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Synthesis and Characterization of the New Cellulose Derivative Films Based on the Hydroxyethyl Cellulose Prepared from Esparto "Stipa tenacissima" Cellulose of Eastern Morocco. II. Esterification with Acyl Chlorides in a Homogeneous Medium

Abderahmane El idrissi,[1] Soufian El barkany,[1,2] Hassan Amhamdi,[2] Abdel-Karim Maaroufi[3]

[1]Laboratory of Applied Chemistry and Environment, Department of Chemistry, Faculty of Sciences (Med I University), 60000 Oujda, Morocco

[2]Physical Chemistry Laboratory of Natural Resources and Environment, Department of Environmental Engineering, National School of Applied Sciences in Al Hoceima, (Med I University), 32 003 Al Hoceima, Morocco

[3]Faculty of Sciences, (Med V University), Department of Chemistry, Rabat, Morocco

Correspondence to: A. El idrissi (E-mail: ab.elidrissi@yahoo.fr) or S. El barkany (E-mail: el.barkany011@gmail.com)

ABSTRACT: Esparto "Stipa tenacissima" cellulose esters derivatives: HECA-COO—C_4H_8—$COOC_2H_5$, HECA-COO—C_8H_{16}—$COOC_2H_5$, and HECA-COO—C_6H_4—$COOC_2H_5$ were successfully prepared in Tetrahydrofuran (THF)/triethylamine system with a degree of substitution (DS), respectively, $DS_{AD\text{-}Et}$=0.32, $DS_{SB\text{-}Et}$=0.22, and $DS_{TRP\text{-}Et}$=0.50 using hydroxyethyl cellulose acetate (HECA; DS_{AC}=0.50) as intermediate product, and we avoided the drawbacks of cellulose solubility. The structural modifications were investigated using Fourier transform infrared spectroscopy (FTIR), Proton nuclear magnetic resonance (^{1}H-NMR), Carbon-13 nuclear magnetic resonance (^{13}C-NMR), and Distortionless Enhancement by Polarization Transfer 135° (DEPT-135). The results from these analyses revealed the presence of the characteristic groups indicating that the grafting reaction was successful. The crystallinity and the structure order changes during the esterification reactions were recorded by X-ray diffraction (XRD), it is found that the crystallinity degree decrease from 63.1% for Esparto "Stipa tenacissima" cellulose to 27.74% for HECA. The thermal stability of the esterified and unmodified cellulose samples was studied by thermogravimetric analysis (TGA)-differential thermal analysis (DTA); the modified HECA exhibits a decrease in thermal stability relatively to the unmodified HECA, and this may be related to the groups grafted. The resulted cellulose esters HECA-P_x (x = 1, 2, or 3) were soluble in THF and present an amorphous structure justified by XRD spectra. It was noted by TGA-DTA analysis that the cellulose esters with low melting range were proved as thermoplastic polymers. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: Esparto 'Stipa tenacissima'; solubility; esterification; plastic films

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INTRODUCTION

Cellulosic materials are generally strong, hydrophilic, and insoluble in water, stable to chemicals, safe to living bodies, reproducible, recyclable, and biodegradable. With these specific and advantageous characteristics of cellulose, the modification techniques to reinforce these original properties or to add new functionalities to cellulose have been investigated,[1–3] and have contributed to the development of cellulose science and technologies. Chemical treatments have been positioned at the center of the field of cellulose modification. Commercial cellulose derivatives having water solubility, organic-solvent solubility, ion-exchanging groups, or hydrophobic groups are used as aqueous thickeners, controlled release systems in pharmaceutics,[4] composite materials[5] and biodegradable plastics,[6] column-supporting materials for chromatography, and others applications. Cellulose carbamates and nitrates are used for determining molecular mass and molecular mass distribution of cellulose to evaluate cellulosic materials by size-exclusion chromatography.[7]

The methods used for cellulose chemical modifications are various, depending on the reactions types. Chemical modification of polysaccharides such as cellulose has become a hot research topic, which is stimulating a rich variety of studies and approaches. Furthermore, as there are still many unsolved and mysterious subjects in cellulose science, chemical modifications

are sometimes used to study fundamental research subjects of cellulose, such as solid-state structures of cellulose (hydrogen bonding patterns, chain conformations, crystal and amorphous structures, etc.), interactions with other substances at molecular levels, and molecular dynamics in solution states. Cellulose has three hydroxyl groups, linked to C-2, C-3, and C-6 of each anhydroglucose unit (AGU). The properties of cellulose derivatives, hence their applications, depend, inter alia, on the functional group introduced, the degree of substitution (DS), and the average degree of polymerization.[8]

Hydroxyethyl cellulose (HEC) is nonionic cellulose ether whose water-solution properties are very useful in many industrial fields. HEC can be also used as a thickening agent, protective colloid, binder, stabilizer, and suspending agent in a variety of industrial applications, including production of pharmaceuticals, textiles, paper, adhesives, coatings, and emulsion polymerization.[9,10] Cellulose ester such as cellulose acetate (CA) is the most successful cellulose derivative in the industrial area. Moreover, the interval of its applications was, recently, much widened, and it used as intelligent materials and optical films.[11] On the subject of esterification, new processes and methods for preparing conventional cellulose esters in laboratory and industrial levels (preparation of new cellulose derivatives, applications to new analytical methods, etc.) have been reported.[12–16] On the other hand, for fundamental aspects, the successful N,N-dimethylacetamide / lithium chloride (DMAc/LiCl) cellulose solvent system has been widely used as a homogeneous esterification medium to prepare new cellulose derivatives or to control DS and distribution of substituents. Cellulose esterification with acyl chlorides is generally limited by their poor solubility in the alkaline medium used as catalyst or as captor of HCl liberated and become insoluble typically in the presence of triethylamine even in the most successful solvent system such as DMAc/LiCl as signaled by Samaranayake and Glasser (Table I).[17] The hydroxyethyl cellulose acetate (HECA) having substitution degree (DS) of acetyl group in average of ~1.5, mixes together the properties of the CA and HEC. The HECA with a lower DS is soluble in ethanol and its thermal stability is similar to that of the CA.

El Idrissi et al.[18] have synthesized a new hydrophobic HECA soluble in THF and owns easy accessible and modifiable Hydroxyl groups, and some successful reactions can be made homogeneously and easily.

In this article, we have used a novel method to modify the HECA derivative in the system THF/triethylamine using different acyl chlorides in order to ameliorate the physicochemical properties of HECA plastic films (solubility, mechanic and thermal properties, etc.) and to avoid the drawbacks of cellulose solubility. Then, new plastic films named HECA-P1, HECA-P2, and HECA-P3 for *HECA-COO—C_4H_8—$COOC_2H_5$*, *HECA-COO—C_8H_{16}—$COOC_2H_5$*, and *HECA-COO—C_6H_4—$COOC_2H_5$*, respectively, have been elaborated.

MATERIALS AND METHODS

Materials

HEC (DS~1.5) was prepared in NaOH/urea aqueous solution[19] starting from cellulose extracted in alkaline medium as mentioned by El Idrissi et al.[20] using "Stipa tenacissima" of Eastern Morocco. The prepolymer HECA with DS_{AC}~1.5, was prepared as mentioned in the first part (Part I: solubility study) of this work[21] and that published by El Idrissi et al.[18] Adipoyl chloride, sebacoyl chloride and terephthaloyl chloride were purchased from Aldrich chemical company. All other chemicals were of analytical grade and are used without further purification and purchased from Aldrich too.

