

New Branched Chain Cellulose Derivatives Based on Esparto "*Stipa tenacissima*" of Eastern Morocco: Synthesis and Characterization

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Abstract

Cellulosic fibers, a renewable raw material, can be successfully modified with functionalized compounds yielding hydrophilic or hydrophobic and biodegradable substrates. Thus, the judicious choice of the polar/nonpolar balance, as well as, the length of the macromolecular segments of the coupling agent gave rise to a variety of interesting modified fibers, which could be tested in different areas of applications. An attempt was made to prepare new hydrophobic cellulose derivatives modified urethane/urea by reaction between various blocked HDI adducts and Hydroxyethyl Cellulose (HEC) prepared from Esparto plant "*Stipa tenacissima*" Cellulose. In the current study, the blocked HDI adducts were synthesized by reacting a series of monoalcohols or monoamines with hexamethylene diisocyanate. Cellulosic fibers were extracted from Esparto plant; their viscosity average molecular weight (Mw) was deduced from the intrinsic viscosity in DMAc/9% LiCl solution and found equal to Mw = 227200. Furthermore, HEC was prepared from these cellulosic fibers with etherification. The conventional spectroscopic structural characterization of the samples was affected by FTIR, 1H NMR and 13C NMR and they were in accordance with the proposed structures. The reaction products (HECU) were also characterized by FTIR, NMR, XRD, TG/TD, and contact angle. The results of data analyses gave sufficient proof of grafting. The crystalline behaviors of the synthesized polymers were investigated and found that crystallinity index decreased when passing from cellulose to HEC and showed a moderate variation in the case of HEC derivatives (urethane and urea).

1. Introduction

Until now, due to shortage of petroleum resources, a great emphasis has been put on the research of alternative biodegradable materials, which could at least partially replace commodity polymers based on petrochemical. Biodegradable materials derived from renewable resources have been carried into the center of public interest for environmental protection and sustainable development [1].

Biodegradable polymers are suitable in many commodities and various applications, but their use is still limited due to their high cost or their low performances [2]. However, A successful method to obtain biodegradable materials is to develop from natural polymers such as cellulose, starch, etc. [3,4], which biodegradable tend readily to degrade in biologically active environments [5]. It is profoundly meaningful to take full advantage of natural cellulose material which is one of the most abundant natural resources in the world.

The effective and utilization of natural fibers as renewable resources are increasingly attracting high interest for scientists due to the consumption and over-exploitation of non-renewable resources and environmental protection. Among available natural fibers, Esparto "*Stipa tenacissima*" is a plant easily cultivated with short renewable times [6] and its annual worldwide production is about 10¹¹ tones [7]. These are mainly used in "simple" applications as ropes, cords, padding, fancy articles, and so forth. Some recent studies also report the possibility of using Esparto "*Stipa tenacissima*" fibers as a source of cellulose [8]. Cellulose which consists of

β -(1 \rightarrow 4)-linked glucose repeating units is the largest renewable biological resources and relatively inexpensive biopolymer [9-11], it has been widely used in numerous industrial domains [12-14]. The use of cellulose for obtaining new classes of engineering plastics is highly motivated by the advantageous properties like relative numerous reactive functional groups, great variety of modification options, moderate biodegradability and compatibility with several basic chemicals. Unfortunately, the cellulose chemical structure and molecular weight are inhomogeneous and depend on the vegetal species and extraction method, giving frequent difficulties in use. What varies from one form of cellulose to another one is, on the one hand, its degree of polymerization, which can span hundreds to thousands, and on the other hand, the supramolecular organization of its chains, which can give rise to amorphous and several types of crystalline structures [15]. Moreover, natural cellulosic fibers are high crystalloid, insoluble in water and common organic solvents. This insolubility is caused by strong inter/intra-molecular hydrogen bonding, and affects their development and utilization. Natural fibers itself cannot satisfactorily replace the functional and physical properties of conventional plastics since cellulose-based plastics exhibit water sensitivity and weak mechanical characteristics [16].

Modified biopolymers can be an interesting alternative for synthetic polymers where long-term durability is not required and a rapid disintegration is an advantage [17]. The surface chemical modification is a typical and classical approach to transform the polar hydroxyl groups sitting at the surface of cellulosic fibers. The properties of the modified cellulosic fibers depend greatly on the degree of substitution (DS) and the length of the introduced alkyl chain. The higher DS and the longer aliphatic chain the better are the hydrophobic properties. Several strategies are reported to overcome the mentioned drawbacks based on derivatization of cellulosic fibers to create low molecular branches via ester, ether, amide and urethane bonds [18-25]. Among these recent works, we can quote the grafting of long chain with isocyanate [26], or chloride acid [27] and the direct grafting of polymeric chains using a grafting process [28, 29] or by using bifunctional coupling agents [30-32]. The chemistry of the urethane bond based on the reaction of isocyanates with alcohols has been largely investigated and many studies have focused on the reaction of cellulose with different isocyanates [33, 35].

To the best of our knowledge, the chemical modification of hydroxyethyl cellulose (HEC) derived from Esparto with isocyanate has not been detailed. The isocyanate reaction presents some important advantages such as relatively high reaction rates, absence of secondary products and chemical stability of urethane moiety [36]. Indeed, the present study is also interested in evaluating the influence of the nature of the cellulose to be grafted and to propose a new grafting technique. The usual carbamate derivatizations are carried out under heterogeneous conditions and the development of homogeneous functionalization methods for cellulose leads to more uniform and stable products [37], and the preparation of HEC urethane and urea derivatives with high DS in DMAc as solvent may be a new approach of homogeneous reaction.

In this paper, investigation results of HEC derived from Esparto which is modified via the addition reactions with alkyl monoisocyanates prepared from hexamethylene diisocyanate (HDI) and monoalcohols (butanol; *HEC-HDI-OBt* and phenol; *HEC-HDI-Oph*) or monoamines (*butylamine*; *HEC-HDI-NHBt* and *benzylamine* *HEC-HDI-NHBz*) in dimethylacetamide (DMAc), are presented. The presence of additional urethane or urea bonds in short modifying branches can affect the urethane cellulose derivatives properties, as compared to those found for polymers obtained with usually applied monoalkyl isocyanates modifiers [38]. The influence of the modifier type as well as the degree of substitution (DS) on some physicochemical properties will be also evaluated. The grafted fibers could represent a new promising route to obtain composite material where the thermoplastic matrix is directly linked on the cellulose fibers surface.

2. Experimental

2.1. Materials

Esparto "*Stipa tenacissima*" cellulosic fibers had been dried in a vacuum oven at 90 °C for 48 hours before they were used for modifications. 1,6-hexamethylene diisocyanate (HDI) (98%) and *n*-butylamine (99.5%) were purchased from (Merck). Ethanol (98%), diethyl ether, acetone and *n*-butanol (98%), products of Aldrich were dried before their use. Ethylene oxide and hexamethylene diisocyanate were used without any further purification. Dimethyl acetamide (DMAc) (Merck) was purified by distillation under reduced pressure over (Na under vacuum) CaH₂ and stored with molecular sieves (4Å). Dibutyltin dilaurate (DBTL 95%) was also obtained from Aldrich and used to catalyze reactions. All other chemicals were of analytical grade and were used without further purification and purchased also from Aldrich.

2.2. Methods

2.2.1. Pretreatments of Esparto “*Stipa tenacissima*” fibers

Native Esparto “*Stipa tenacissima*” fibers used in this work were purchased from Oriental (eastern) Morocco. Cellulose was extracted according to the *El Idrissi et al.* method [39]. Esparto fibers were cut until fine particulates were obtained. Then, the fibers were treated with a 1N NaOH solution at 80 °C for 2 hours under mechanical stirring. This treatment was done three times in order to purify cellulose by removing other constituents. After each treatment, fibers were filtered and washed with bleach (NaClO) and distilled water until the alkali was completely eliminated and washed again with ethanol and diethyl ether three times. A subsequent bleaching treatment was carried out to bleach the fibers under mechanical stirring and was repeated 4 times at 80 °C for 4 hours. After each treatment, the fibers were filtered and washed with distilled water. The solution used in this treatment consists of equal parts of acetate buffer, aqueous chlorite (1.7 wt % in water) and distilled water.

