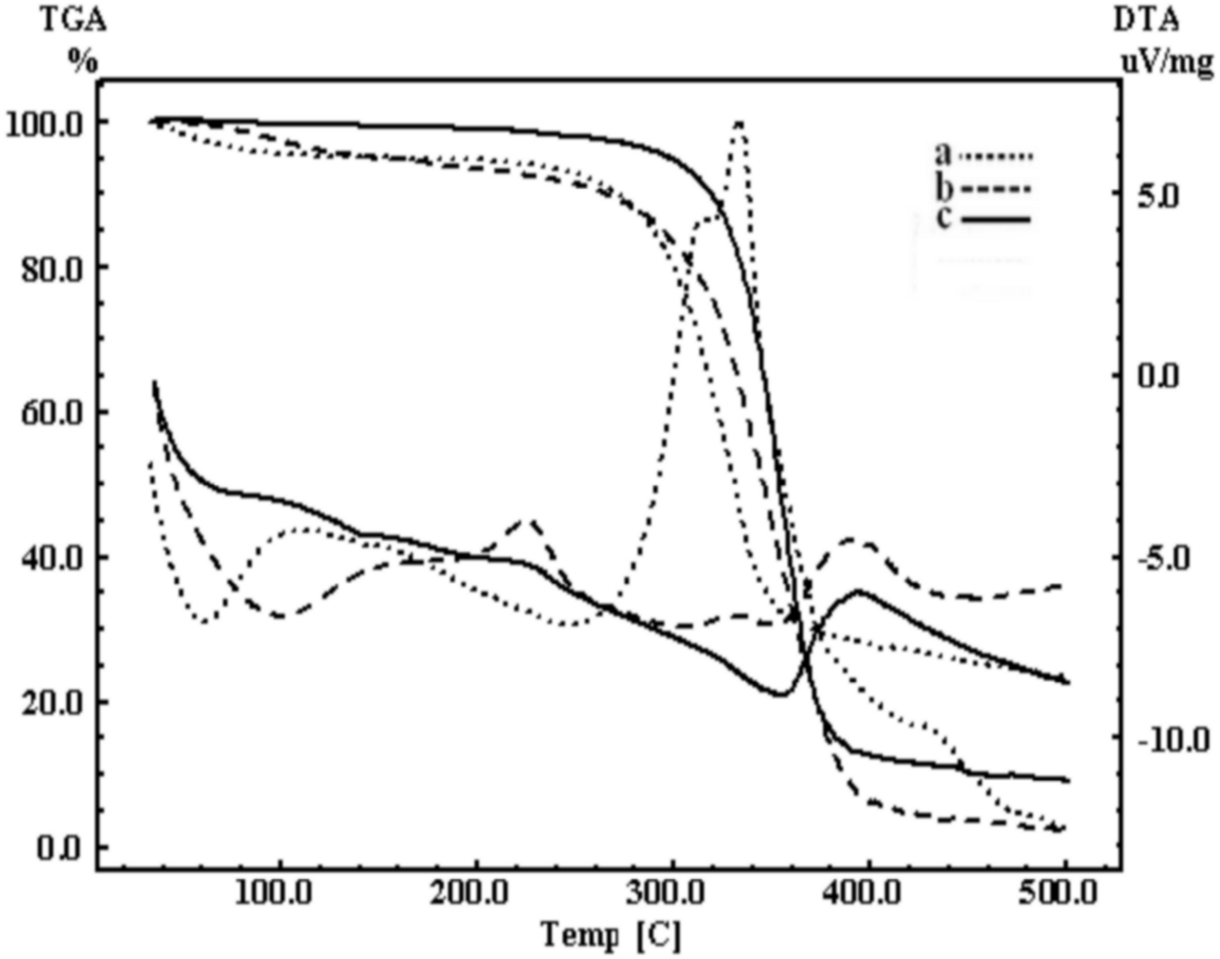

Fig. 6. Thermograms of unmodified HEC (a), HECA DS=0.72 (b) and HECA DS= 2.4 (c).

The TDA Thermograms of unmodified HEC (a), HECA DS = 0.72 (b) and HECA DS = 2.4 (c) are presented also on figure 6. The first endothermic phase transition may be attributed to the glass transition temperature (Tg). Then, Tg of the unmodified HEC appeared at ~62°C **[31]**, while, the Tg values of HECA (DS=0.72) and HECA (DS=2.4) are higher than HEC value. It can be suggested that the acetyl group (CH_3) in the HECA samples influences the intermolecular interaction and a diminution in crosslink density.

The thermal degradation of HEC showed two peaks at 315 °C and 333 °C attributed to the degradation of the cellulose non modified part and cellulose modified part respectively, because this phenomenon is influenced by the DS of the Hydroxyethyl group contained in HEC main chain. The increase of the exothermic peak temperature at high DS could be explained by the disappearance of the hydrogen bonding and the ordered regions, though this suggestion will be correlated by the XRD data.

Conclusion

Resuming the carried out investigation we can conclude the following:
1- Samples HECA with various DS were fabricated from HEC which was prepared from cellulose extracted in basic medium using «Stipa Tenacissima" of Eastern Morocco. The resulted compounds were characterized by spectroscopy techniques (FTIR, NMR). The DS values were obtained from direct titration method, especially the FTIR and NMR techniques respectively. The effect of acetic anhydride equivalent numbers added to the reaction mixture, the temperature and the time of reaction have respectively a high influence on the DS value.
2- HECA samples thermal behaviors were investigated by thermogravimetric analysis (TGA) under nitrogen. The results indicated some differences in glass transition temperature (Tg) and thermal degradation of HEC and HECA, these thermal temperatures were influenced by the DS values. The HECA cellulose derivative exhibited more heat resistant property compared with starting HEC; we can conclude that HECA is thermally more stable material than HEC and common cellulose. Specific focus should be placed on modification of the cellulose backbone as a means of enhancing solubility and stability.

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