Table I. Qualitative Solubility of Esterification Agents in DMAc/LiCl Solvent System

Acid derivative	DMAc/LiCl	DMAc/LiCl triethylamine	DMAc/LiCl pyridine
Propionyl chloride	Soluble	Insoluble	Soluble
Hexanoyl chloride	Soluble	Insoluble	Insoluble
Stearoyl chloride	Soluble	Insoluble	Insoluble

Methods

Preparation of Precursors ClCO-R-$COOC_2H_5$. After placing each compound *ClCO-R-COCl* (adipoyl chloride 1.2 g, sebacoyl chloride 1.58 g, or terephthaloyl chloride 1.34 g) and 10 mL of THF into a reaction flask, an equimolar amount of ethanol (0.3 g) and of triethylamine (0.66 g) in 10 mL of THF was added dropwise (drop by drop). The reaction was carried without using catalyst and was kept under stirring and inert atmosphere (N_2) at room temperature. The crude products *ClCO-R-$COOC_2H_5$* (P_1: (R= —$(CH_2)_4$—), P_2: (R= —$(CH_2)_8$—), P_3: (R= —C_6H_4—) were isolated from the mixture and characterized, then they were subsequently used for the modification of HECA.

Preparation of HECA-COO-R-$COOC_2H_5$ (HECA-P_x). The cellulose derivatives HECA-P_x were prepared by modification of the prepolymer HECA using the precursors previously prepared *ClCO-R-$COOC_2H_5$*. In a three-necked round-bottomed flask equipped with a thermometer, a mechanical stirrer, and a reflux condenser, an excess of the precursor *(ClCO-R-$COOC_2H_5$)* was introduced, then 1 g of HECA (DS_{AC}~1.5) dried at 40°C during 24 h (equaling to 4.386 mmol of AGU and 6.578 mmol of hydroxyl functionality in HECA) and 0.66 g of triethylamine in 20 mL of THF were added slowly to the mixture containing the precursor previously introduced when the temperature of the system reached 80°C.

The reaction mixture was kept under stirring for 2 h. After the elimination of the solvent (THF) under vacuum (in Rota-vapor), the modified cellulose derivatives were precipitated into 30 mL of cold water filtered and washed with cold methanol and cold ether to remove all impurities, and the triethylamonium chloride (salt) was eliminated by filtration. The resulted products were dried at 40°C to a constant mass. Afterward, The HECA-P_1, HECA-P_2, and HECA-P_3 samples were purified a second time by the dissolution–precipitation method in THF/cold methanol and washed by cold ether. The product was dried first at 60°C for 24 h and second in desiccators for 1 week with P_2O_5. The samples recovered were characterized and studied by using different techniques, and DS was determined using ^{1}H-NMR spectra.

X-Ray Diffraction. The crystallinity of the samples were investigated by x-ray diffraction (XRD), the analysis was performed with a Panalytical X'Pert Pro MPD-Ray Diffractometer, using Copper radiation Kα (λ = 1.5418 A°), voltage of 40 kV, and operation current of 30 mA. All essays were performed with 2θ = 5°

and $2\theta = 40°$, pitch 0.05° s^{-1}. The crystallinity index I_c was calculated from the formula (1):[22]

$$I_c = 1 - (I_{min}/I_{max}) \quad (1)$$

Where I_{min} is the intensity minimum between $2\theta = 18°$ and 19° and I_{max} is the intensity of the crystalline peak at the maximum between $2\theta = 22°$ and 23°. The samples were pressed into pellets (25 mm in diameter) by compression of ~0.25 g in mould under 50 MPa.

Spectroscopic Measurements. The chemical structures of HECA-P_1, HECA-P_2, and HECA-P_3 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 grounded samples. Twenty scans were taken of each sample recorded from 4000 to 400 cm^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on an AVANCE Bruker 300 MHz spectrometer at 360K by Technical Scientific Research National Centre at Rabat-Morocco, using Tetramethylsilane (TMS) as internal standard and DMSO-d_6 as solvent.

Thermal Analysis. Thermal study of the samples was performed using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a Shimadzu DTG-60 simultaneous DTA-TG apparatus. The sample weight was between 8 and 12 mg. Two scans were run from room temperature to 500°C at a rate of 10°C min^{-1} under nitrogen flow.

DS Determination. ^{1}H-NMR method can be used as tool to calculate the DS of cellulose derivatives based on proton integrations of typical signals. The following equations [eqs. (2)–(5)] may be used to deduct the DS value of HEC, HECA, HECA-P1, HECA-P2, and HECA-P3:

$$DS_{HEC} = \frac{I_{-CH2-(HEC)}}{2I_{-CH2-(C6)}} = 1.55 \quad (2)$$

$$DS_{HECA} = \frac{2}{3}\frac{I_{-CH3(AC)}}{I_{-CH2-(\alpha ESTER)}} = 1.5 \quad (3)$$

$$DS_{AD-Et}(DS_{SB-Et}\ Or\ DS_{TRP-Et}) = \frac{I_{-CH3(Et)}}{I_{-CH3(AC)}} DS_{HECA} \quad (4)$$

$$DS_{AD-Et}(DS_{SB-Et}\ Or\ DS_{TRP-Et}) = \frac{I_{-CH3(Et)}}{I_{-CH3(AC)}} 1.5 \quad (5)$$

Casting. The films with thickness of 1 mm were prepared by casting the modified HECA solution on Teflon plates. About 1 g of the HEC, HECA, HECA-P1, HECA-P2, and HECA-P3 samples was, respectively, dissolved in 30 mL of THF to reach complete dissolution, except HEC was dissolved in distillated water. Each solvent was eliminated by evaporation process under vacuum.

RESULTS AND DISCUSSION

FTIR Spectra

FTIR spectroscopy has been extensively used in cellulose research and it allows obtaining easily direct information on chemical changes that occur during various chemical treatments.[23] Figure 1 shows respectively, the FTIR spectra of unmodified cellulose extracted from Esparto "Stipa tenacissima" (a), HEC with $DS_{HEC} = 1.5$ (b), and HECA having a DS of acetate group about ~1.5 (c). The absorbencies at 3380, 2926, 1643, 1429, 1375, 1163, 1060, 1028, and 900 cm^{-1} noted at the spectrum (a) are associated with cellulose. The strong absorption band around 3380 cm^{-1} is due to the stretching of O—H groups and that one at 2926 cm^{-1} is assigned to the C—H stretching. The band at 1643 cm^{-1} corresponds to the bending mode of the naturally absorbed water.[20,24–27] The spectrum shows also the absorption bands around 1429 and 1375 cm^{-1} which are attributed respectively to the —CH_2 and to the O—H bending.[28] The bands around 1335 and 1262 cm^{-1} are allotted to the vibrations of C—C and C—O (osidic link) characteristics of the cellulose skeleton.[29,30]

The absorption band at 1163 cm^{-1} relates to C—O antisymmetric bridge stretching. The C—O—C pyranose ring skeletal vibration occurs in the region 1076–1023 cm^{-1}, whereas the band at 903 cm^{-1} is originated from β-glucosidic linkages between glucose units in cellulose.[31,32] In the spectrum (b), the intensity of the peak at 2873 cm^{-1} for ν_s (—CH_2—) slightly increased due to the replacement of hydroxyl groups of AGU by —O—$(CH_2)_2$—OH. Moreover, the increasing of the intensity of the absorption band of primer O—H bending at 1350 cm^{-1} indicates a successful etherification. More importantly, the spectrum (c) gives evidence of acetylation by showing the presence of the new three acetyl ester bands; the carbonyl area around 1743 cm^{-1} was associated with the formed ester group (C=O ester), a new absorption band at 1377 cm^{-1} was assigned to the C—CH_3 stretch vibration, and C—O stretching band at 1246 cm^{-1}.[33] Furthermore, the intensity of peak located at 3380 cm^{-1}, assigned to O—H stretching of the HEC component, decreased after the chemical acetylation of HEC. On the other hand, it should be noted that the successful modification of the half of HEC hydroxyl groups was thereby indicated also by the dislocation of the band characteristics attributed to O—H stretching from 3380 to 3470 cm^{-1}, where the concentration of O—H groups decreases.

