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Physicochemical Characterization of Celluloses Extracted from Esparto "*Stipa tenacissima*" of Eastern Morocco

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ABSTRACT: Increasing ecological concerns have given rise to renewed interest in the use of natural materials, considering their renewability and possibility of disposal at the end of their life cycle without damage to the environment. In this study, we examined the isolation of cellulose from Esparto "*Stipa tenacissima*" of Eastern Morocco by two different ways; the first one using an acetic acid solution catalyzed by nitric acid. The objective is to determine the optimum amount of this catalyst needed to the extraction. The second way consists to study the cellulose extraction with change of the alkaline solution concentration in order to choose the required value. The cellulosic samples were characterized by *FT-IR* spectroscopy and *X-ray* diffraction, the morphology of the isolated fibers was investigated by optical microscopy. Thermal analysis (*DT-TGA*) were carried out to study the thermal behavior of the cellulose isolated compared with the control sample. The degree of polymerization (DP) of the samples extracted is estimated from the intrinsic viscosity value using the Mark-Houwink equation in two different solutions (DMAc/9%LiCl) and (6%NaOH/4%urea/90%H_2O). We have demonstrated that the extraction using an acetic acid solution has been very successful by adding 2% in volume of nitric acid (HNO_3). However, the extraction process using an alkaline solution (NaOH; 1M) is preferable because of the absence of acetylating reaction and the high purity and the nondegradation of the resulted fibers. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

Although plastics are vital to the economy and quality of life, their limited waste disposal issue has created the need for biodegradable plastics to be used for this purpose. Furthermore, the shortage of fossil resources, the need for sustainable development and environmental protection are profoundly receiving interest of scientists as well as of socioeconomic operators.[1,2] Moreover, synthetic fibers, such as nylon, amid, glass, and carbon are widely used as reinforcement in polymer matrix composite materials. However, these fibers are not biodegradable and they are often very expensive, increasing the cost of the part being manufactured. Textile and other industries using fibers have been attempting to find new sources of natural fibers that could; compare with the performance properties of major natural fibers like cotton, linen, etc.; reduce the dependence on other resources required to produce fibers, and compete in terms of cost and availability with currently available fibers.[3–5] Natural polymers can be a good candidate to substitute the synthetic polymers and they have to offer comparable qualities. Cellulose and wood are most abundant in nature, and they are produced in a sustainable way and offer many possibilities for use, because they are renewable, biodegradable, biocompatible, and derivatizable.[5] Though the forest cannot satisfy the demand for perpetual growth today any more, because of the disappearance of 30 Million Hectares of trees every year (FAO, 1997).[6] Then during the last decades, the research has been directed to exploit new sources of cellulose from the remainders of the human activities such as residues of *Maize*,[7] *Banana*,[8,9] *Hibiscus cannabinus L*,[10] *Opuntia Ficusindia*,[11] etc.

Many attempts were made to utilize the biomass efficiently by applying chemical treatments to obtain a new class of high performance green polymers.[12] Among available natural fibers,

Esparto "*Stipa tenacissima*" is a plant easily cultivated with short renewal times[13] and their annual worldwide production is about 10^{14} kg[14] and in Morocco about 5.7125 10^8 kg (*Moroccan Society of Agricultural Land Management; SOGETA, 1983*). They are mainly used in "simple" applications as ropes, cords, padding, fancy articles, and so forth. Therefore, using resource such as Esparto will become more and more interesting and popular. Some recent studies also report the possibility of using Esparto fibers as a source of cellulosic fibers.[15] Therefore, Esparto shows greater promise in providing large quantities of natural cellulosic fibers with significant economic benefits than any other agricultural product. In addition, the process of fiber extraction from Esparto requires relatively lesser energy and is also environmentally friendly. Cellulose which consists of β-(1 $\rightarrow$ 4)-linked glucose repeating units is the main plants cell wall constituent and is the largest renewable biological resources and relatively inexpensive biopolymer,[16–18] it has been widely used in industrial domains such as fiber, paper, polymer, textile, food industries and bioactive and biocompatible materials.[19–21] 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, good adhesive, adsorption and solution properties, and compatibility with several basic chemicals.

The extraction of cellulose starting from a vegetal material (biomass) can be carried out in acid or alkaline medium.[22] The principle consists of the progressive impoverishment of the cellular walls of the plants. The diffusion of the alkaline (or acid) solution between the chains of a vegetal breaks the physical interactions such as *Van deer Waals* especially the hydrogen bonds. Moreover, the elimination of the intermolecular interactions facilitates the delignification and the elimination of non-cellulosic constituents. Cellulose has been already extracted from Esparto,[23] but much work is still needed before it can be directly employed industrially or derivatized under heterogeneous or homogeneous solution conditions.

The cellulose chemical structure and molecular weight are inhomogeneous and depend on the vegetal species and extraction method, giving frequent difficulties in use.[24] The determination of the molecular mass parameters (M_n, M_w, and polydispersity), the chemical uniformity, the degree of crystallinity, as well as the thermal properties, etc. of this type of cellulose have not be determined before and is necessary. In this article, we report the role of extraction conditions (acidic and alkaline pretreatments), particularly its effect on the degree of polymerization (DP) and the nature of the cellulose obtained (I, II, or III). Various extraction parameters, such as reaction time, amount of nitric acid added were studied in order to obtain fibers with high purity and avoiding their degradation. Chemical characterizations and some physico-chemical properties of the fibers isolated from Esparto are also presented and we will demonstrate their suitability for high value applications. The results obtained will be compared with those of the same family (extracted from the Esparto) using acidic and alkaline treatments respectively. We suggest that the introduction of such fibers in the market will create a new class of natural fibers and will find different application domains.