2.2.2. Preparation of hydroxyethyl cellulose (HEC)

Hydroxyethyl cellulose (HEC) was prepared in NaOH/urea aqueous solution starting from ethylene oxide and cellulose extracted in basic medium as mentioned by *A. El Idrissi et al.* [39] and *Qi Zhou et al.* [40]. 6 g of NaOH and 4 g of urea were dissolved in 80 g distilled water. 2 g of cellulose were then added with stirring to get slurry. This solution was held at -20°C for 5h and then thawed with stirring in an ice-water bath to obtain a transparent solution. Ethylene oxide - with known amount - was added by portions of the homogeneous cellulose solution with stirring at 0°C. The solution was kept under stirring at 50°C for 4h. The solution was precipitated after neutralizing with acetic acid. The precipitate was filtered out, washed with acetone and dried in vacuum at 70°C.

2.2.3. Preparation of blocked HDI adducts

After placing HDI and 10 mL of DMAc into a reaction flask, an equimolar amount of monoalcohol (phenol/butyl alcohol) or monoamine (butyl amine/ benzyl amine) was added dropwise. The reaction temperature was kept below the boiling point of the added substance under inert atmosphere (N₂) until the intensity of NCO band became constant with time. The synthesis was catalyzed using DBTL, and it was noted that the amine compounds are more reacted than alcohols. The resulted products (HDI-OBt, HDI-NHBt, etc.), were subsequently used for Hydroxyethyl cellulose (HEC) modification.

2.2.4. Preparation of hydroxyethyl cellulose urethane /urea (HECU)

In a three-necked round-bottomed, flask equipped with thermometer, mechanical stirrer and a reflux condenser, 3 g of Hydroxyethyl cellulose (HEC) in 20 mL of DMAc were placed. The system was kept under nitrogen atmosphere. 1.5 equivalent of *blocked HDI adducts* (4.74 g of HDI-OBt, 4.71 g of HDI-NHBt, 5.13 g of HDI-Oph and 3.51 g of HDI-NHBz) was then added slowly (dropwise) when the temperature of the system reached 80 °C. To speed up the reaction, a single drop of dibutyltin dilaurate (DBTL) was used as catalyst. The temperature was then increased up to 110 °C, and it was kept for 4 hours. The modified cellulose derivatives were precipitated into 50 mL of acetone filtered and washed with acetone to remove amine formed during the reaction and the isocyanates were unreactive. Afterwards, the modified material was washed with acetone and diethyl ether, and dried at 60 °C to a constant mass. The cellulose urethane and urea-derivative films were processed by a casting/evaporation technique. The procedure was performed twice to check the reproducibility. The synthesized products were characterized by FTIR, ¹H NMR, ¹³C NMR and substitution degree (DS) was determined using ¹H NMR spectra.

2.2.5. Viscosity measurements

The viscosity average molecular weight of Esparto’s cellulose was deduced from the intrinsic viscosity, as described in the literature [41]. To calculate the average molecular weight, we measured the relative viscosity with an Ubbelohde capillary viscosimeter instrument in DMAc/9% LiCl solution at 25.0 ± 0.1 °C. With the intrinsic viscosity results, the Mark–Houwink equation was used to evaluate the DP of cellulose [42]. DMAc/LiCl solvent systems were chosen because it is known for dissolving cellulose without residue, detectable chain degradation and derivatization. One of the factors influencing the polymer dissolution is the polymer molecular weight. It was found that the dissolution rate decreases with increased polymer molecular weight:

$$[\eta]_{\text{int}} = 0.054 \times DP^{1.19} \quad (1)$$

Where $[\eta]_{\text{int}}$ is in the unit of $\text{cm}^3 \cdot \text{g}^{-1}$

2.2.6. Spectroscopic measurements

NMR spectroscopy

The chemical structure of samples was evaluated by FTIR, ^{13}C NMR and ^1H NMR spectroscopy techniques. ^1H and ^{13}C NMR spectra were recorded on a *Bruker Advance- 300 MHz* spectrometer at 360 °K by National Centre for Technical and Scientific Research at Rabat-Morocco. Chemical shifts (δ) were given in ppm using TMS as internal standard and deuterated dimethyl sulfoxide DMSO- d_6 as solvent.

FTIR spectroscopy

FTIR spectroscopy was used to follow the reactions and to compare modified and unmodified cellulose derivatives. FTIR experiments were performed using a Shimadzu Fourier transform infrared spectrometer FTIR-8400S using a KBr disc containing 2% fine samples. Twenty scans were taken of each sample recorded from 4000 to 400 cm^{-1} .

X-ray analysis

X-ray analysis was performed using a Panalytical Xpert-Pro MPD-Ray diffractometer with Ni-filtered using Copper Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) generated at a voltage of 40 kV and operation current of 30 mA, and scan from $2\theta = 5^\circ$ to 40° , pitch $0.05^\circ/\text{s}$. The crystallinity Index was evaluated using the Buschle-Diller and Zeronian equation [43].

$$I_c = 1 - (I_{\text{min}}/I_{\text{max}}) \quad (2)$$

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

Thermal analysis

Thermal study 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.

2.2.7. Casting

The films with thickness of 1 mm were prepared by casting the modified HEC (HECU) solution on Teflon plates. 1 g of the HECU samples was dissolved in 30 ml of DMAc to reach complete dissolution of the sample, and the solvent was eliminated by evaporation process under vacuum.

2.2.8. Contact angle measurements

The static contact angle (θ) was measured by a sessile drop method at constant room temperature (20 °C) using the drop shape analysis (DSA) *G 10 goniometer of Kruss GmbH*, equipped with software for a drop shape analysis. Diiodomethane (analytically pure) and deionized water were applied as test liquids. The image of liquid drop (volume of 2–3 μl) was recorded by video camera and fitted by means of mathematical functions. Each given θ value was the average of at least five measurements and the precision was 1° . Water absorption (%) and equilibrium degree of swelling were determined following the method as described in the literature [44].

3. Results and discussion

Before the preparation of HEC as an intermediate product, we had determined the degree of polymerization DP of the cellulosic fibers extracted from Esparto plant in DMAc/ 9% LiCl solution at 25.0 ± 0.1 °C using the viscosity technical and Mark-Houwink equation. The intrinsic viscosity was derived from the inherent and the reduced viscosity at zero concentration as shown in figure 2 and is equal to $[\eta]_{\text{int}} \sim 300 \text{ cm}^3 \cdot \text{g}^{-1}$. The values of DP_w and M_w calculated are respectively $\text{DP}_w \sim 1402$ and $M_w \sim 227200$.

Cellulose has a complex structure with both crystalline and amorphous regions making it difficult to be dissolved in normal solvents. In this work, hydroxyethyl cellulose (HEC), a representative cellulose derivative, was prepared by a totally homogeneous hydroxyethylation of cellulose using 6 wt % NaOH/4 wt % urea aqueous solvent systems. This solvent system, as a homogeneous reaction medium for the etherification of

cellulose, leads to better results. The preparation of the above material was relatively easily to be carried out. The structure of the compound obtained was examined using the spectroscopy techniques, and the relative DS value was determined from the ratio between peak areas.

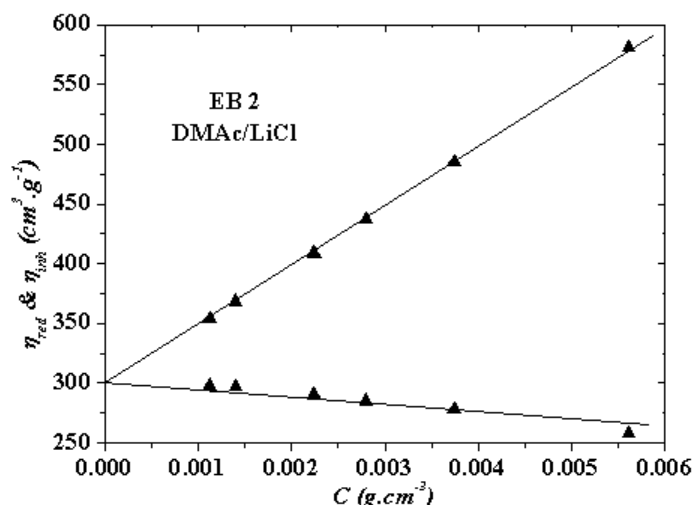


Figure 1: Inherent and reduction viscosity of the extracted cellulose from Esparto (in alkaline medium (NaOH, 1N)) in the solvent system DMAc/9%LiCl.