The chemical structures of HECA and the grafted HECA (HECA-P_1, HECA-P_2, and HECA-P_3) are very similar to each other. The spectra of HECA (c) and the products prepared [HECA-P_1 (d), HECA-P_2 (e), and HECA-P_3 (f)] are presented in Figure 1. The similarity between the three spectra (c), (d), and (e) is obvious at the first glance; this is not surprising as no novel functional group has been formed during the grafting reaction. The vibration of the carbonyl group at 1743 cm^{-1} is very strong as well as the bands associated with the C—O vibration at 1052 cm^{-1}. Additional vibrations can be assigned to the aliphatic —CH— and —CH_2— and aromatic —CH— groups included into the chain of HECA. A more through comparison reveals several differences between the four spectra; the most important are the decrease of the relative intensity of the OH absorption (3470 cm^{-1}) and the increase of the intensity of the peak at 2945 and 2881 cm^{-1} attributed to —CH_2—.[34] In addition, in the spectrum (e), the intensity of the absorption band at 1583 cm^{-1} correspond to the aromatic ring vibrations $(C=C)_{arm}$ and the absorption bands at 732, 806, and 875 cm^{-1} are attributed to C—H bending of parabisubstituted benzene, which indicate that the phthaloyl group was introduced into the backbone cellulosic chains. As expected, the absence of absorption bands at 1815 and 1690 cm^{-1} in the spectra (e, d, and f) confirmed that the

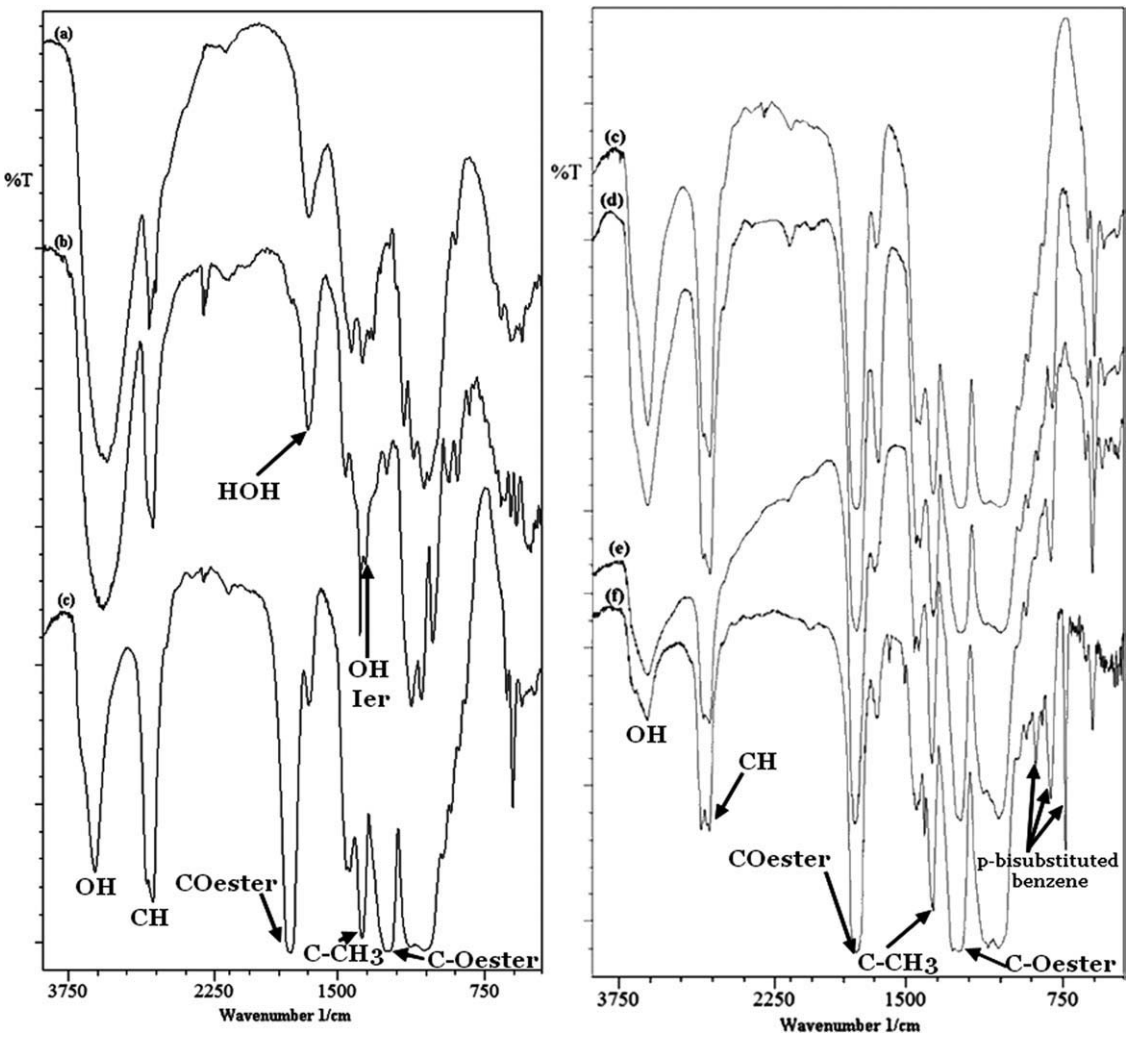

Figure 1. FTIR spectra of Esparto "Stipa tenacissima" cellulose (a), HEC (b), HECA(c), HECA-P_1 (d), HECA-P_2 (e), and HECA-P_3 (f).

products HECA-P_1 (d), HECA-P_2 (e), and HECA-P_3 (f) are free of the unreacted chloride precursors (adipo-, sebaco-, and phthaloyl chloride) and free of carboxylic acid groups, which can be formed by saponification reaction of precursors chlorides.