EXPERIMENTAL

Materials

The Esparto "*Stipa tenacissima*" used in this study was collected from the field of the Eastern Morocco region. It was dried in sun light and then cut in small pieces. The cut Esparto was crushed in a crusher type Herzog to prepare mesh size particles (500–900) μm. The resulted product was dried at 60°C during 16 h (or 5 h at 105°C) before use. Its composition (%,w/w) is: cellulose (42.7%), lignin (17.19%), ashes (7.72%), silica (2.7%), water (7.72%) and other constituents present about 23.84–25.84%.[5] Acetic acid (80%), nitric acid, sodium hydroxide, urea and lithium chloride (LiCl) were purchased from Aldrich and were employed without any further purification. The solvents: dimethylacetamid (DMAc), toluene (Tol.), tetrahydrofurane (THF), ethanol (ETOH), etc., are of analytical grade and were used as received from commercial suppliers. Moreover, all the chemicals used were of laboratory grade.

Methods

Determination of Dry Matters Content. We introduced 2 g of the crushed Esparto "*Stipa tenacissima*" into a bottle and we placed them at 105°C, then we follow the weight variation with the time. The constant weight was reached after 5 h of drying at 105°C or 16 h at 60°C. Then the container was covered by a lid (before leaving it in the drying oven), and then stored in a desiccator for 30 min. The content of dry matter X (%) was calculated using the eq. (1); where W and W' are respectively the weight of Esparto samples before and after drying.

$$X(\%) = \frac{W'}{W} \times 100 \quad (1)$$

This test was repeated three times to confirm the reproductivity. The value (91.8%) obtained represents the average of three tests, and the content of water is about 8%. Similar results were reported in the literature.[5]

Determination of the Extractable Content. Totally, 10 g of Esparto "*Stipa tenacissima*" were placed in a 250 mL of Pyrex glass flask and heated in distilled water at 100°C for 5 h, after cooling at room temperature, 60 mL of a mixture of solvents (THF/ETOH) (v/v; 1/1) was added to the flask. The mixture again was stirred at 60°C for 24 h. After vacuum filtration and washing three times with ethanol, the solid phase rich in cellulose was recovered. Three tests were carried out for each sample. The extractable products percentage X' contained in the sample was calculated using the eq. (2):

$$X'(\%) = \frac{W''}{W} \times 100 \quad (2)$$

where W and W'' represent respectively the weights of dried Esparto and the weight recovered after 24 h of stirring in the mixture (THF/Ethanol; 1/1) at 60°C. This experiment shows that Esparto enclosed 3% of extractable products and is used to remove contaminants from the raw materials.

Isolation of the Cellulose

In Acid Medium. Different treatments have been used to obtain cellulose enriched residues from Esparto fibers. The

various substrates had cellulose content 500 mg/g and were contaminated by residual lignin and heteroxylans. Esparto was purified using the method described below. When the extractable products were eliminated, 30 mL of glacial acetic acid (CH_3CO_2H, 80%) with various fractions in volume of nitric acid (HNO_3) used as catalyst were added to the remainder solid phase. This mixture was stirred during 2 h at 80°C. After cooling by addition of 20 mL of distilled water, the mixture was filtered under vacuum, washed again with distilled water until the filtrate was neutral in order to remove the soluble impurities, then at the last state with ethanol. The second solid phase rich in cellulose was isolated and heated at 105°C until constant weight was reached and dried over phosphorus pentoxide in a desiccators (sample noted AE).

In Alkaline Medium. After removal of extractable products using a solvent mixture (same protocol than extraction in acidic medium), the Esparto's remainder residue was introduced in a 250 mL Pyrex glass flask, then 30 mL of sodium hydroxide solution, at different concentrations in mol/L were added respectively. The mixture was stirred at 100°C for 2 h, then filtered and washed twice with a bleaching agent, then several times with distilled water and finally with ethanol. The resulted product was heated at 105°C until constant weight was reached and dried over phosphorus pentoxide in a desiccators (sample noted EB). The concentration, time and temperature of the chemical treatments can be chosen in order to not damage the cellulose fibers and to produce them with the desired quality.

Fiber Bleaching. Esparto fibers obtained from the chemical extraction were bleached using equal parts of acetate buffer, aqueous sodium hypochlorite (NaClO, 2.0 wt % in water) and distilled water at 80°C with about 7% (w/v) of fibers in the bleaching solution. The mixture was kept under stirring for 4 h and the operation was repeated four times. After bleaching, the fibers were washed and dried at ambient temperature. The natural yellow color of the fibers was eliminated by this treatment.

X-ray Diffraction. The crystallinity of the extracted samples (AE and EB) was investigated by X-ray diffraction (XRD), the analysis was performed with a *Panalytical X'Pert Pro MPD-Ray* Diffractometer, using Cu Kα radiation ($\lambda = 1.5418$ Å), voltage of 40 kV and operation current of 30 mA. All tests were performed in the range $2\theta = 5°–40°$, pitch 0.05°/s. The crystallinity index I_c was calculated from the formula (3)[26]:

$$I_c = 1 - \frac{I_{\min}}{I_{\max}} \quad (3)$$

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.

Optical Microscopy. Optical micro-photographs were taken using a spectrographic microscope *Leitz CY*, equipped with a camera and polarizer. The enlarging is of 500 times for all the photographs.

Intrinsic Viscosity. This part is devoted to determining the molecular weight of some previously extracted cellulosic samples. Viscosimetry is the most convenient and simplest method for determining the molecular weight. Intrinsic viscosity determination was carried out with an Ubbelohde viscometer at 25 ± 0.05°C in 6% NaOH/ 4% urea/90% H_2O and DMAc/9%LiCl solutions, respectively. Lithium chloride (LiCl) was dried at100–105°C overnight and then stored in a desiccator before use. Temperature maintenance was done by using a thermostat. The *Mark–Houwink* equation is used to calculate the molecular weight $[\eta] = k.M^a$, where k and a are constants for a particular polymer–solvent pair at a particular temperature. Cellulosic samples obtained as above were characterized in order to determine their DP and the results are reported in Table II.

***DMAc/ 9%LiCl Cellulose Solution.** Totally, 112 mg of cellulose was put into 20 mL of DMAc under stirring via a magnetic stirrer, the mixture was heated to 150°C for 30 min, then cooled to 100°C and LiCl of 9 w% DMAc was then added to the system. The resulted mixture was then kept at 50°C for about 15 h under stirring, and thus the cellulose in DMAc/ 9%LiCl solution was obtained.