3.1. NMR Study

The NMR spectra were also in accordance with the proposed structure. In the first, the modification of cellulose was clear on figures 2 and 3. Furthermore, the spectrum represented on figure 2 shows the HEC methylene proton signals between ~3.5 ppm and ~3.6 ppm which were overlapped with the broad ring proton signals (2.8~5.6 ppm) of the cellulose skeleton. The degree of substitution of HEC (DS_{HEC}) was estimated using the equation (3) where I_{-CH_2-HEC} is the HEC methylene proton integration and $I_{-CH_2-C_6}$ is the integration C6 methylene of cellulose skeleton:

$$DS_{HEC} = \frac{I_{-CH_2-HEC}}{2 I_{-CH_2-C_6}} = 1.5 \quad (3)$$

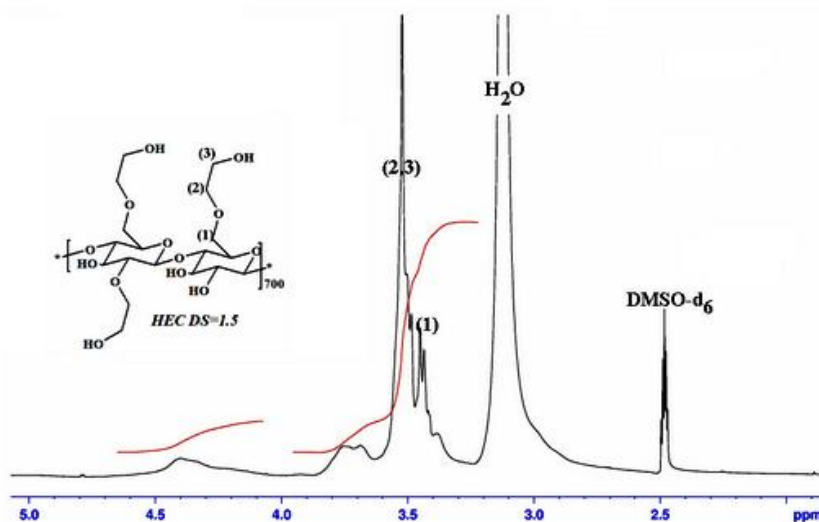


Figure 2: 1H NMR spectra of HEC $DS_{HEC} = 1.5$

The passage from cellulose to HEC can also be proved by the ^{13}C NMR spectra. The figure 3 presents the ring carbon of HEC ($DS = 1.5$), in DMSO- d_6 .

The successfully etherification of cellulose was revealed, as seen on the ^{13}C NMR spectra (figure 3), by the presence of the carbon methylene at 61, 70 and 72 ppm. According to *Qi Zhou et al.* [40] and *Jun li et al.* [49], the other peaks are assigned to the cellulose carbon in the region (60–105 ppm). The C_{6s} and C_{2s} are due to the C-6 and C-4 carbons bearing a substituted hydroxyl group respectively.

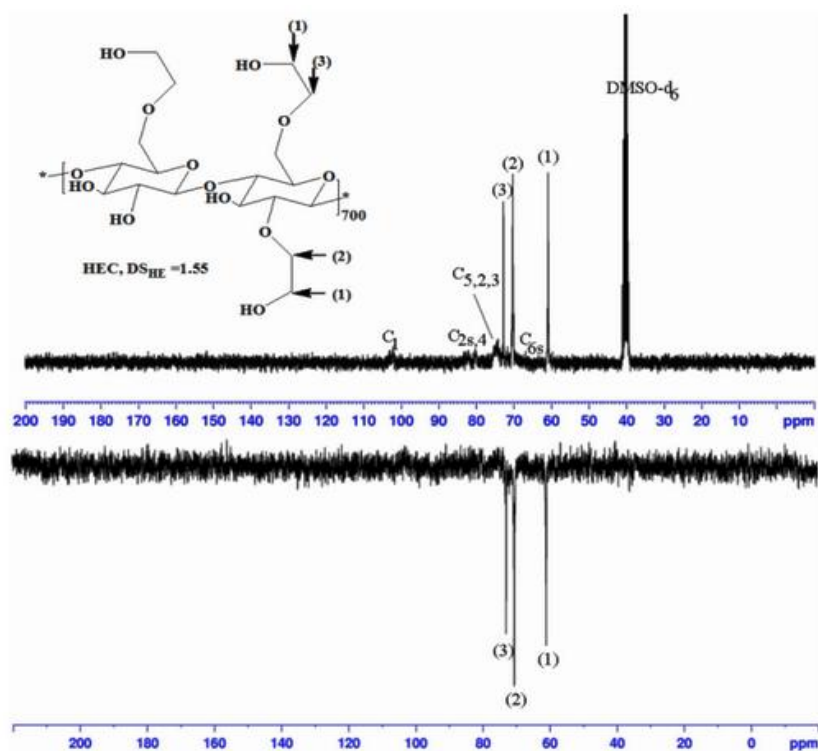


Figure 3: ^{13}C NMR and DEPT spectra of $\text{DS}_{\text{HEC}} = 1.5$

3.2. HDI derivatives as HEC modifiers

HEC modification presented in this paper is a two-step process and the chemical reactions that took place are illustrated in figure (4). At the first stage, the HEC modifiers were synthesized and were prepared by classical reaction between hexamethylene diisocyanate and monoalcohol or monoamine using DBTL as catalyst and the blocked urethane or urea-monoisocyanate derivatives were obtained (figure 4a). At the second stage, urethane–urethane or urethane–urea cellulose derivatives were synthesized (figure 4b). HDI has been chosen because it is harmless to environment [45].

In order to control the content of blocked HDI derivatives in the urethane/ urea cellulose derivatives (HECU) ^1H NMR spectra were recorded, because it is a powerful tool for monitoring the progress of the reaction using area methylene peak in α of urethane groups. Since HDI is a bifunctional reagent, the disubstituted derivatives may also be formed. ^1H NMR spectroscopy allowed determining the ratio of mono-/disubstituted derivatives. The main products of both controlled syntheses (HDI/*n*-butyl alcohol and HDI/*n*-butyl amine) are the monosubstituted derivatives (ca. 80% wt of HDI monoisocyanate) [46]. HDI derivatives were also characterized by FTIR spectroscopy.

3.3. Characterization of the Grafting Occurrence

Figure 5 shows FTIR spectra obtained for cellulosic fibers, HEC, blocked HDI in the case of butanol (HDI-OBt), and HECU (HEC- HDI-OBt) respectively. The last product results from the reaction between HDI-OBt and HEC. Before the chemical modification, the Cellulosic fibers display characteristic bands at 3400 cm^{-1} (O–H), 1110 cm^{-1} (C–O of secondary alcohol), and $2856/2920\text{ cm}^{-1}$ (C–H). After isocyanate additions, a strong increase of the band characteristics of the grafted alkyl chain ($-\text{CH}_3$ and $-\text{CH}_2-$ groups) at 2856 and 2920 cm^{-1} , which correspond to asymmetric and symmetric $-\text{CH}_2-$ stretches, respectively is observed. The addition reaction was confirmed by the characteristic absorption due to the carbamate groups in the ^1H NMR and IR spectra. In the case of FTIR spectra, the strong absorption at 1702 cm^{-1} can be attributed to the C=O absorption of the carbamate groups. Other characteristic peaks at 3362 and 2925 cm^{-1} can be assigned to the NH and CH absorptions. The 3340 cm^{-1} peak and the 1645 cm^{-1} peak, are assigned respectively to the NH and C=O urea groups formed by the reaction between NCO and NH_2 function. At the end of the reaction, the presence of the peak at 2270 cm^{-1} indicates that these compounds bear an NCO function which makes it suitable for further grafting to cellulose fibers. Some characteristic peaks appeared also in ^1H NMR and ^{13}C NMR showing successful formation of urethane and urea groups ($-\text{NHCOO}-$ aromatic urethane: $8,03$ and $153,4\text{ ppm}$); ($-\text{NHCONH}-$ aromatic urea: $6,0$ and $154,3\text{ ppm}$); ($-\text{NHCOO}-$ aliphatic urethane: $8,03$ and $157,8\text{ ppm}$); ($-\text{NHCONH}-$ aliphatic urea: $6,0$ and $160,8\text{ ppm}$).