NMR Study

The NMR spectra also were in accordance with the proposed structures. First, the modification of cellulose was clear on the Figure 2, the spectra presented on Figure 2(a) shows the HEC methylene proton signals between ~3.5 and ~3.6 ppm, which were overlapped with the broad ring proton signals of the cellulose skeleton at (2.8~5.6 ppm). The DS of HEC (DS_{HEC}) was estimated from the ratio between the HEC methylene proton integration $I_{-CH2-(HEC)}$ and the integration of methylene situated in α of C_6 in cellulose skeleton $I_{-CH2-(C6)}$ using the following equation [eq. (6)]:

$$DS_{HEC} = \frac{I_{-CH2-(HEC)}}{2I_{-CH2-(C6)}} = 1.5 \quad (6)$$

The NMR spectrum of HECA was performed in DMSO-d_6. The different signals can be classified in three parts: 15 HEC main chain protons are located between 3.2 and 5.6 ppm, where H_4 HEC proton (the proton attached to the carbon 4 of the AGU) hidden by water protons at 3 ppm [Figure 2(b)], and methyl protons appeared at 2 ppm. ^{1}H-NMR method can also be used as tool to calculate the DS_{AC} of HECA based on proton integrations of acetyl methyl group and HEC methylene protons located in α of ester. The eq. (7) obtained from the NMR investigation may be used to deduct HECA DS value:

$$DS_{HECA} = \frac{2}{3}\frac{I_{-CH3(AC)}}{I_{-CH2-(\alpha ESTER)}} = 1.5 \quad (7)$$

in which:

$I_{-CH3(AC)}$= acetyl methyl protons integration

= integration of HEC methylene protons located in α of ester

The ^{1}H-NMR spectra of cellulose derivatives HECA-P_1 and HECA-P_2 are presented on Figure 2(c,d); they reveal two distinct regions; the protons signals of the grafted chain appear between 1.81, 2.18 ppm and at 4.11 ppm, whereas the protons

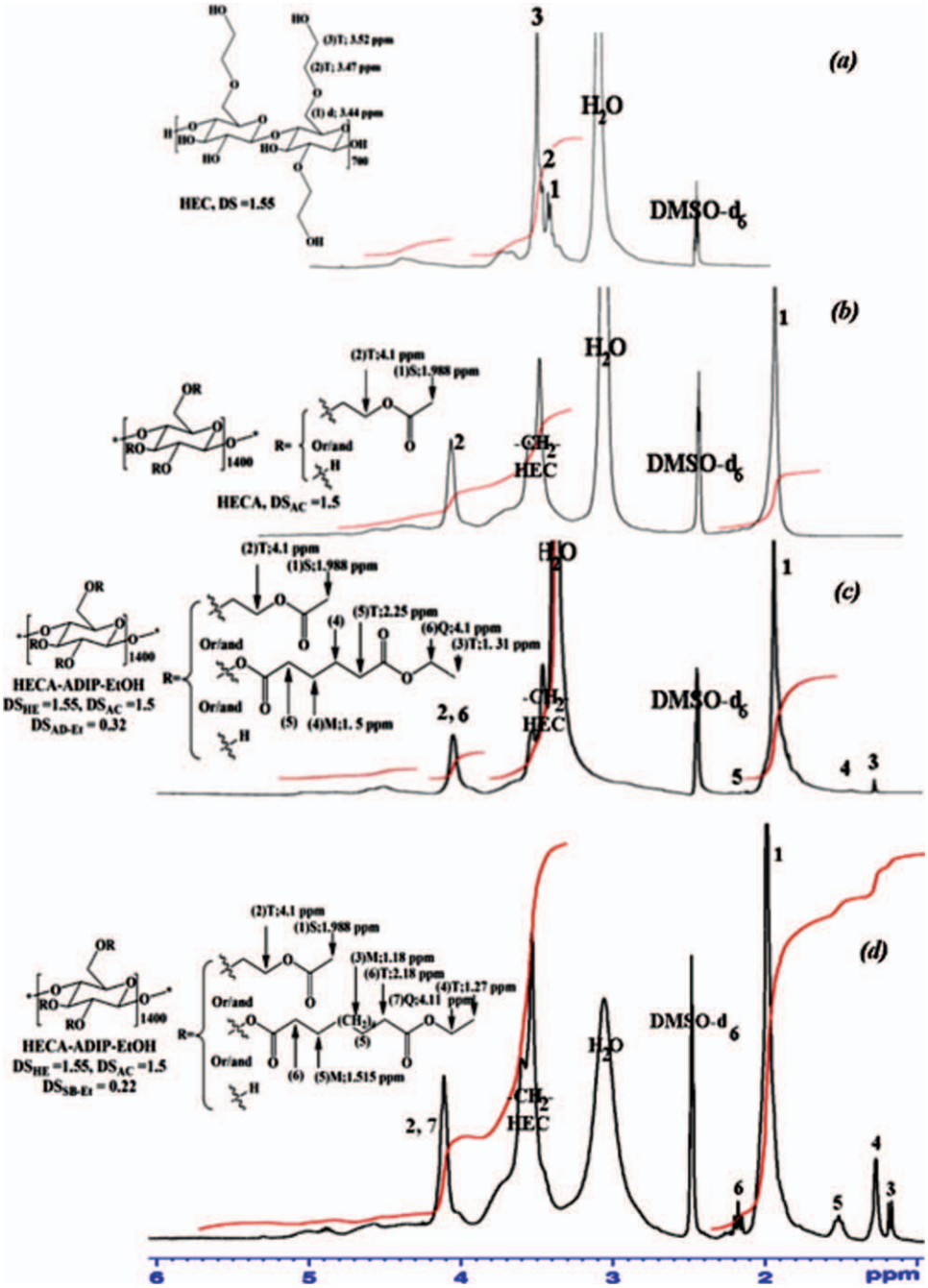

Figure 2. [1]H-NMR spectra of hydroxyethyl cellulose (HEC) (a), hydroxyethyl cellulose acetate (HECA) (b), HECA-P1 (c), and HECA-P2 (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

signals of the HECA backbone chain appear between 3.0 and 5.5 ppm and the acetyl protons at 2.0 ppm.

Figure 3(e) shows the [1]H-NMR spectrum of HECA-P3. Three obvious signals appeared at 1.32, 4.32, and 8.06 ppm were assigned to methylene protons, the protons in position α of ester alkoxyl and aromatic protons, respectively. Moreover, no peak was observed around 10–13 ppm, showing the absence of the carboxylic acid residues. The DS was also calculated from the proton NMR integration ratio. In our case, the DS value was determined by taking the integration of the methylene protons of grafted chain $I_{-CH3\text{-}Et}$ and the methylene protons integration of the acetyl group $I_{-CH3\text{-}AC}$ using the following equations [eqs. (8)–(10)]:

$$DS_{AD-Et} = \frac{I_{-CH3(Et)}}{I_{-CH3(AC)}} 1.5 = 0.32 \quad (8)$$

$$DS_{SB-Et} = \frac{I_{-CH3(Et)}}{I_{-CH3(AC)}} 1.5 = 0.22 \quad (9)$$

$$DS_{TRP-Et} = \frac{I_{-CH3(Et)}}{I_{-CH3(AC)}} 1.5 = 0.5 \quad (10)$$

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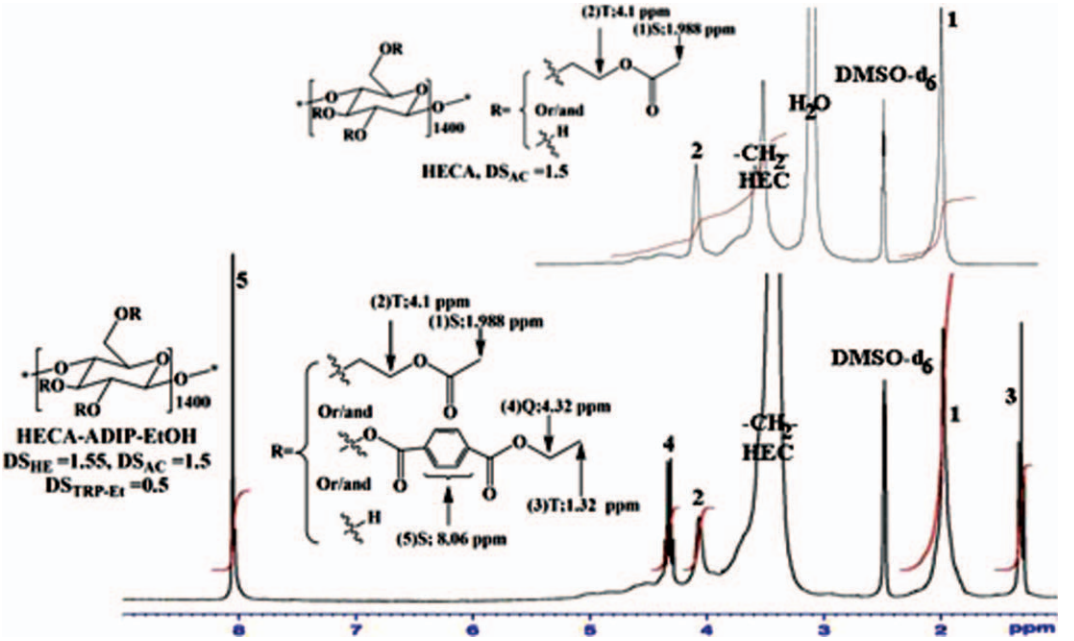