*** 6 wt % NaOH/ 4 wt %% Urea/90 wt % H_2O Cellulose Solution.** Totally, 3 g of NaOH and 2 g of urea were dissolved in 45 g of distilled water, 1 g of cellulose was then added with stirring to get a slurry. In order to prepare a clear and homogeneous solution and avoid cellulose gel formation, a freeze-thaw cycle was employed in the cellulose dissolution. The cellulose slurry was held at the freezer for 24 h and then thawed with stirring in an ice-water bath to obtain a transparent solution.

Every prepared solution for cellulosic samples was diluted to five different concentrations and kept at 25°C for 15 min using a water bath before the intrinsic viscosity $[\eta]$ measurements.

Spectroscopic Measurements. The chemical structure of the cellulosic samples was evaluated by FTIR. The experiments were performed using a Shimadzu Fourier transform infrared spectrometer FTIR-8400S using a KBr disc containing 2% finely samples. Twenty scans were taken of each sample recorded from 4000 to 600 cm^{-1}.

Thermal Analysis. Thermal study of the cellulosic samples was performed using thermo-gravimetric analysis and differential thermal analysis DT-TGA 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. The fiber samples were oven dried at 100°C for 12 h.

Water Absorption Test. Water absorption studies were performed following the *ASTM D 570-98* method. Water absorption of the cellulosic fiber samples was determined after immersion in distilled water at different temperatures (30, 45, 60, and 75°C). The period of immersion varies between 1 and 9 day. The dried samples weighted with a precision of 0.0001 g were placed in distilled water. At the end of the immersion period, the samples were removed and their surfaces were dried by pressing with a tissue paper and then weighed. The error

involved in this test was about ±2%. The percentage of water absorption was calculated using eq. (4):

$$X'(\%) = \frac{W_w - W_0}{W_0} \times 100 \quad (4)$$

Where W_w and W_0 are respectively the weight of the sample after and before immersion period.

RESULTS AND DISCUSSION

Extraction in Acid Medium

The principle of the method used here was already described by Crampton and Maynard 1938, then by Brendel et al., 2000.[27] We plan in this study to improve the conditions of extraction on modifying the procedure steps in order to minimize the reagent's concentration and to determine exactly the optimal catalytic quantity of nitric acid (HNO_3) necessary for this operation. The obtained results after different treatments are reported on Figure 1.

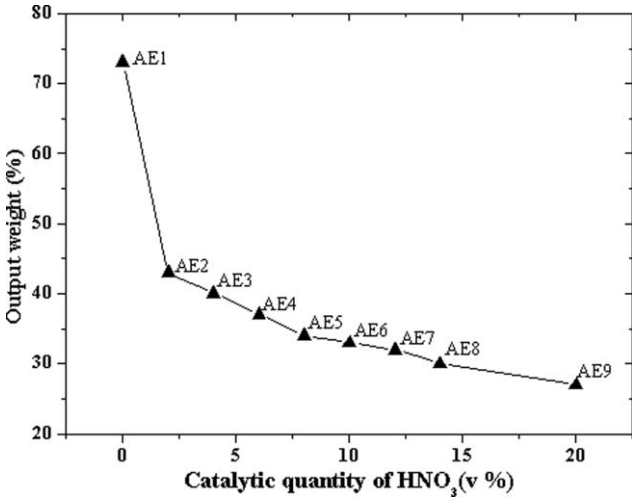

Figure 1. Variation of the weight output according to the catalytic quantity of HNO_3.

The progressive increase of the nitric acid concentration shows a brutal reduction in the weight output from 73% (AE1) to 43% (AE2). This last value (43%) is quite comparable to that of the cellulose contained in the Eastern Morocco's Esparto which is reported in the literature.[5] It's possible to consider that 2% in volume of nitric acid is an optimal catalytic value for the isolation of cellulose starting from the Esparto fibers. The slow variations of the mass output between the other tests (samples: AE3, AE4, AE5 … AE9) and the sample AE2 may be due to the degradation of the cellulose chains by oxidation and to the osidic bonds hydrolysis.

During the reaction, the nitric acid gives oxygen, dioxide nitrogen, and water according to the subsequent eq. (5):

$$2HNO_3 \rightarrow 2NO_2 + 1/2O_2 + H_2O \quad (5)$$

The oxidation of the lignin and the disruption of the osidic bonds by the acetic acid treatment become easy in the presence of the oxygen and increase with increasing the temperature.

The addition of HNO_3 as catalyst to the mixture removes the residue coagulations of the lignin and the hemicelluloses from cellulosic fibers (AE2). The Figure 2(a) shows the picture of a fiber obtained after this chemical treatment. On the Figure 2(b), the degradation of the cellulosic fibers was observed, when the nitric acid catalytic amount exceeds the optimal value (2%). The nitric acid excess, generally, leads to the nitrogen dioxide, water, and oxygen. This reaction is usually accompanied by more or less significant chain degradation, leading to a decrease in degree of polymerization (DP) of the polysaccharide.

On the Figure 3, are presented the FTIR spectra of the cellulosic samples extracted from Esparto in acid medium 80% using variable percentage of nitric acid [0% (AE1), 2% (AE2), 6% (AE4), and 20% (AE9)]. According to these spectra, the absorption bands characterizing the lignin (1600, 1510, and 1410 cm^{-1}) are presented only in the spectrum of the sample (AE1). This is due to the absence of the nitric acid in the mixture which oxidizes the lignin and leads to their dissolution. It is well clear that the complete dissolution of hemicelluloses is justified, in other spectra, by the absence of their characteristic absorption band around 1040 cm^{-1}.[28,29]