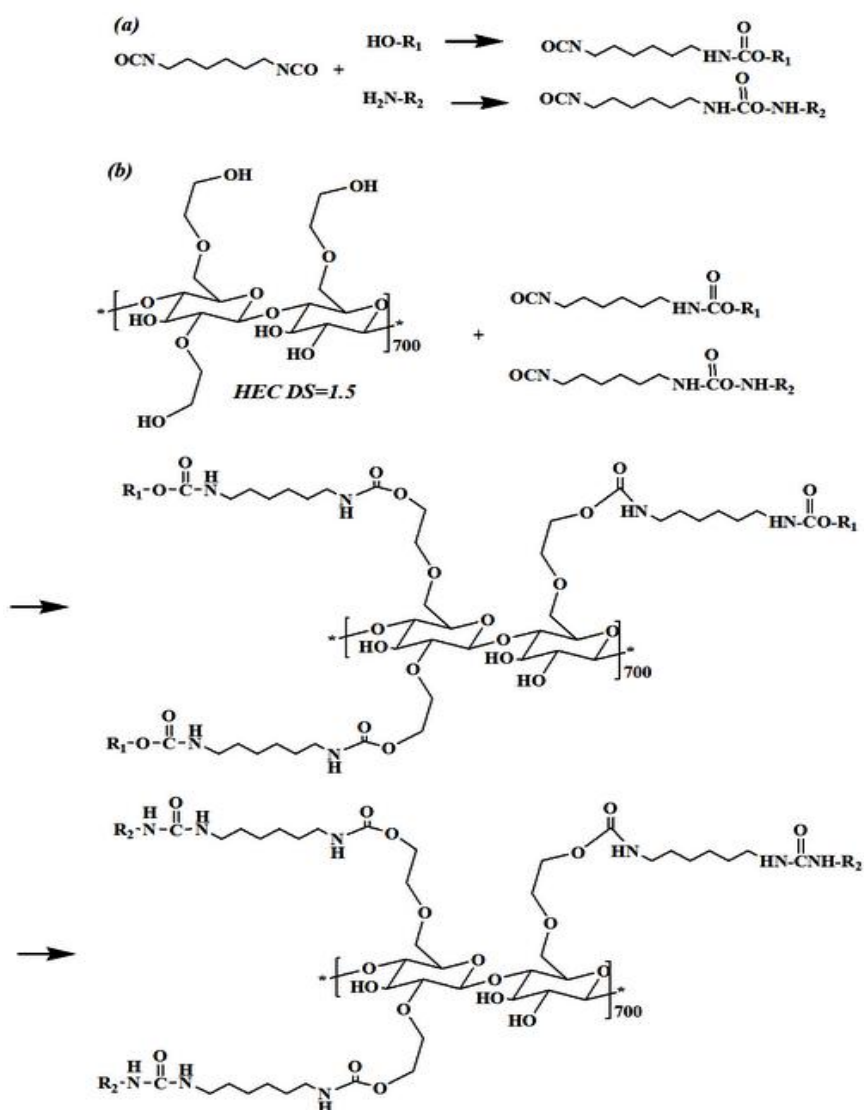


Figure 4: (a) Reaction between HDI and monoalcohol or primary amine, respectively, urethane- or urea-derivative is formed. (b) Reaction between HEC unit and HDI/mono alcohol or HDI/mono amine modifiers.

As can be observed in figure 6, in all HECU samples a decrease in the intensity of OH/NH band is observed in the region $3300\text{--}3500\text{ cm}^{-1}$. Other difference of the characteristic bands for urethane and urea cellulose derivatives are located in the range $1545\text{--}1575\text{ cm}^{-1}$ (amide) and the carbonyl group bands appeared between 1620 and 1707 cm^{-1} .

The signals at 1622 cm^{-1} and 1543 cm^{-1} , assigned to the amide I and amide II vibrations respectively, are interpreted as the presence of ureic linkage formed during the reaction. Two especial regions are of main interest providing a powerful method to evaluate the confirmation change of urethane polymers: the C=O stretching vibration and the N-H stretching vibration corresponding to free, disordered hydrogen bonded and ordered hydrogen bonded urethane carbonyl group. A band is assigned to NH bonded to carbonyl groups at 3327 cm^{-1} . The C=O stretching band at around 1687 cm^{-1} was resulted from the hydrogen bonded formed from the NH of urethane and C=O of urethane carbonyl group [47]. We can also notice the absence of the signal at 2270 cm^{-1} corresponding to the isocyanate functions, which is expected after several washing steps. Even if we are working in an anhydrous environment, long-chain amine could be produced as a byproduct, because isocyanates are highly sensitive to moisture. However, no signal corresponding to NH_2 (at 3563 cm^{-1} and 3472 cm^{-1}) is clearly observed, mainly because this signal is overlapping with bands ascribed to OH groups still present at 3400 cm^{-1} . Moreover, the excess of isocyanate is not very important. Thus, it cannot lead to the formation of allophanate as described by *Stenstad et al.* [48] and proved by FTIR. This allophanate is in fact obtained by the reaction of a new isocyanate on the urethane linkage and needs a huge excess of isocyanate.

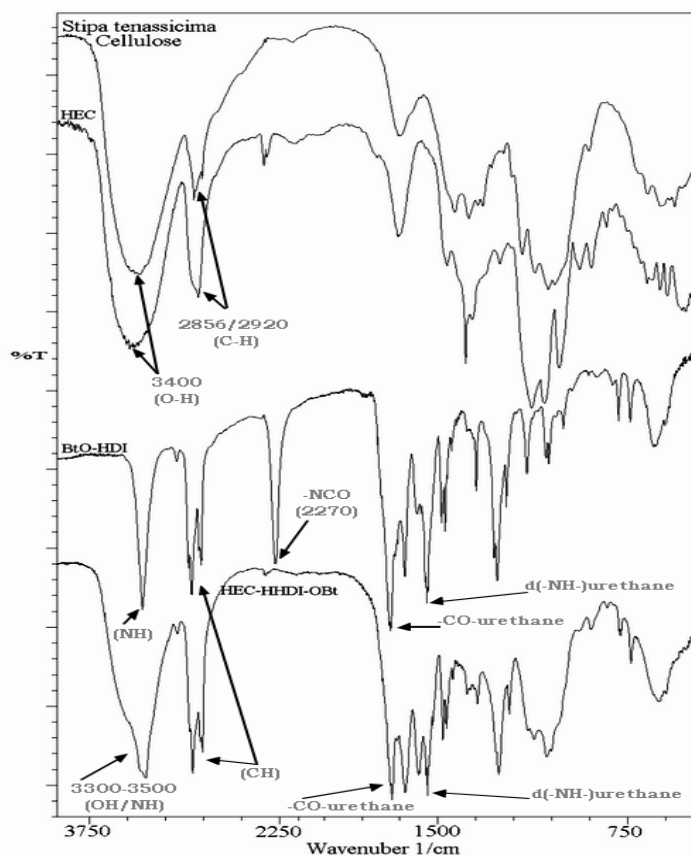


Figure 5: FTIR spectra of cellulose extracted from Esparto, HEC, BtO-HDI and the hydroxyethyl cellulose modified by HDI-OBt (HEC-HDI-OBt).