Figure 3. ^{1}H-NMR spectra of hydroxyethyl cellulose acetate (HECA) (b) and HECA-P3 (e). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4(a) shows the ^{13}C-NMR and DEPT-135 spectra of HEC prepared from the modification of Esparto "Stipa tenacissima" fibers. The spectra exhibit the signal characteristics of cellulose skeleton. Thus, the C1 (103 ppm) and C4 (82 ppm) represent the carbons of the glucopyranose rings within amorphous regions. The peak around 88 ppm assigned to C4 of crystalline cellulose disappeared completely indicating that the crystalline structure of cellulose was disrupted by breaking hydrogen bonds in cellulose during dissolution and modification.[35] Moreover, the peak attributed at C6s (C6 carbon bearing a substituted hydroxyl group) shifted to 67 ppm indicating that all hydroxyl groups attached to C6 were totally substituted. The intensity diminution of the peak at 74 ppm assigned to C2, and the appearance of the C2s (C2 carbon bearing a substituted hydroxyl group) around 80 ppm indicate that the etherification reaction occurred at the C6 and the half of the C2 carbons.

The monomeric repeat unit of cellulose (anhydroglucose) reveals three hydroxyl groups having different reactivity in accordance with intramolecular and intermolecular interactions and their electronic environments. The authors in the literature are agree that the C6 hydroxyl group of AGU is the more reactive than the others at C2 and C3;[36–39] it should be noted that the primary alcohol is more important from reactivity point of view. The first main to introduce into the monomeric repeat unit of cellulose (anhydroglucose), more primary hydroxyl, is the destruction of the crystalline order, and the accessibility of the reagents increases. The second one is to increase the hydrophobicity of polymer by acetylating some hydroxyl groups with acetic anhydride without solvent to obtain HECA (DS_{HECA} ~1.5) soluble in THF (Scheme 1).

Finally, the modification of the nonacetylated hydroxyls present in HECA with different chloride precursors P_1, P_2, and P_3 was occurred homogeneously in the mixture THF/triethylamine (Scheme 2).

The primary hydroxyl groups, grafted on cellulose such as hydroxyl ethyl, were more accessible than the secondary hydroxyl groups attached to the C2 and C3 glucopyranose units. This suggestion was justified by the comparison of ^{13}C-NMR and DEPT-135 spectra of HEC and HECA. The signals at 60.9, 70.3, and 72.8 ppm assigned to the grafted ethylene carbon [1, 2, and 3 in Figure 4(a)] of HEC, shifted after acetylation, to 63.6, 68.8, and 70.34 ppm, respectively [Figure 4(b)]. The presence of carbonyl ester group peaks at 170.6 ppm and the methylene groups at 20.92 ppm indicates that the chemical modification reaction shown in Scheme 1 occurs successfully.

^{13}C-NMR and DEPT-135 spectra of esterified cellulose fibers (HECA-P_x) were presented in Figure 4(c–e). The appearance of new resonances in the spectra of HECA-P_1 and HECA-P_2, typical aliphatic (14–36 ppm) and carbonyl ester groups around 171 ppm, give additional evidence of the occurrence of the esterification reaction. The DEPT-135 spectra are complementary to the NMR spectra, it distinct the —CH_2— carbon from others carbon types. Additionally, the appearance of the signal assigned to C3s (substituted carbon at position 3 of glucopyranose unit) at 83 ppm, and the no displacement of the ethylene hydroxide carbon [1, 2, and 3 in Figure 4(a)] of HEC indicated that the esterification was occurred at the unacetylated hydroxyl groups attached to the carbons C3 and C2. The NMR results are in good accord with the proposed structure in Scheme 2.

Particularly, the modification of HECA by an aromatic group is very clear on ^{13}C-NMR and DEPT-135 spectra, because novel characteristic signals have been appeared. Figure 4(e) shows ^{13}C-NMR and DEPT-135 spectra of HECA-P3. The signals at