The large absorption band around 3420 cm^{-1} is characteristic of the elongation vibration of the hydroxyl groups. In the same way, the band at 2940 cm^{-1} is associated to the CH bonds elongation, and the absorption band at 1646 cm^{-1} corresponds to naturally absorbed water.[30,31] The spectrum shows also the absorbance bands around 1440 cm^{-1} and 1388 cm^{-1} characterizing respectively the deformation bands of CH and OH.[32] The bands around 1335 cm^{-1} and 1262 cm^{-1} are allotted to the vibrations of C—C and C—O characteristics of the cellulose skeleton.[33] The peak at 1169 cm^{-1} was attributed to the C—O antisymmetric vibration, while that at 1073 cm^{-1} was assigned to the C—O—C vibration of the pyran-cycle (X.F. Sun et al., 2004), whereas the band at 903 cm^{-1} is a characteristic of the β-glucidic bond.[34,35]

The extraction of the cellulose fibers using an acetic acid solution in the presence of the nitric acid as catalyst, can give place to acetylating reactions under controlled conditions of temperature and HNO_3 concentration.[36] The IR spectra of the resulting compounds reveal three characteristic absorption bands of acetylated ester; 1745 cm^{-1} ν (C=O), 1388 cm^{-1} ν (C—CH_3) and ν (C—O) to 1262 cm^{-1}. The IR spectrum of the commercial product shows some absorption bands at 3412, 2912, 1641, 1429, 1379, 1334, 1163, 1057, and 902 cm^{-1} and they are the same of thus observed in the case of the extracted cellulose witch indicating there similarity.

Extraction in Alkaline Medium

The Figure 4 shows that the degradation level of the Esparto's cellular wall in a sodium hydroxide solution with a concentration of 0.5*M* was 49%. However, the variation of the weight output with increasing the concentration from 0.5 to 1.5*M* was practically negligible.

The cellulosic fibers extracted in alkaline medium (Figure 5) are quite separated one from others and have a smooth and free

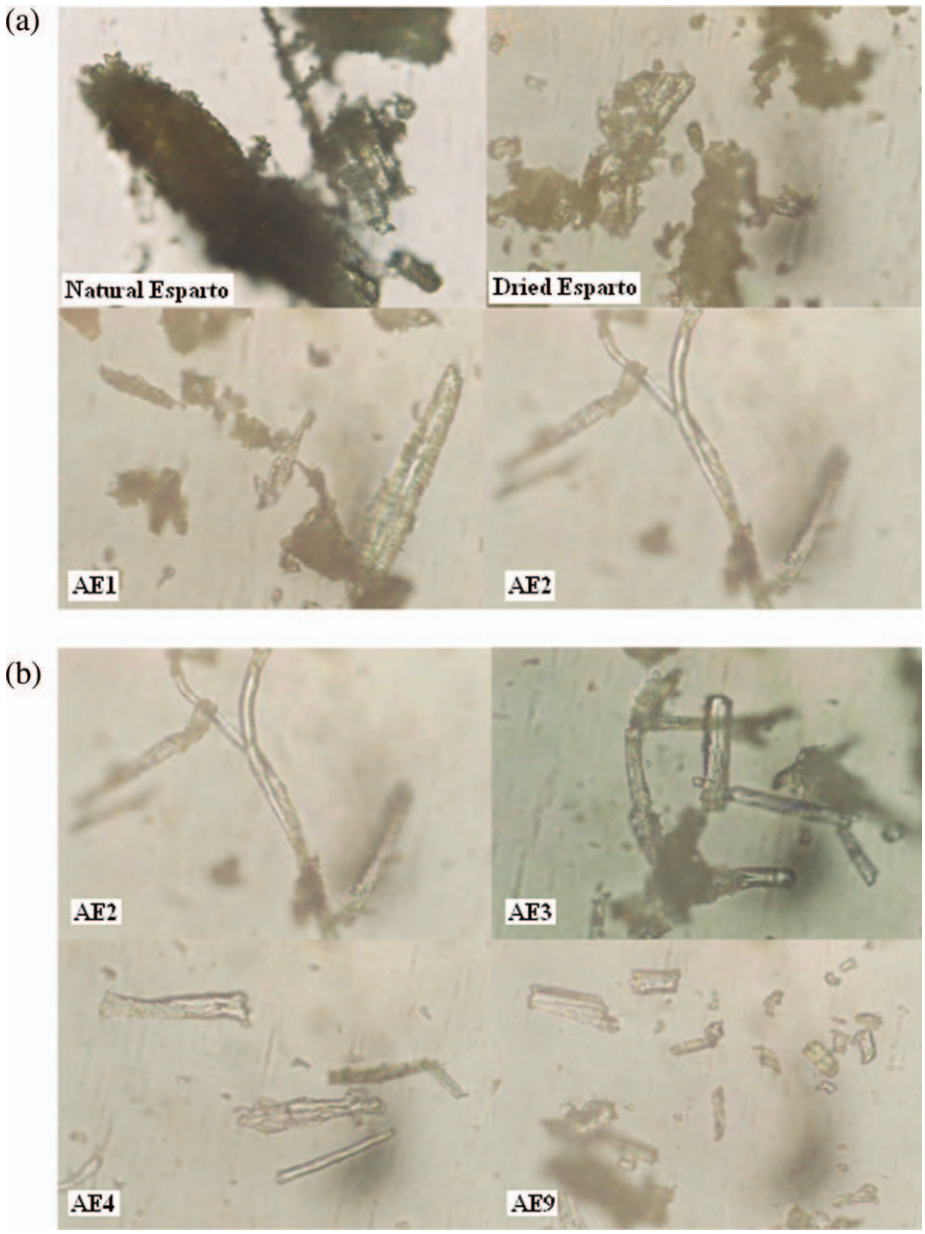

Figure 2. (a) Optical microscopic pictures of natural and dried Esparto, and cellulose fibers extracted in the acid medium without catalyst (AE1) and in presence of 2 v% of HNO_3 (AE2). (b) Optical microscopic pictures of cellulose fibers extracted in the acid medium and catalyzed by 2 v% of HNO_3 (AE2), 4 v% of HNO_3 (AE3), 6 v% of HNO_3 (AE4), and 20 v% of HNO_3 (AE9). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surface, indicating the total elimination of the lignin and the hemicelluloses derivatives without degrading the cellulosic chains. The chemical extraction of the non cellulosic polysaccharides leads to a cellulose enriched residue containing about 500 mg/g of cellulose extracted in alkaline medium.