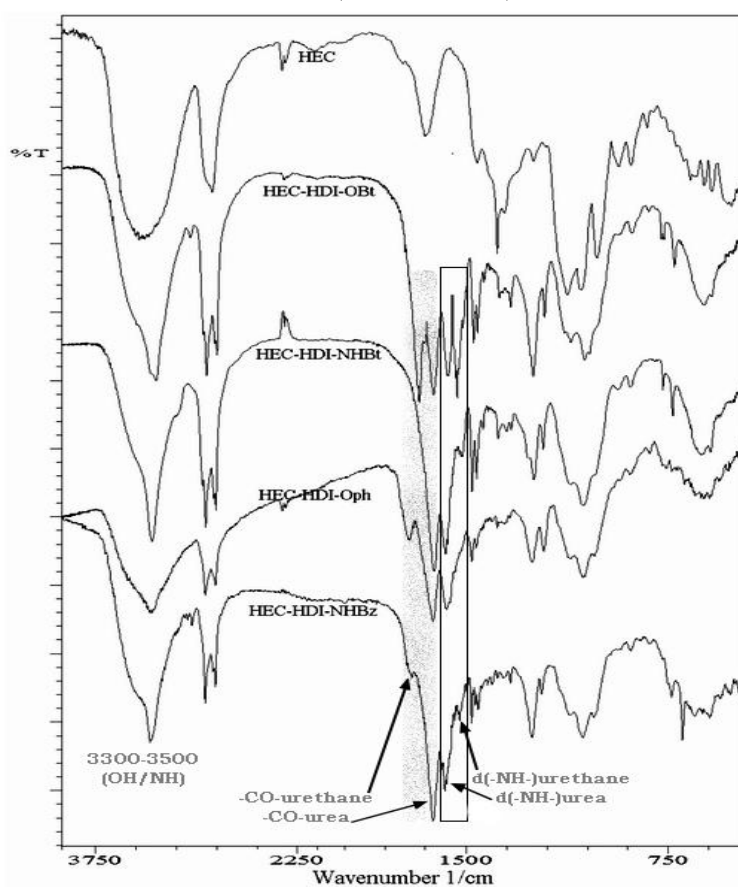


Figure 6: FTIR spectra of HEC modified by HDI/butyl alcohol (HEC-HDI-OBt), by HDI/butyl amine (HEC-HDI-NH₂Bt), by HDI/phenol (HEC-HDI-Oph) and by HDI/benzyl amine (HEC-HDI-NH₂Bz)

However, an alternative reaction of isocyanate on the primary amine byproduct could occur and form the corresponding di-urea in homogeneous media. We can obviously admit that this long-chain di-urea is produced at very low quantity and should stay in reaction media in which it is soluble. Nevertheless, the ensuing aliphatic urea could also be adsorbed at the fiber surface through hydrogen bonding, and hence be detected by FTIR. Therefore, to conclude on FTIR measurements, changes in the surface chemistry were observed after a strong washing of the modified HEC (which should eliminate all byproducts), thus, proving the grafting of n-alkyl hexamethylene isocyanate. In spite of these results, other analyses have been performed to indubitably confirm the chemical modification of cellulose and HEC. The NMR, XRD, TGA/DTA, etc., present the advantage of determining the relationship between the structure (composition) and the properties.

Figure 7 represents ^1H NMR spectra of the synthesized HEC urethane and HEC urea derivatives and confirms the grafting of HDI/alcohol or HDI/ amine onto HEC. The urethane proton signal ($-\text{NHCOO}-$) was observed at around 6.6 ppm, except in the case of HEC-HDI-Oph it appears at 9.1 ppm; This exception may be due to the aromatic effect [50]. The urea protons ($-\text{NHCONH}-$) were detected at around 5.6 ppm. The apparition of urea characteristic peak at 5.6 ppm in the urethane spectra (HEC-HDI-OBt and HEC-HDI-Oph) due to the formation of the urea linkage results from the non-totally anhydrous system. Some other new peaks were observed in the range 0.86-1.38 ppm and 2.75-4.27 ppm attributed respectively to the methylene protons $-\text{CH}_3$, $-\text{CH}_2$, $-\text{CH}_2\text{O}-$, $-\text{CH}_2\text{OCO}-$ and $-\text{CH}_2\text{N}-$, support the formation of HEC urethane and HEC urea (figure 7a, 7b, 7c and 7d), while the majority peaks of the cellulose skeleton are highly overlapped. Moreover, the formation of the allophanate compounds ($\text{ROCO}-\text{NR}'-\text{CO}-\text{NHR}''$) could be followed by the appearance of a characteristic peak at 10.1 ppm [51]. However, when the reaction temperature was kept below $100\text{ }^\circ\text{C}$, almost no allophanate compounds were observed. In the case of the aliphatic grafted urethane and urea (HEC-HDI-OBt/ HEC-HDI-NHBt), the HECU degree substitution (DS_U) was estimated from the ratio between the HEC methylene protons peak integration ($I_{-\text{CH}_2-\text{HEC}}$) at 3.4 – 3.6 ppm and the methylene ($-\text{CH}_3$) protons peak integration of the urethane or urea chains at 0.88 ppm ($I_{-\text{CH}_3}$) using the equation (4):

$$\text{DS}_U = \frac{8I_{-\text{CH}_3}}{3I_{-\text{CH}_2-\text{HEC}} + 2I_{-\text{CH}_3}} \quad (4)$$

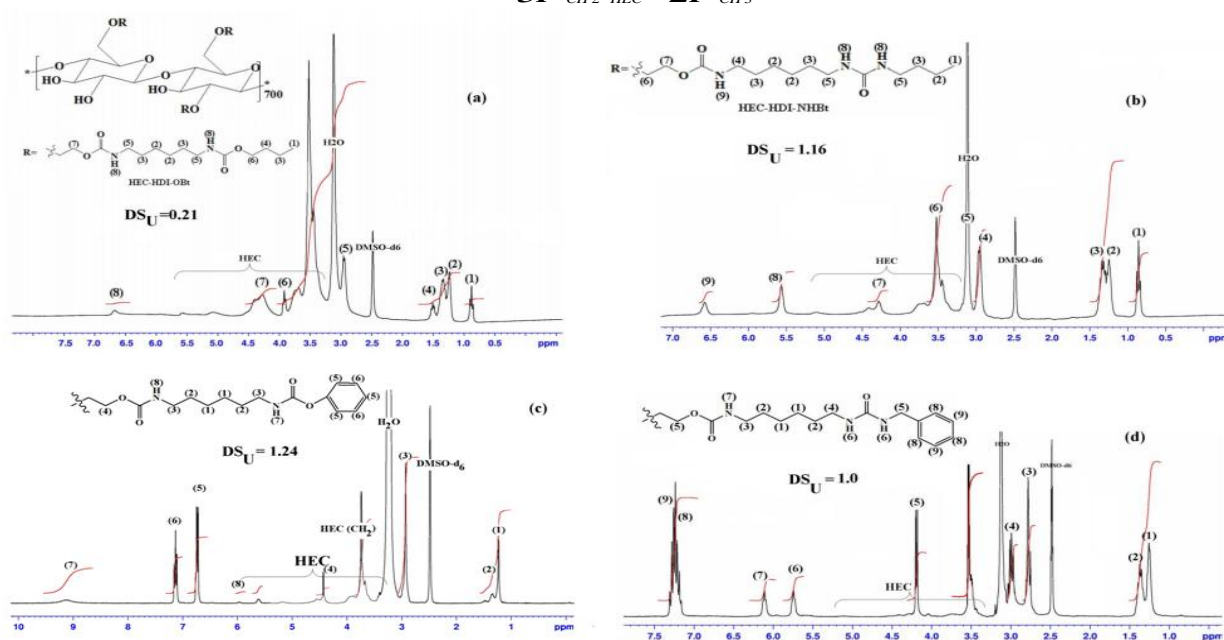


Figure 7: ^1H NMR spectra of (a): HEC-HDI-OBt, (b): HEC-HDI-NHBt, (c): HEC-HDI-Oph and (d): HEC-HDI-NHBz

The same approach was also used for the aromatic ones (HEC-HDI-Oph) and (HEC-HDI-NHBz) respectively. The HECU degree of substitution (DS'_U) was estimated using similar procedure from the ratio between the HEC methylene protons peak integration ($I_{-\text{CH}_2-\text{HEC}}$) at 3.4 – 3.6 ppm and the aromatic protons peak integration of the urethane or urea chains between 6.72-7.28 ppm (I_{Ar}) using the equation (5):

$$\text{DS}'_U = \frac{8I_{Ar}}{5I_{-\text{CH}_2-\text{HEC}} + 2I_{Ar}} \quad (5)$$

The ^{13}C NMR -DEPT-135 and the assignment of different peaks of HEC-HDI-OBt, HEC-HDI-NHBt, HEC-HDI-Oph, and HEC-HDI-NHBz are reported on figure 8a, 8b, 8c and 8d respectively. The modification of the HEC is clear on the ^{13}C NMR spectra by the appearance of characteristic peaks of urethane and urea grafted chains at 13.9 – 43 ppm and 115 – 153 ppm which were assigned to range owners of $-\text{CH}_2-\text{CH}_3$ and aromatic carbons respectively. These results are also confirmed by DEPT-135 spectra. These results are also confirmed by DEPT-135 spectra.