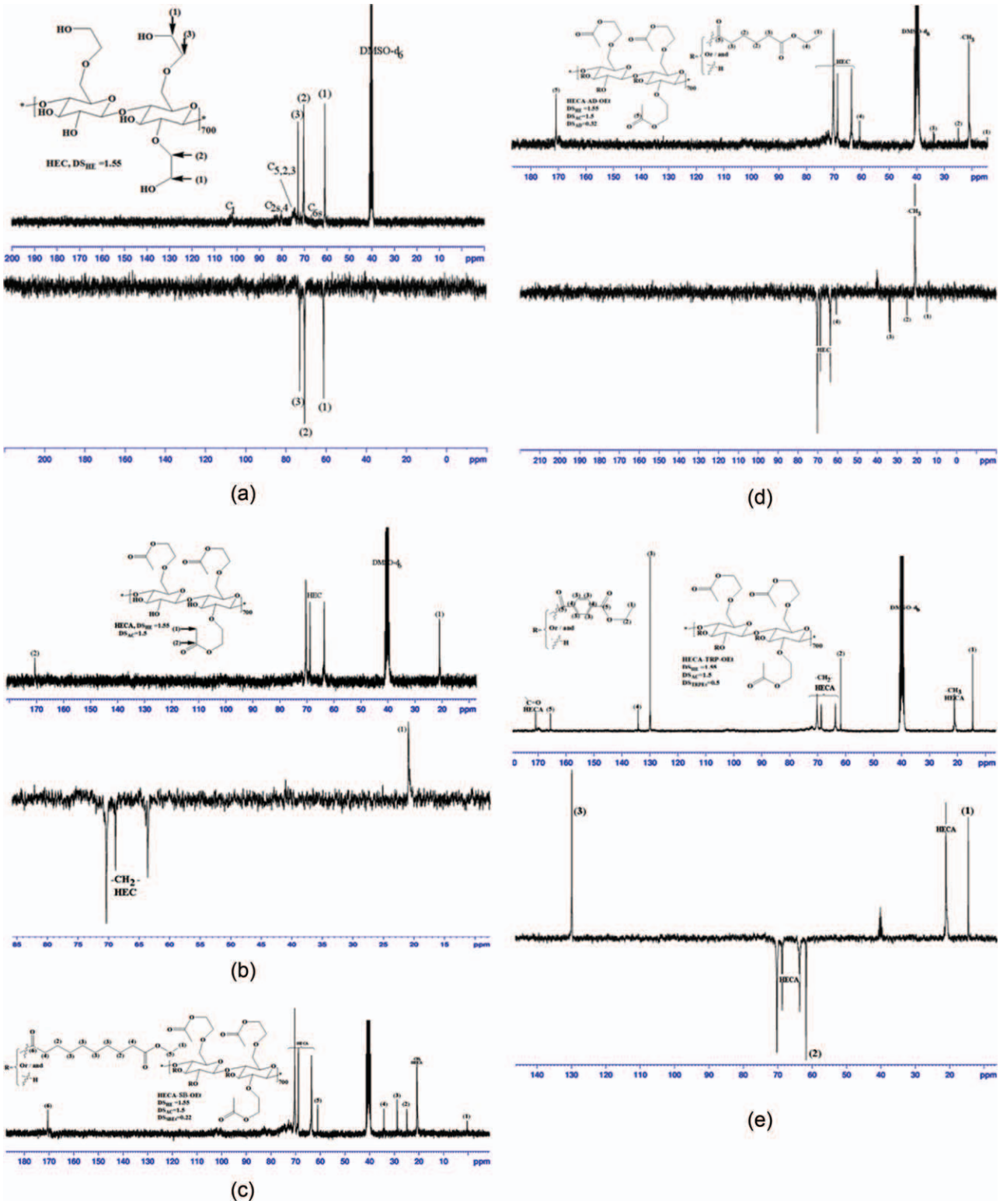

Figure 4. ^{13}C-NMR and DEPT-135 spectra of (a) hydroxyethyl cellulose (HEC) and (b) hydroxyethyl cellulose acetate (HECA). (c) ^{13}C-NMR and DEPT-135 spectra of HECA-P1. (d) ^{13}C-NMR spectrum of HECA-P2. (e) ^{13}C-NMR and DEPT-135 spectra of HECA-P3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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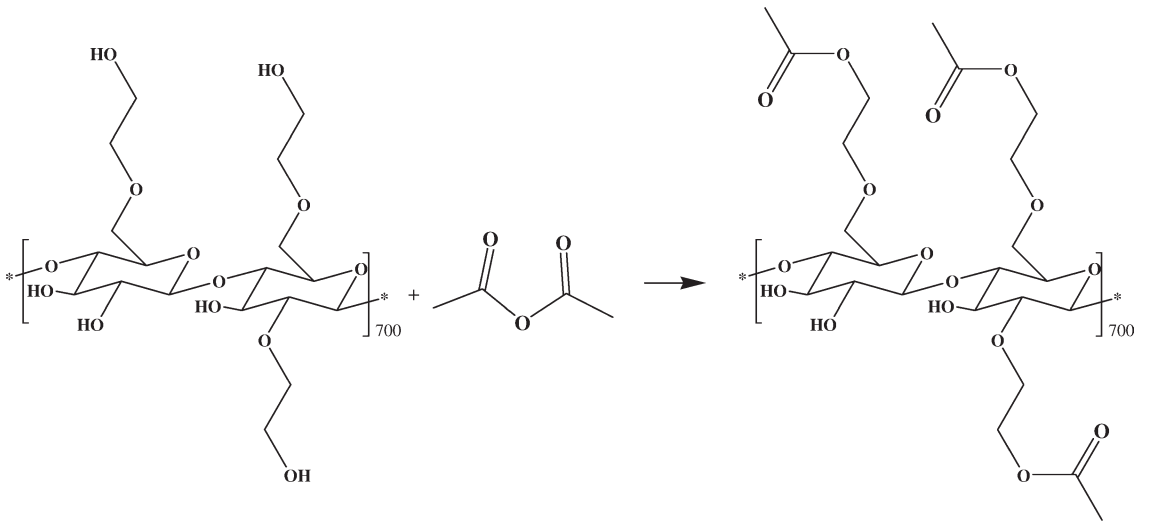
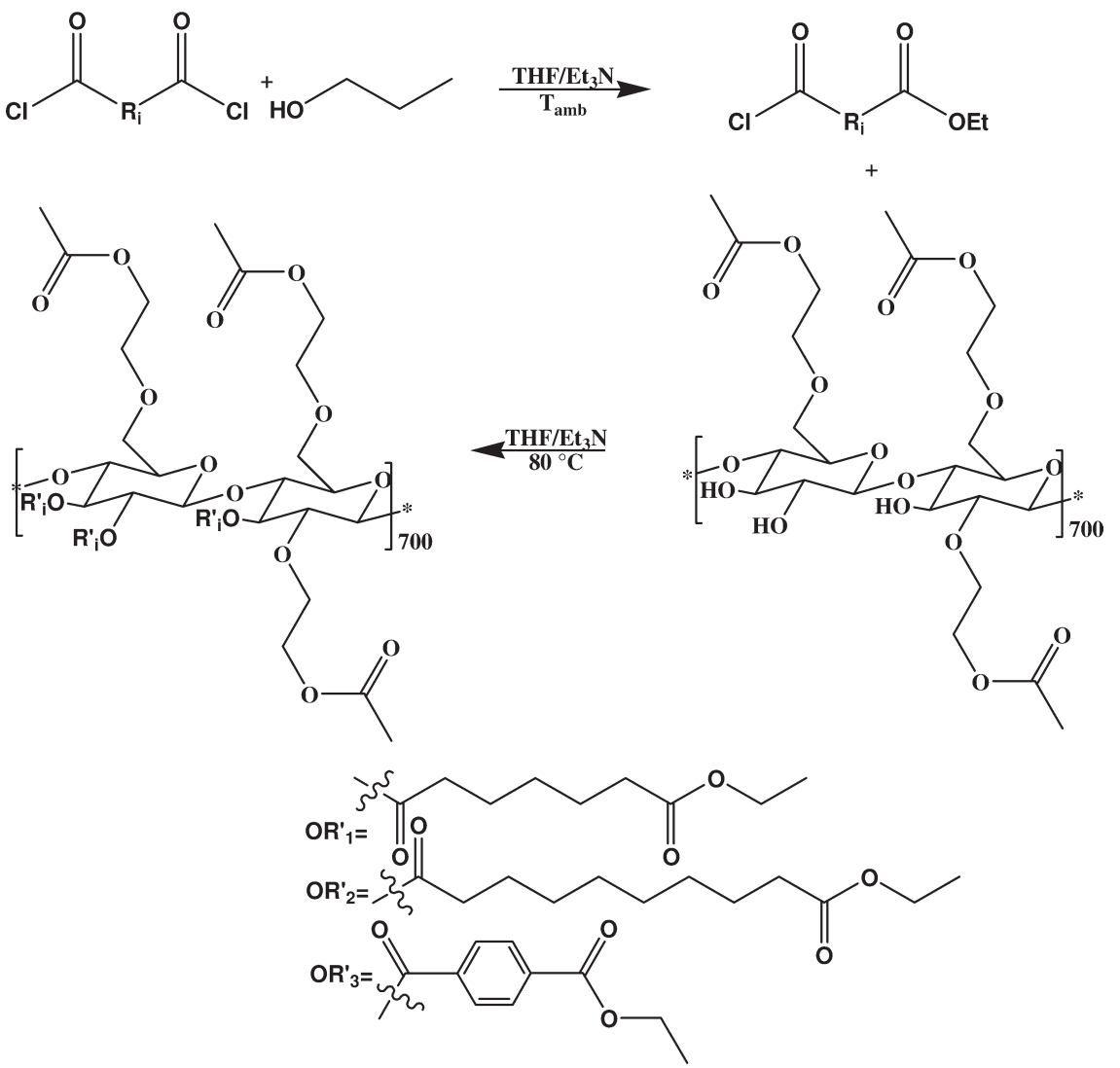


Scheme 1. Preparation of hydroxyethyl cellulose acetate (HECA); $DS_{HECA} = 1.5$.