All FTIR spectra on the Figure 6 indicate the absence of the absorption band around 1745 cm^{-1} characteristic of the acetate carbonyl. The band which appears at 1645 cm^{-1} is assigned to naturally water absorption.[36] The band at 1563 cm^{-1} corresponding to the residual lignin products (EB1) has been disappeared from the spectra of the cellulose extracted in the alkaline solutions 1.0*M* (EB2) and 1.5*M* (EB3). This disappearance confirms the complete elimination of the lignin, and the cellulose extracted is with high purity. All others absorption bands characterizing the cellulosic fibers are also present on the spectra of the samples EB2 and EB3. These results were compared with those of the commercial cellulose spectrum and are similar. Bleaching of Esparto fibers results in removal of their natural yellow color, therefore, more weak bindings in the Esparto fiber were removed during bleaching, resulting in a decrease in denier and an increase in strength. Moreover, if the bleaching conditions are well controlled, the damage to the fiber through oxidation could be minimized.[37]

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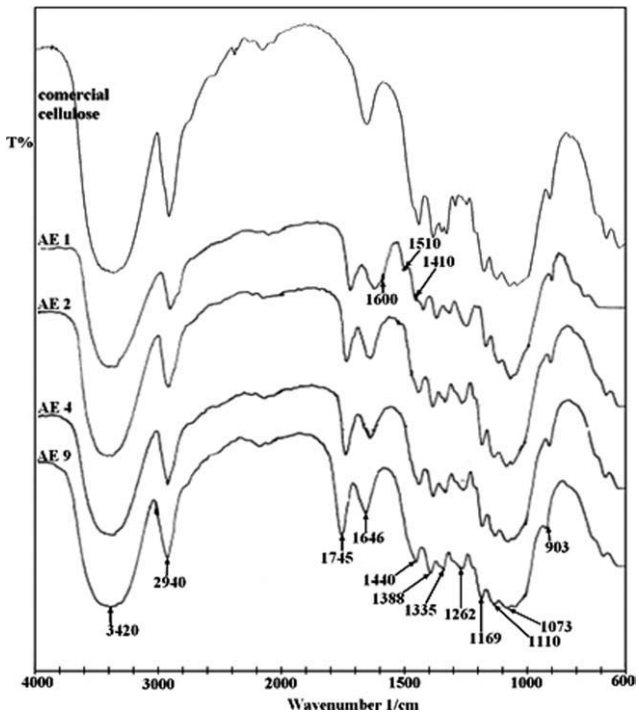

Figure 3. FTIR spectra of commercial cellulose and cellulose fiber samples extracted from Esparto "*Stipa tenacissima*" in acid medium in presence of nitric acid as catalyst [0% (AE1), 2% (AE2), 6% (AE4), and 20% (AE9)].

X-ray Diffraction. Cellulosic fibers are composed of microfibrils with 3–15 nm in thickness and 10–30 nm in width, containing semicrystalline bundles of finer, nanoscale threads termed fibrils having 2–6 nm in width.[38,39] These microfibrils are organized helically along the fiber axis and ultimately form annular layers within the fiber cross section.[40,41] X-ray diffraction studies have identified four types of cellulosic polymorphs (I, II, III, and IV) which can coexist simultaneously.[42,43] Native cellulose, such as cotton is termed Cellulose I, whereas modified cellulose such as rayon and mercerized cotton, is classified as Cellulose II. The transition from Cellulose I to Cellulose II (mercerization) is obtained by treating the cellulose with sodium hydroxide solution.[43] Generally, polymer chains are organized in an antiparallel configuration which allows for intersheet hydrogen bonding and a more stable morphology.[44–46] Other morphologies can be derived from Cellulose I depending on the type of swelling agents, temperature, and time of treatments.[45,46] Cellulose III is derived from Cellulose I using a finishing treatment in liquid ammonia.[44–46] Transformation from Cellulose III back to Cellulose I may occur upon

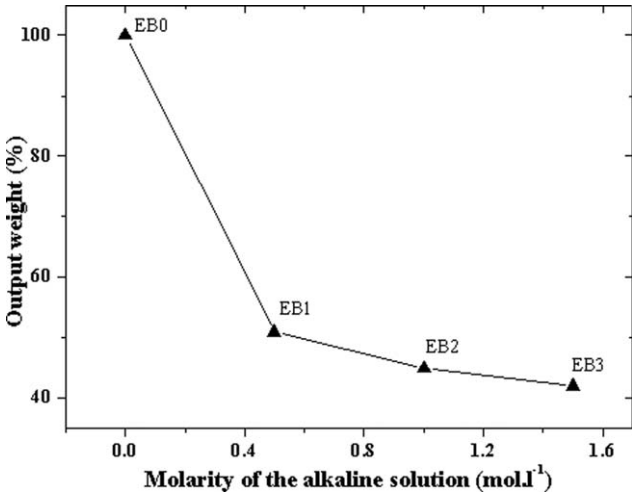

Figure 4. Variation of the output weight according to the concentration of the alkaline solution.