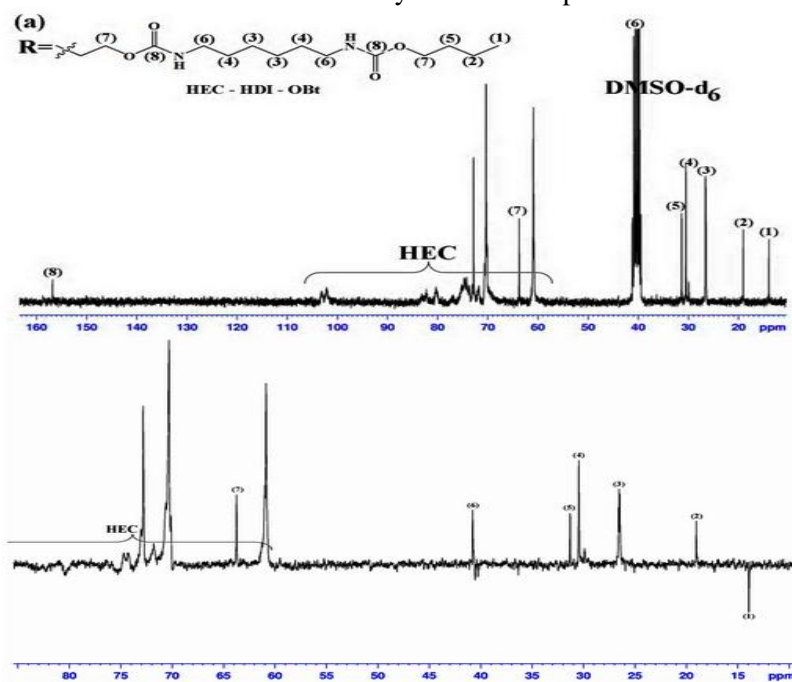


Figure 8a: ^{13}C NMR and DEPT-135 spectra of HEC-HDI-OBt.

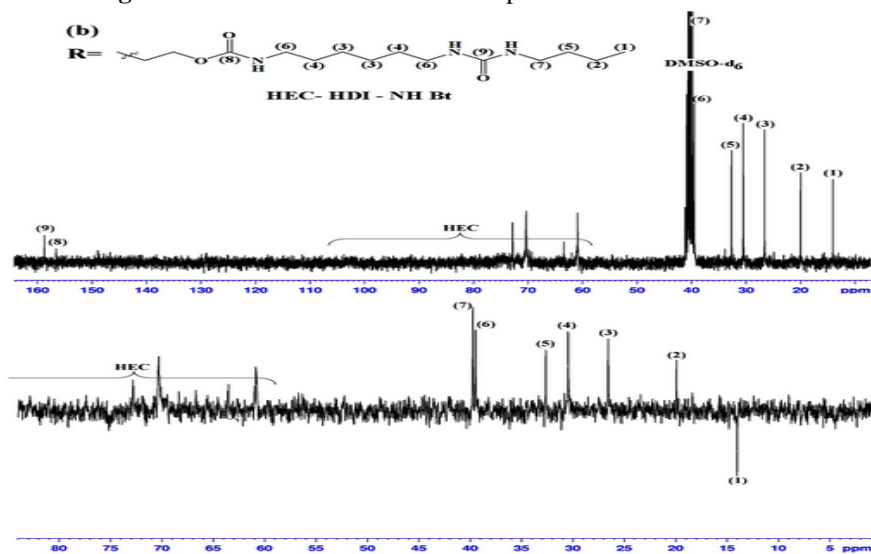


Figure 8 b: ^{13}C NMR and DEPT-135 spectra of HEC-HDI-NHBt

The shifting of the characteristic peak of $-\text{CH}_2$ group linked at HEC and in α of urethane from 60 ppm to 63 ppm was a strong indication that the grafted reaction was successful. No other changes were noted indicating that no change in the HEC main chain was occurred. Grafting is still shown by the appearance of new peaks characteristic of (C=O) urethane and (C=O) urea between 156.77 – 157.75 ppm and 158.43 – 158.68 ppm respectively.

X-ray diffraction analysis

X-ray diffraction measurements were performed to check if the chemical modification altered the crystallinity of cellulose and its derivatives. Figure 9, presents respectively the X-ray diffraction patterns of Esparto's cellulose, (HEC), HEC-HDI-OBt, HEC-HDI-NHBt, HEC-HDI-Oph and HEC-HDI-NHBz. The diffraction pattern of Esparto's cellulose shows well-defined four peaks around 15° , 16.3° , 22.6° and 34.5° corresponding respectively to the (101), (10-1), (002) and (040) hkl plan which derived from cellulose I [52].