Scheme 2. Syntheses of HECA-P1, HECA-P2, and HECA-P3.

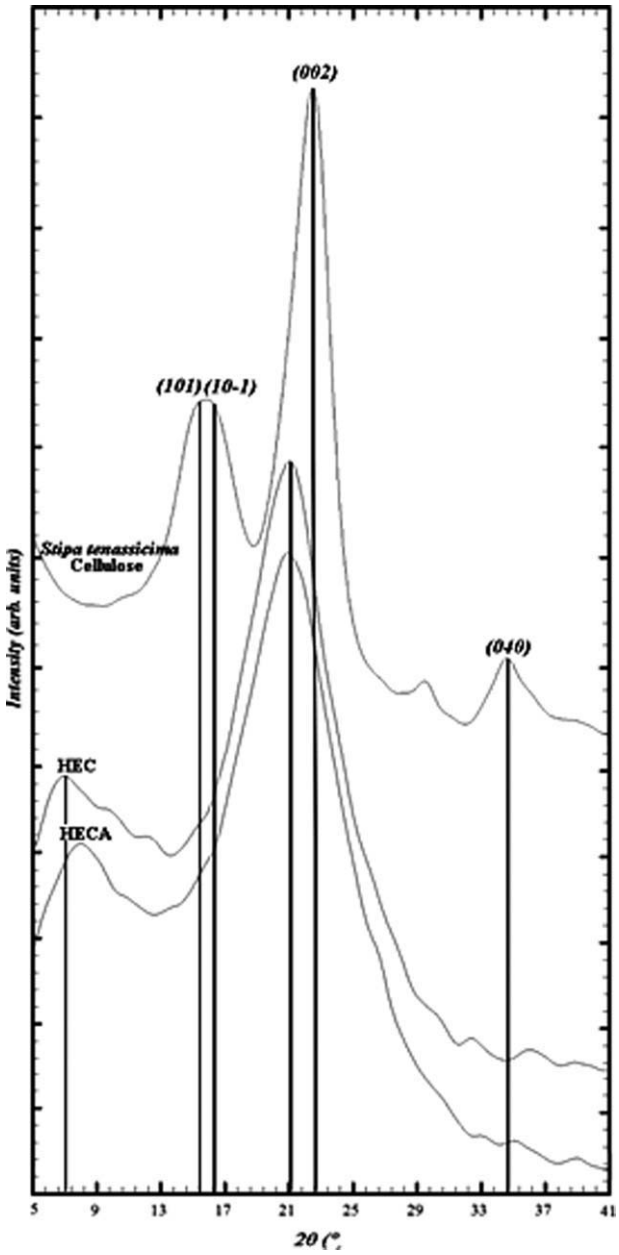


Figure 5. X-ray diffractograms of Alfa "Stipa tenacissima" cellulose fibers, hydroxyethyl cellulose, (HEC), and hydroxyethyl cellulose acetate (HECA).

14.1 and 61 ppm are assigned to the methylene and ethylene carbons, and these at 130 ppm is attributed to the =CH aromatic carbons. The important differences between the spectra of HECA and HECA-P3 are the presence of peaks at 134 and 165 ppm characterizing the quaternary aromatic ring carbon and the novel carbonyl ester formed between HECA and the group included into the chain, respectively. The aromatic ring effect renders the carbonyl more electrophilic. Hence, this effect increases the reactivity of phthaloyl chloride and the DS obtained ~0.5 is higher than in the case of aliphatic chain giving a DS $\leq$ 0.3.

X-Ray Diffraction Measurements

The unmodified cellulose fibers derived from Esparto "Stipa tenacissima" displayed the typical XRD pattern of cellulose I,[40] with the main diffraction signals at around 2θ = 15°, 16.3°, 22.6°, and 34.5° attributed, respectively, to the (101), (10-1), (002), and (040) hkl diffraction planes.

The polymorphic transition of the cellulose was detected when the concentration of sodium hydroxide solution is high more than 10%.[41] However, XRD signals of cellulose II are not observed on XRD pattern of Esparto "Stipa tenacissima" cellulose extracted in alkaline medium as mentioned by El Idrissi et al.[20] The changes in the crystalline structure of cellulose as result of the modification depend on the degree of the substitution (DS) and on the nature of grafted groups.

The X-ray diffractograms of modified cellulose fibers (Figure 5) showed a progressive decrease in the intensities of the signals attributed to the 002 and 040 planes, and the absence of the signal characteristics assigned to the (101) and (10-1) diffraction planes. These changes indicate a destruction of the crystalline order, which occurs during dissolution and modification. However, the disappearance of the crystalline order in the cellulose structure is accompanied by the appearance of newly ordered region associated to the cellulose ether (HEC) and cellulose ester (HECA) at the diffraction angles 2θ between 7° and 21°.

The crystallinity index decreases from 63.1% for Esparto "Stipa tenacissima" cellulose to 30.86% for HEC indicating a significant content of the amorphous regions, this allows modification to occur easily. A small variation in the crystallinity index between HEC and HECA was observed. Crystallinity index was calculated for each sample using the formula (1) and the results are reported in Table II.

Thermal Analysis

The effect of the etherification of cellulose and acetylation of HEC on the thermal behavior was also studied by TGA and DTA in the temperature range between 35 and 500°C. Figure 6(a) shows the TGA and DTA Thermograms of unmodified Esparto "Stipa tenacissima" cellulose, HEC (DS~1.55) and HECA (DS~1.5). From the above figure, it can be seen that the etherification of cellulose by hydroxyl ethyl groups decreases the thermal degradation temperature, from 291°C for Esparto "Stipa tenacissima" cellulose to 280°C for HEC (DS~1.55). This diminution in the thermal degradation temperature between cellulose and HEC is due, probably, to the destruction in the crystalline region. Also, a similar phenomenon[42] was observed in the acetylating reaction of HEC. However, the thermal decomposition temperature (T_d) was increased from 280 to

Table II. The Percent Crystallinity of Alfa "Stipa tenacissima" cellulose fibers, Hydroxyethyl Cellulose (HEC), and Hydroxyethyl Cellulose Acetate (HECA)

Sample	% I_c
Alfa 'Stipa tenacissima' cellulose	63.1
HEC)	30.86
HECA	27.74

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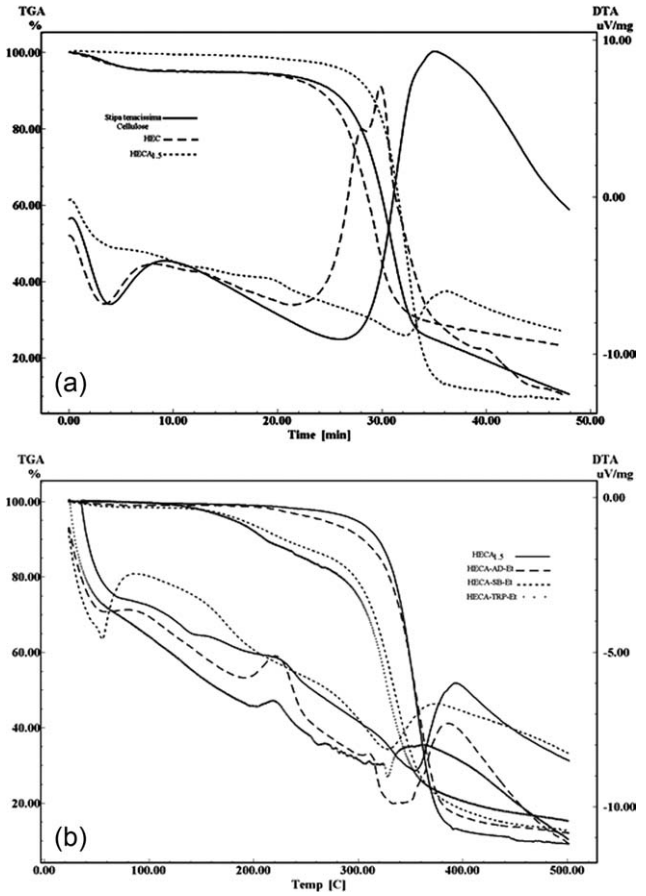