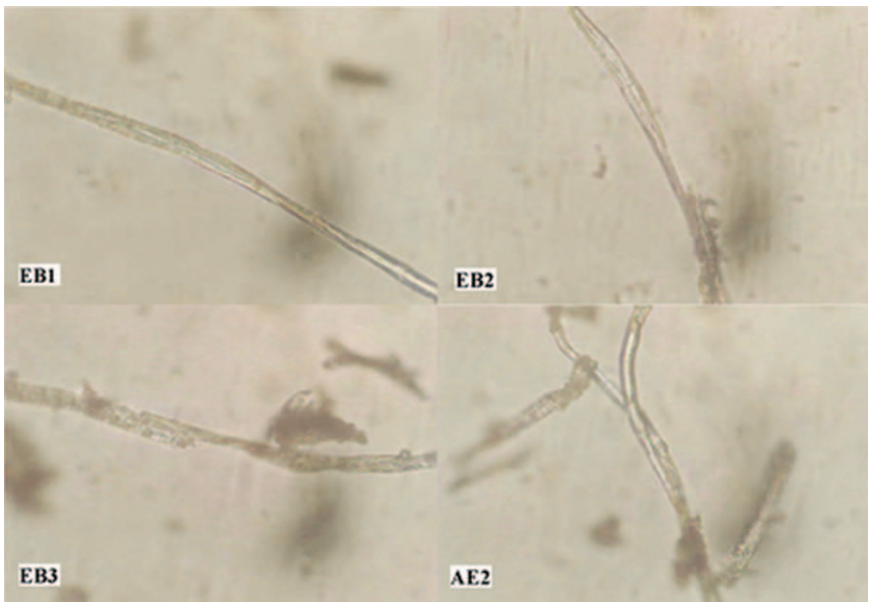

Figure 5. Optical microscopic pictures of cellulose fiber extracted in the acid medium catalyzed by 2% of HNO_3 (AE2) and in alkaline medium 0.5*M* (EB1), 1*M* (EB2), and 1.5*M* (EB3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

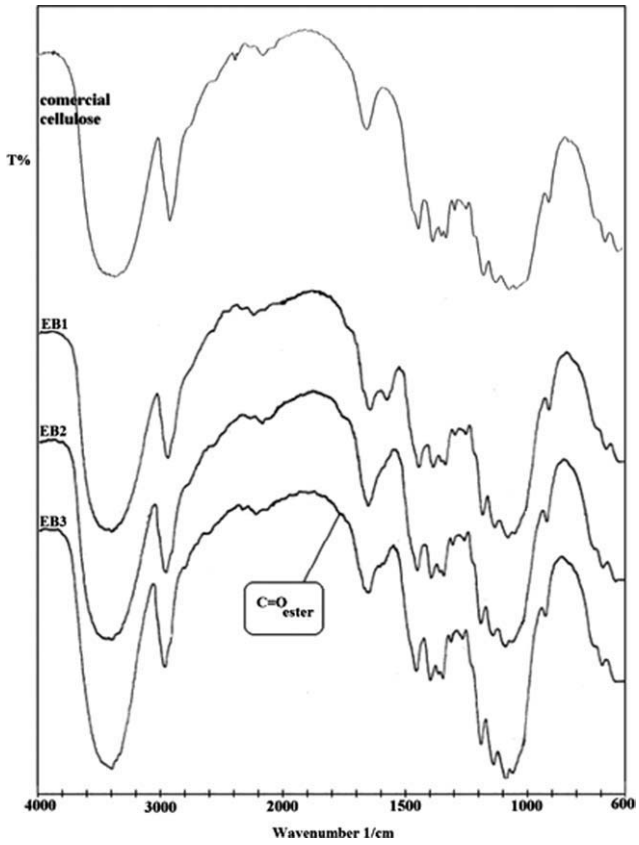

Figure 6. FTIR spectra of commercial cellulose and cellulose fiber extracted from esparto "*Stipa tenacissima*" in alkaline medium 0.5*M* (EB1), 1*M* (EB2), and 1.5*M* (EB3).

laundering or with an additional heat treatment. Treatment of the Cellulose I with ethylene diamine and subsequently boiling in formamide yields Cellulose IV. Hot glycerol is known to convert Cellulose II and III to Cellulose IV.

Figure 7, shows the X-ray diffraction patterns of the commercial cellulose, the samples AE2 [acid medium (HNO_3 = 2%)], AE9 [acid medium (HNO_3 = 20%)] and EB2 sample [alkaline medium (1.0*M*)]. The diffraction patterns of all the cellulosic samples (Figure 7) show only four peaks at 2θ = 15°, 16.3°, 22.6°, and 34.5° assigned respectively to the (101), (10–1) (002), and (040) hkl plans characterizing the Cellulose I polymorph.[49] The polymorphic transition of the Cellulose I was detected when the concentration of the sodium hydroxide solution is high more than 10%.[50] However, Cellulose II is not observed on X-ray diffraction patterns in the case of the sample EB2. The values of crystallinity index are calculated using the formula (3) and are regrouped in Table I.

Some osidic bonds in the amorphous regions of cellulosic fibers, on one hand, can be hydrolyzed in acid medium giving glucose unit soluble in liquid phase. This phenomenon enhances the crystallinity degree and explains the difference between the crystallinity index (Ic) in the case of EB2 (63.1%), EA9 (67.7%) and EA2 (69.6). The decrease in the crystallinity index may be caused also by the alkaline treatment; this experiment reduces the crystallinity of cellulose in the range 7–11%.[39,44] This type of compounds is of commercial importance due to the resulting improvement in strength, reagent uptake, and fiber luster.[39,43]

Intrinsic Viscosity and Molecular Weight. Generally, the physico-chemical and mechanical properties depend widely on the molecular weight of the macromolecule. Cellulose is a commercially important material, and the determination of its molecular mass (MM) parameters (average M_w, M_n, and I_p) as well as the chemical uniformity is necessary. The characterization of the cellulose extracted from Esparto will increase its utilization as an alternative to expensive products which are discouraged due to environment conservative regulations. Viscosity study is often used to characterize the interaction between two different polymers in a common solvent.[51,52] It is generally accepted that macromolecule conformation and molecular weight play a fundamental role, through their relationships with the molecular dimensions and shapes, in determining the value of intrinsic viscosity.[53] The η_{int} value can be considered as an indication of the dimension of the macromolecular chains in different solvents.

The viscosity-average DP of the cellulose is estimated from the intrinsic viscosity η_{int}. The experiments were realized in two different solutions at 25 ± 0.1°C using an Ubbelohde capillary viscometer. In the (DMAc/ 9%LiCl) solvent system, the equation giving η_{int} and DP_w is reported in the literature $\eta_{int} = 0.054 \times DP_w^{1.19}$.[54] The M_w value of the isolated cellulose samples is also measured using other solvent system (6% NaOH/4% urea/90% H_2O) applying the Mark-Houwink equation $\eta_{int} = 2.45 \times 10^{-2} M_w^{0.815}$.[55] The intrinsic viscosity was derived in each case from the inherent and the reduce viscosity at zero concentration as shown in the Figure 8(a–d). The results obtained are regrouped in the Table II.