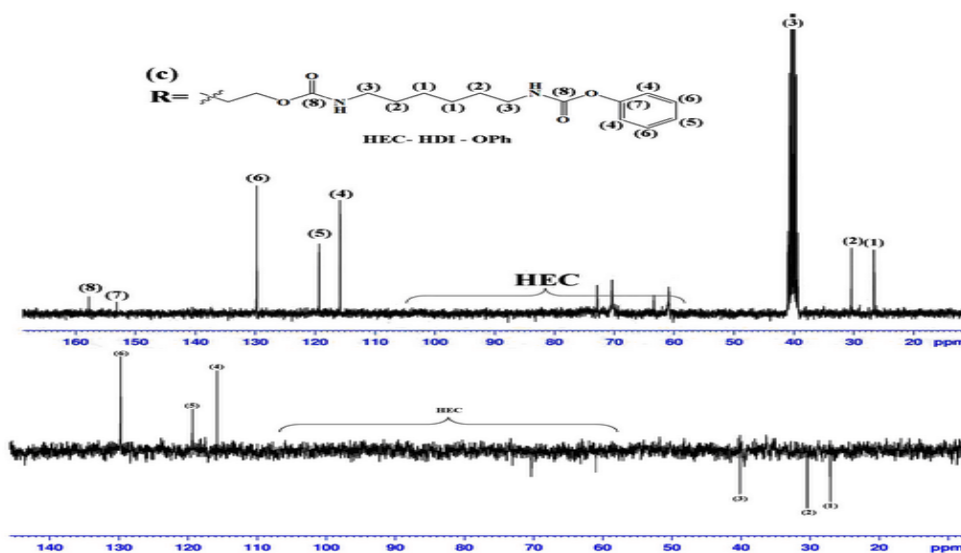


Figure 8c: ^{13}C NMR and DEPT-135 spectra of HEC-HDI-Oph

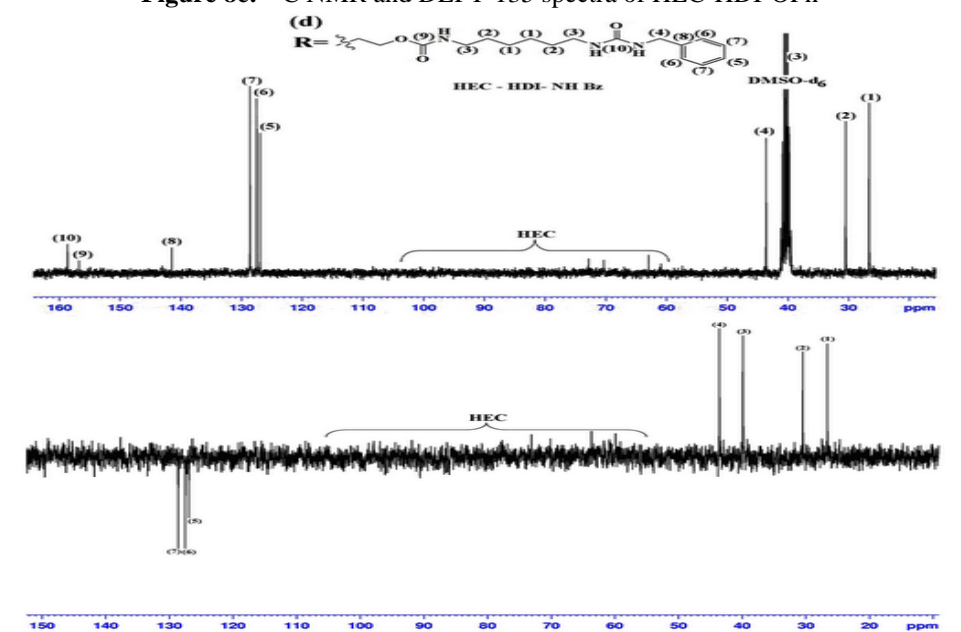


Figure 8d: ^{13}C NMR and DEPT-135 spectra of HEC-HDI-NHBz

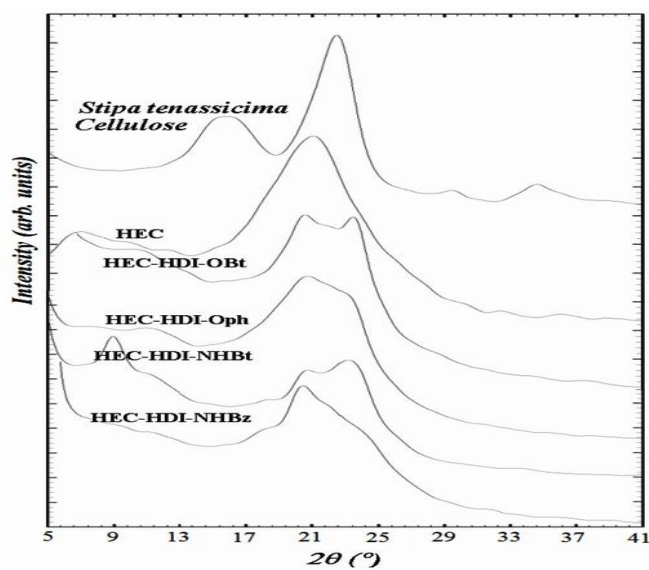


Figure 9: X-ray diffraction patterns of Esparto cellulose, (HEC), HEC-HDI-OBt, HEC-HDI-NHBt, HEC-HDI-NHBz and HEC-HDI-Oph.

X-ray diffraction pattern results of HEC indicate that with the etherification processing, the crystalline structure of cellulose was destroyed, and the degree of crystallinity is decreased from 63.1 % for Esparto's cellulose to 30.8 % for hydroxyethyl cellulose. This alteration may be explained by the fact that the inter- and intra-molecular hydrogen bonds are responsible of its highly ordered crystalline structure. During the etherification reaction, the ethylene ether groups have substituted some hydroxyl groups on cellulose backbone, reducing the formation of the intra- and inter-molecular hydrogen bonds, and a decrease in the ordered crystalline structure was noted, the proportion of amorphous regions increases.

Table 1: Degree of crystallinity determined from X-ray diffraction experiments.

Samples.	Degree of crystallinity I_c (%)
Esparto cellulose	63.10
HEC	30.86
HEC-HMDI-OBt	34.00
HEC-HMDI-NHBt	37.30
HEC-HMDI-Oph	23.63
HEC-HMDI-NHBz	21.96

The viscosity and crystallinity measurements results show that cellulosic fibers extracted from Esparto cellulose have a high degree of polymerization ($DP \sim 1400$) and an important value of crystallinity index ($I_c \sim 63.10\%$), making their solubility very difficult and requires considerable efforts. It is worth noting that increasing the amorphous percentage enhances the cellulose solubility without pretreatments, avoiding expensive solvents and reducing the price of final product. This intermediate product (HEC) can create an easy path for modifying the cellulose and therefore the development of new biodegradable compatible cellulose-based materials.

It can be seen in figure 9, that the HEC-urethane and HEC-urea display a similar defined pattern which differs from HEC XRD-pattern by the appearance of two new peaks at 10.6° and 23.5° suggesting that in the progress of the reaction other ordered regions were formed and may be due to the formation of a new hydrogen bonds established between the (-NH) and (-C=O) urethane and urea groups respectively. This idea can explain the increase of the crystallinity level of HEC-HDI-NHBt and HEC-HDI-OBt from 30.8 % (HEC) to 37.3 % and 34.0 % respectively. In the case of aromatic urethane and urea compounds, we note that the peaks' intensity at 10.6° and 23.5° decreases sharply, indicating a decrease in their crystallinity from 30.8 % (HEC) to 23.6 % and 21.9 % respectively (table 1). This observation may be ascribed to the aromatic effect. However, the sharpness in crystalline peaks is increased from the aromatic to aliphatic character. The X-ray diffraction studies showed that crystallinity depends greatly on the structure of the reagents and the reaction conditions.

Thermal analysis

The etherification effect on the thermal behavior of HEC was also studied by TGA and DTA in the temperature range from 35°C to 500°C . Figure 10a shows the TGA and DTA thermograms of unmodified Esparto's cellulosic fibers and HEC. From the above figure, it can be seen that the thermal degradation temperature decreases from 291.08°C for Cellulose to 280°C for HEC respectively. This low decrease could be explained by the disappearance of the hydrogen bonding and the decrease of ordered regions in HEC chain backbone. This result correlates better with the XRD data. Moreover, HEC was measured in the form of dry powder; it still contains approximately 4.5% of moisture in their molecules, showing the initial weight loss observed in its TG curve. The DTA thermo grams of HEC show two peaks at 315°C and 333°C attributed to the degradation of the modified part and non-modified part respectively, because this phenomenon was influenced by the amount of the hydroxyethyl groups contained in HEC main chain (figure 10a).

Thermogravimetric analysis of HEC-urethane and HEC-urea samples were also developed in order to characterize their thermal behavior. The TGA thermograms of *HEC-HDI-OBt*, *HEC-HDI-NHBt*, *HEC-HDI-NHBz* and *HEC-HDI-Oph* obtained from room temperature to 500°C are shown in figure 10b. In this figure, three weight loss steps can be identified; the first weight loss occurs between 140°C and 300°C attributed to the decomposition of the grafted urethane and urea chains. The second weight loss step occurs around $300\text{-}380^\circ\text{C}$ ascribed to the decomposition of the HEC, followed by a slight weight loss, practically negligible, observed from 420°C , indicating that 420°C is the limit temperature of degradation where the HEC thermal degradation is complete. In the case of HEC-urethane thermograms, especially in the aliphatic ones, no major weight loss was observed until 270°C confirming the high thermal stability of alkyl urethane bonds. This increase in the

thermal stability from HEC to HEC- urethane and HEC-urea may be explained by the stability of the urethane and urea bonds.

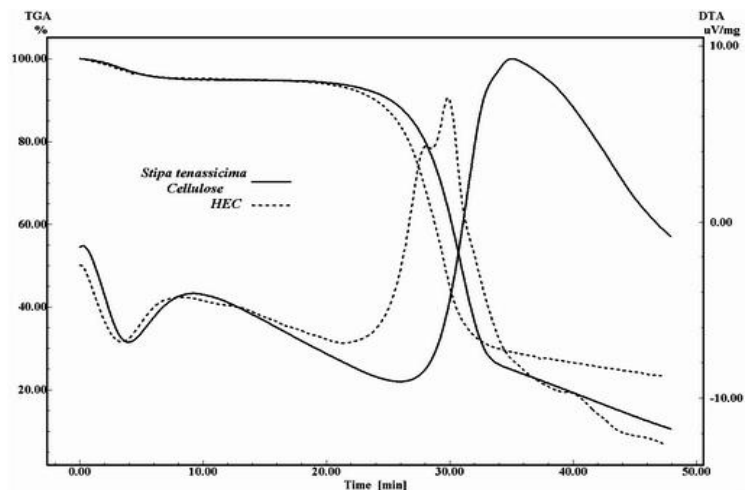


Figure 10a: TGA and DTA curves for Esparto cellulose and HEC.