Figure 6. TGA-DTA thermograms of (a) Esparto "Stipa tenacissima" cellulose fibers, HEC, and HECA and (b) unmodified intermediate polymer HECA and cellulose derivatives (HECA-P_1, HECA-P_2, and HECA-P_3).

320°C for HEC (DS ∼ 1.55) and HECA (DS ∼ 1.5), respectively. At 50% weight loss, the decomposition temperature occurs at 333°C for unmodified Esparto "Stipa tenacissima" cellulose and 330°C for HEC. The absence of the difference in the thermal degradation temperature at 50% weight loss between cellulose and HEC indicates that at this temperature, they have an identical structure corresponding to the cellulose skeleton. The invariance of the $T_{d,}$ at 50% weight loss, was not available between HEC and HECA. The $T_{d,}$ at 50% weight loss, increased to 353°C for HECA. It must be noted that the thermal stability of HECA increases with the DS values as we are mentioned in part I (solubility study) of this work.[21]

The DTA thermograms of unmodified Esparto "Stipa tenacissima" cellulose, HEC, and HECA are presented also on Figure 6(a). The differential thermal analysis thermogram of cellulose illustrates two major areas, an initial shoulder peak appears about 295–346°C, and it was related to the thermal depolymerization of cellulose. The major second stage of weight loss ranging from 346 to 500°C is attributed to further degradations of cellulose and inorganic compounds. At 500°C, the cellulosic sample has a residual weight of about 10.7%. In inert atmosphere, the end products of the decomposition of cellulose are carbonaceous residues.[43] The thermal degradation of HEC showed two peaks at 315 and 333°C attributed to the degradation of the cellulose nonmodified 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 at high DS could be explained by the disappearance of the hydrogen bonding and the ordered regions level decreases, this suggestion is in accord with the XRD data.

Two thermal characteristics of cellulose esters are commonly identified in studding their thermal behaviors. The first transition is the glass temperature $T_{g,}$ i.e., the temperature at which the polymer changes from a glassy to rubbery state, from this temperature the material become moldable. The second is the decomposition temperature T_d at which thermal degradation is observed.

The glass transition temperature of cellulose was not observed in this thermogram [Figure 7(a)]. It is known that T_g detection for cellulose is very difficult and only, on using particular scan conditions, it is possible to determine it with DSC[44] and DTA techniques.[45] This result confirms the high degree of crystallinity in this type of cellulose. Generally, the glass transition temperatures (T_g) of cellulose esters are located between 75 and 200°C.[46] By comparing the DTA Thermograms of HECA and other cellulose esters, we have observed that the T_g has shifted from ∼62°C for HEC[47] to 140°C for HECA. The T_g values of HECA are higher than the HEC one. It can be suggested that the acetyl group (—$COCH_3$) in the HECA samples influences the intermolecular interaction. The T_g transitions of the cellulose esters HECA-P_1, HECA-P_2, and HECA-P_3 were not identified, probably because their variations were too small and overlapped by the first endothermic variation attributed to the solvents elimination.

The TG/DTA was performed to evaluate the effect of the chemical modification on the decomposition patterns and thermal stability of cellulose derivatives HECA-Px, as well as to verify the success of the grafting process. As can be seen in the Figure 6(b), two weight loss steeps can be identified on Thermograms of HECA-P_1, HECA-P_2, and HECA-P_3. The HECA-P_1 was degraded in two steps, at 213 and 322°C, corresponding to the decomposition of the adipic group and disintegration of HECA, respectively. We have also noted that the modified HECA by sebasic (HECA-P_2) and phthalic (HECA-P_3) groups showed two degradation profile steps, the first degradation step is due to the elimination of the sebasic and phthalic-grafted groups at 150 and 130°C, respectively. The second step can be attributed to the HEC main-chain disintegration taking place at 295°C for HECA-P_2 and at 290°C for HECA-P_3. The third degradation step observed from 400°C was a small weight loss (∼6%). This decrease in the stability thermal may be due to the breaking of the intramolecular and intermolecular interactions between chains and causing a diminution in the crystallinity of the polymer and creating a novel order.

At 50% weight loss, the decomposition temperature occurs at 357°C for HECA-P_1. The 50% weight loss for the compounds HEPC-P_2 and HECA-P_3, take place at 335 and 328°C, respectively. We can conclude that the thermal stability of sebasic

cellulose and phthalate cellulose is lower than that of HECA. Similar results are reported also by Liu et al.[48] Figure 6(b), also gives the DTA curves of HECA, HECA-P_1, The HECA-P_2, and HECA-P_3. It is noted that the exothermic peaks are asymmetric and thus is due to the overlapping endothermic responses from the both unreacted and reacted product.[49] Generally, each product is characterized by two exothermic peaks; the first is attributed to the degradation of the grafted groups and the second is attributed also to the thermal disintegration of HECA chain backbone.

CONCLUSIONS

The conversion method of Esparto "Stipa tenacissima" cellulose to HECA was successfully used as an intermediate steep to elaborate others cellulose derivatives in homogeneous medium (THF) avoiding the drawbacks of cellulose solubility. The HECA with $DS_{AC} \sim 1.5$ soluble in THF can be obtained easily by the acetylation of the HEC prepared from Esparto "Stipa tenacissima" cellulose of Eastern Morocco. Then, it is possible to elaborate new and different families of plastic films based on HECA (e.g., HECA-COO—C_4H_8—$COOC_2H_5$, HECA-COO—C_8H_{16}—$COOC_2H_5$, and HECA-COO—C_6H_4—$COOC_2H_5$) in the system THF/triethylamine using different reaction ways.

The structural modifications were investigated using FTIR, ^{1}H-NMR, ^{13}C-NMR, and DEPT-135. The results from these analyses revealed the presence of the characteristic groups indicating that the grafting reaction was successful. The crystallinity and the structure order changes during the esterification reactions were recorded by XRD, it is found that the crystallinity degree decrease from 63.1% for Esparto "Stipa tenacissima" Cellulose to 27.74% for HECA. The thermal stability of the esterified and unmodified cellulose samples was studied by TGA-DTA; the modified HECA exhibits a decrease in thermal stability relatively to the unmodified HECA, this may be related to the groups grafted. The physicochemical properties (solubility, mechanic and thermal properties, softness, etc.) of HECA plastic films were ameliorated. The resulted cellulose esters HECA-Px were soluble in THF and present an amorphous structure justified by XRD spectra. It was noted by TGA-DTA analysis that the cellulose esters with low melting range were proved as thermoplastic polymers. The modification by aliphatic and aromatic ester moiety could decrease the thermal stability of the HECA in nitrogen atmosphere.

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