It's well known that the cellulose solubility depend scarcely on its degree of polymerization DP. This phenomenon was justified on testing the cellulose solubility in the chosen solvent systems (DMAc/9% LiCl) and (6% NaOH/4% urea/90% H_2O). The sample EB2 extracted in alkaline medium was found to be soluble in the (DMAc/9% LiCl) system to form a genuine dilute solution without suffering obvious degradation under adequate conditions, but in the case of solvent system (6% NaOH/4% urea/90% H_2O), we have observed only a swilling phenomenon. The commercial cellulose chosen such as control sample was soluble in the (6% NaOH/4% urea/90% H_2O) system, subsequently a better solubility is shown in the other solvent system (DMAc/9%LiCl). In the case of the sample EB2, both different values of M_w (227166; 48068) are obtained in the both solvent systems (DMAc/9% LiCl) and (6% NaOH/4% urea/90% H_2O), respectively. This result can be interpreted taking into account the solubility behavior in the solvent systems used. The sample (EB2) has showed a perfect solubility in (DMAc/9% LiCl), but only a moderate solubility in the second system (6% NaOH/4% urea/90% H_2O). The solubility of the cellulose fraction with high DP is hard and needs a suitable solvent system, this fraction was eliminated by filtration during the preparation of the viscosity solution, because it was not soluble in (6% NaOH/4% urea/90% H_2O) system. The cellulosic solution in this last solvent system

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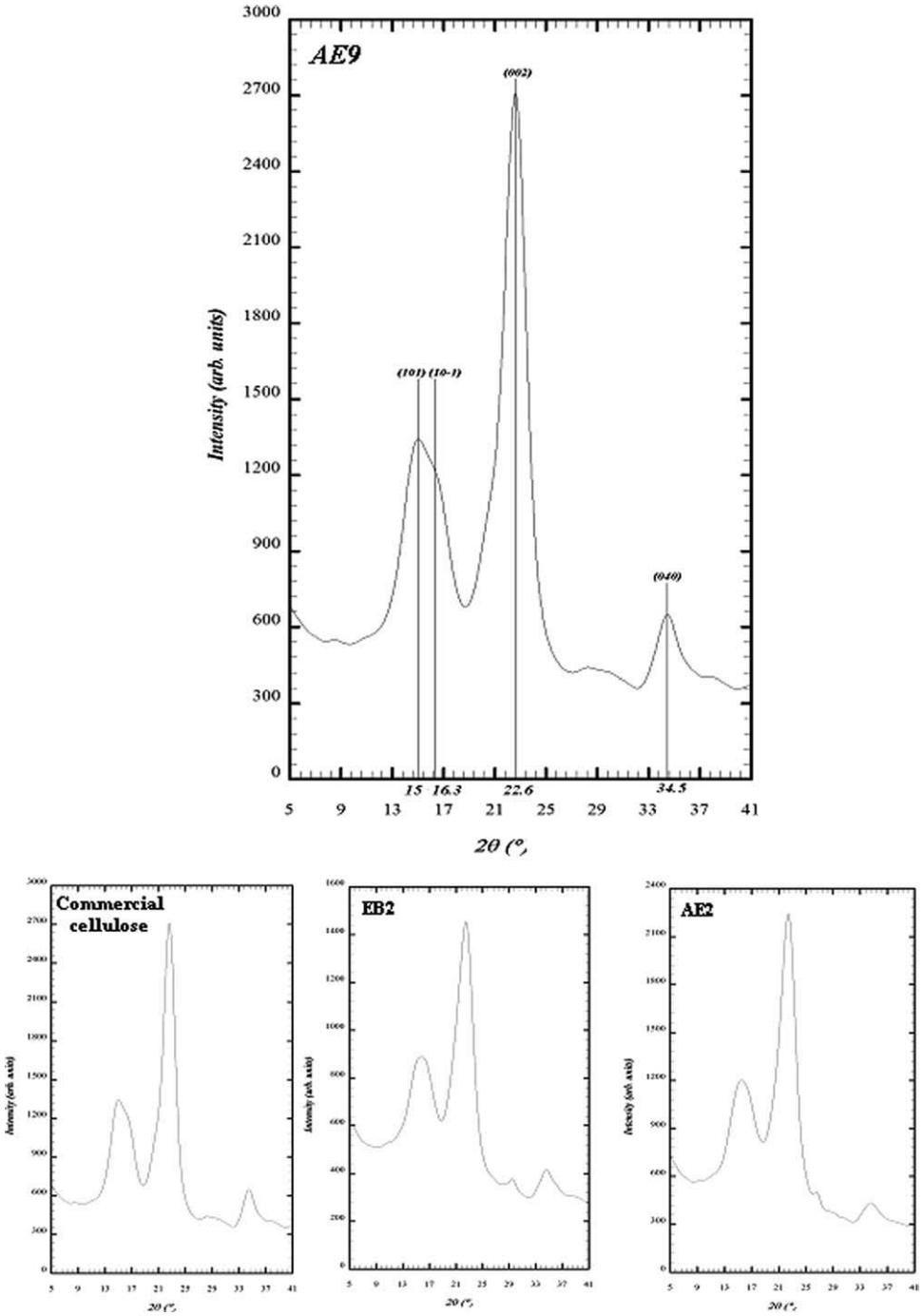

Figure 7. X-ray diffraction pattern of the commercial cellulose, AE2, AE9, and EB2.

contains only the fraction with a small DP, because they are easier soluble in this system in contrast to the fraction with high DP. However, the sample EB2 is totally soluble in the adequate solvent system (DMAc/9% LiCl) and the fraction with high DP is not eliminated by filtration. We suggest that no degradation takes place under these conditions. The stronger the interaction between cellulose and solvent molecules the bigger dimension of the chains. At last, we conclude that the cellulose extracted from Esparto is characterized by its higher