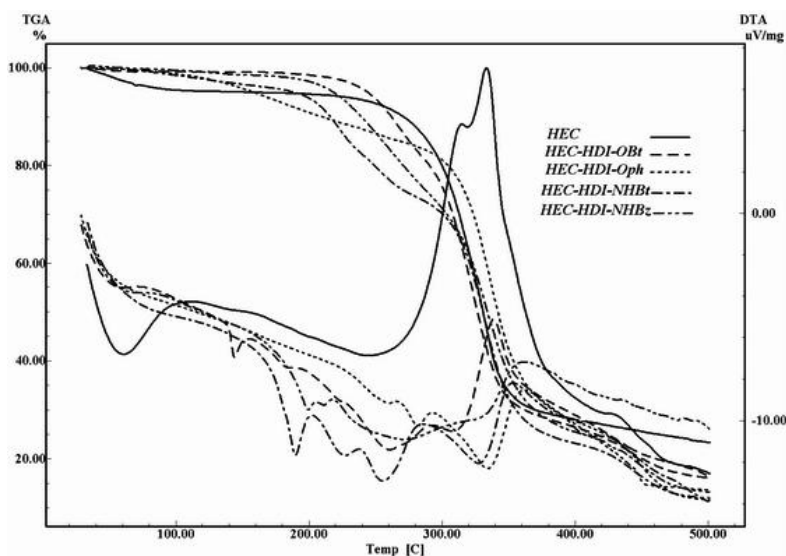


Figure 10b: Thermogravimetric and thermodifferential curves for HEC, HEC-HDI-OBt, HEC-HDI-NHBt, HEC-HDI-NHBz and HEC-HDI-Oph.

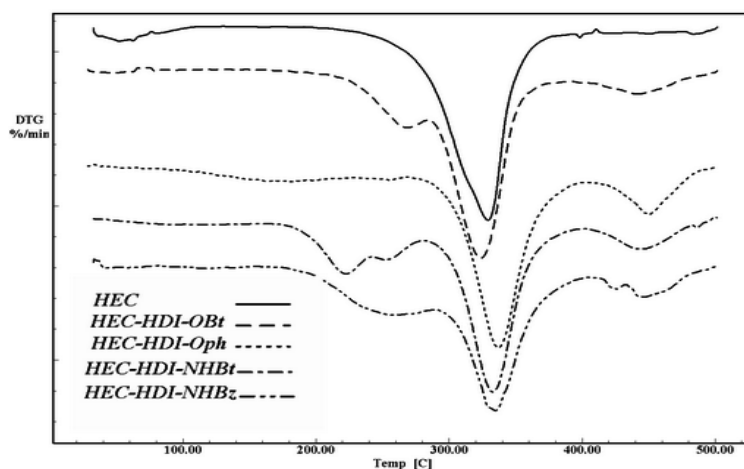


Figure 10c: DTG curves for HEC, HEC-HDI-OBt, HEC-HDI-NHBt, HEC-HDI-NHBz and HEC-HDI-Oph.

The stage characteristics of the HEC-urethane and HEC-urea samples can be observed clearly in the DTG curves on figure 10c. The maximum decomposing rate temperature (T_{max}) appears clearly and the detailed results are given in the table 2.

Table 2: The thermal degradation data of cellulose, HEC and HECU result products

Compounds	T _d (°C)	T _{max1} (°C)	T _{max2} (°C)	T _{max3} (°C)	T _{50%} (°C)	Residue at 500 °C
Esparto cellulose	291.08	-----	332.15	-----	332.76	10.16
HEC	280°C	-----	329.60	-----	330.77	23.22
HEC-HDI-OBt	229.89	267.96	324.70	442.16	326.34	15.97
HEC-HDI-NHBt	202.95	222.42 and 254.41	332.64	444.02	330.77	11.98
HEC-HDI-Oph	112.48	255.11	337.54	450.33	342.63	11.55
HEC-HDI-NHBz	215.91	258.15	334.15	446.60	334.51	13.16

Contact angle measurements

The contact angle measurements of liquid droplets on material surfaces are used to characterize surface properties of modified fibers to provide information regarding the evolution of hydrophilic/hydrophobic character induced by different functionalization. The low contact angle value of original fibers, about 25°, results from high hydrophilic character of the surface as a consequence of the high density of the surface hydroxyl groups on cellulosic fibers, and decreases rapidly with the time. The water drop disappears both because of the spread and/ or penetration into the porous structure of the substrate. The fibers treated with HDI/mono alcohol or HDI/mono amine modifiers reached a contact angle between 81°-92° for both aliphatic/aromatic structure and urethane/urea groups, denoting a highly hydrophobic surface which is the sign that the grafting chains thoroughly hide the cellulose surface hydroxyl groups. We have noted the stability of the water drop on the modified surface and constant angle with time. The increase of the contact angle value after chemical modification is more significant for urea derivatives than for urethane ones and for aliphatic than aromatic structures. It is found to be around 92° and 81° respectively. It is an indication that chemical grafting induced important changes in surface polarity and wettability for cellulosic fibers. Comparing the contact angle value obtained for unmodified cellulose to the values obtained for modified compounds, it clearly appears that the surface chemical modification successfully occurs. Indeed, it is reported that the surface properties of polymeric materials are dictated by the surface configuration of the molecule and their atoms spatial arrangement at the top surface.

These data are confirmed by the values of dispersive and polar contributions to the surface energy of these substrates. In fact, virgin model cellulose displayed dispersive and polar components of the surface energy around 25 and 35 mJm⁻², respectively. The data obtained shows that cellulosic fibers have a surface energy close to that of similar materials reported in the literature [22, 53]. After modification, the dispersive component remained roughly constant, while the polar contribution to the surface energy decreased drastically and reached very low values. This phenomenon is due to the fact that any increase in contact angle values leads to decrease in surface energies. In other words, a solid surface can be made more wettable either by lowering the surface tension of the liquid or by increasing the surface energy of the solid.

As expected, the decrease in the surface energy after modification was essentially due to the reduction in its polar component, because of the replacement of the surface hydroxyl groups by non polar chains. The polar contribution to the surface energy of all the modified fibers decreased with respect to that of the untreated fibers, but the extent of this reduction depended on the nature of grafting chains and the reaction time.

Conclusion

Cellulosic fibers, a renewable raw material, can be successfully modified with functionalized compounds. Thus, the judicious choice of the polar/nonpolar balance as well as the length of the coupling agent gave rise to a variety of interesting modified fibers, which could be tested in different areas of applications. Generally, the cellulose derivatives with the degree of substitution in a range of 1.6–1.8 exhibit acceptable bulk hydrophobic properties and melt flow features in hot press test.

An attempt was made to prepare new hydrophobic HEC derivatives modified urethane/urea by reaction between a various blocked HDI adducts and HEC. The blocked HDI adducts were synthesized by the reaction of monoalcohol or monoamine and hexamethylene diisocyanate. Firstly, cellulosic fibers have been extracted from Esparto plant, their viscosity average molecular weight (M_v) was deduced from the intrinsic viscosity and found equal to $M_v = 227200$ g/mol then these fibers have been etherified in order to prepare HEC. The conventional spectroscopic characterization with FTIR, ¹H NMR and ¹³C NMR were in accordance with the proposed structures. HEC was chemically modified using blocked HDI adducts that have been never reported in the literature to broaden its range of different applications areas. An innovative process for the surface chemical

grafting has been developed. It consists of a procedure that appears as a good solution to avoid problems of inhomogeneous reaction. The reaction products (HECU) have been characterized by FTIR, NMR, XRD, TG/TD, and contact angle measurements which give sufficient proof of grafting.

The crystalline behavior of these biopolymers was investigated and the crystalline decreased from cellulose to HEC and shows a moderate variation in the case of HECU samples (urethane/urea). Investigation of structure-property relationship for these derivatives showed that the main determining factors for observed properties were physical effective crosslink density, hydrogen bonding, thermal stability and nature of blocked HDI adducts. The effect of modification percentage on hydrophobicity was measured through contact angle and it was found that it increases with increasing the amount of grafting moieties. The equilibrium degree of swelling and water absorption were affected by chemical composition of the final HECU compounds.

The modified HECU biopolymers can be used as filler in biodegradable cellulose based materials due to better dispersion and compatibility, and it can be concluded that the synthesized products could be a potential candidate as biodegradable materials which are biocompatible and non-toxic.

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