Table I. The Crystallinity Percent of Commercial Cellulose, EA2, EA9, and EB2

Sampl.	% Ic
Commercial cellulose	78,8
EA2	69,6
EA9	67,7
EB2	63,1

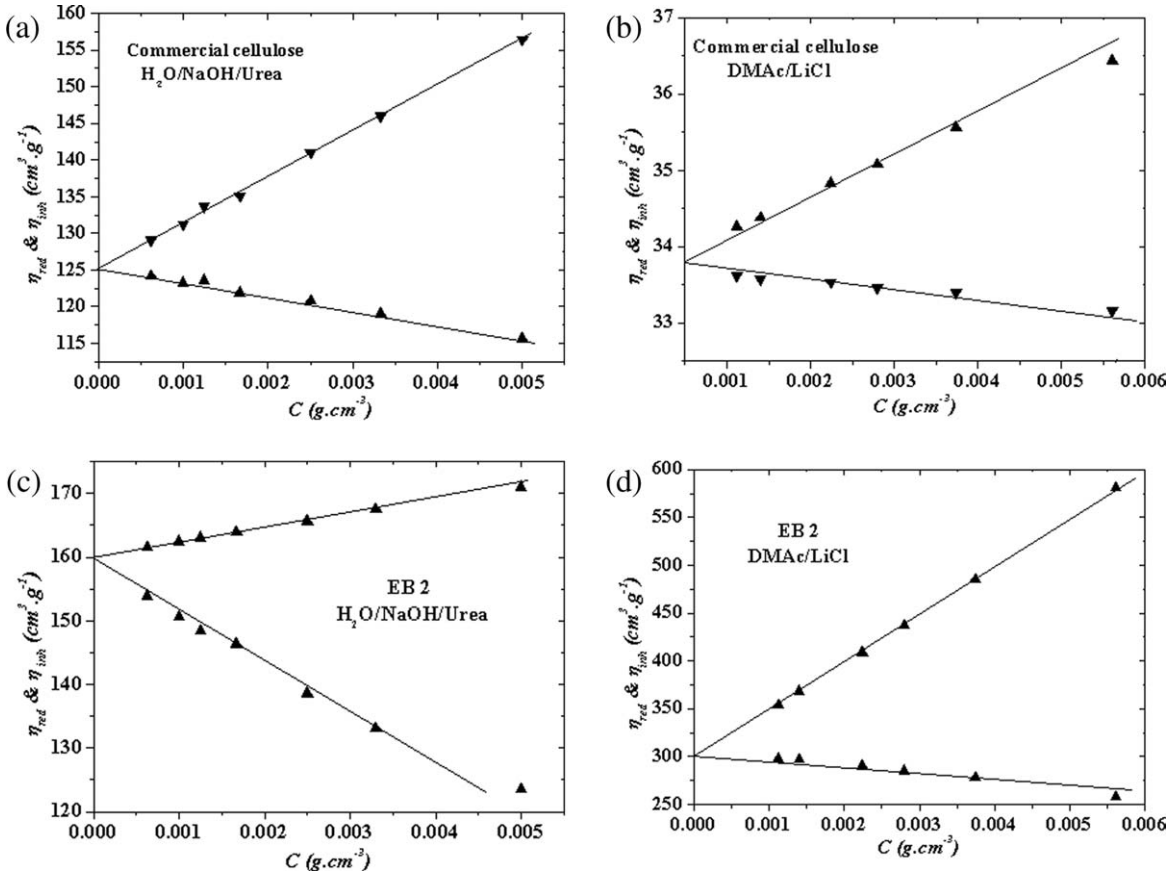

Figure 8. (a) Inherent and reduce viscosity of cellulose commercial in the solvent system (6% NaOH/4% urea/90% H_2O). (b) Inherent and reduce viscosity of cellulose commercial in the solvent system (DMAc/9%LiCl). (c) Inherent and reduce viscosity of EB2 in the solvent system (6% NaOH/4% Urea/90% H_2O. (d) Inherent and reduce viscosity of EB2 in the solvent system (DMAc/9%LiCl).

macromolecular weight ($M_w \sim$ 227,166) and can be used in many applications. The higher the macromolecular weight the better properties. The (DMAc/9% LiCl) can be chosen as solvent system for this type of cellulose in order to study its properties and correct results will be obtained. The commercial sample (cell.com.) viscosity study was undertaken in (DMAc/9% LiCl) solvent system under the same conditions and the perfect solubility was observed. The value of M_w obtained ($M_w \sim$ 36,268.89) is practically the same of that calculated in 6% NaOH/4% urea/90% H_2O system, and it was very small than these calculated in the case of EB2 sample ($M_w \sim$ 227,166), this difference may be explain by the dissimilarity of the source of each sample.

Thermal Analyses

The thermogram curves (TG/DTA) of the extracted cellulosic samples A E and EB in acid and alkaline medium respectively are shown in Figure 9(a–c). The thermogram of the acid medium extraction samples (AE1, AE3, AE7, and AE9) presented in Figure 9(a) shows only one event in the decomposition process covering the interval of temperature from 274 to 370°C corresponding to a mass loss of ~90%. Initial decomposition (T_d) takes place at 274°C for AE1; 313°C for AE3; 307°C for AE7 and 293 °C for AE9. The degradation of the cellulosic chains increases with increasing the amount of catalyst (nitric acid). The thermal study confirms this result and revels that the thermal stability of the cellulosic samples (EA1… EA9)

Table II. M_w and DP_w of Commercial Cellulose and EB2

Sampl.	Solvent system	η_{int} ($cm^3\ g^{-1}$)	DP_w	M_w
Commercial cellulose	DMAc/9%LiCl	33.8	223.882	36,268.89
Commercial cellulose	6%NaOH/4%Urea/90%H_2O	125.36	220	35,555.89
EB 2	6%NaOH/4%Urea/90%H_2O	160.28	296.72	48,068.08
EB 2	DMAc/9%LiCl	300	1,402.26	227,166.12

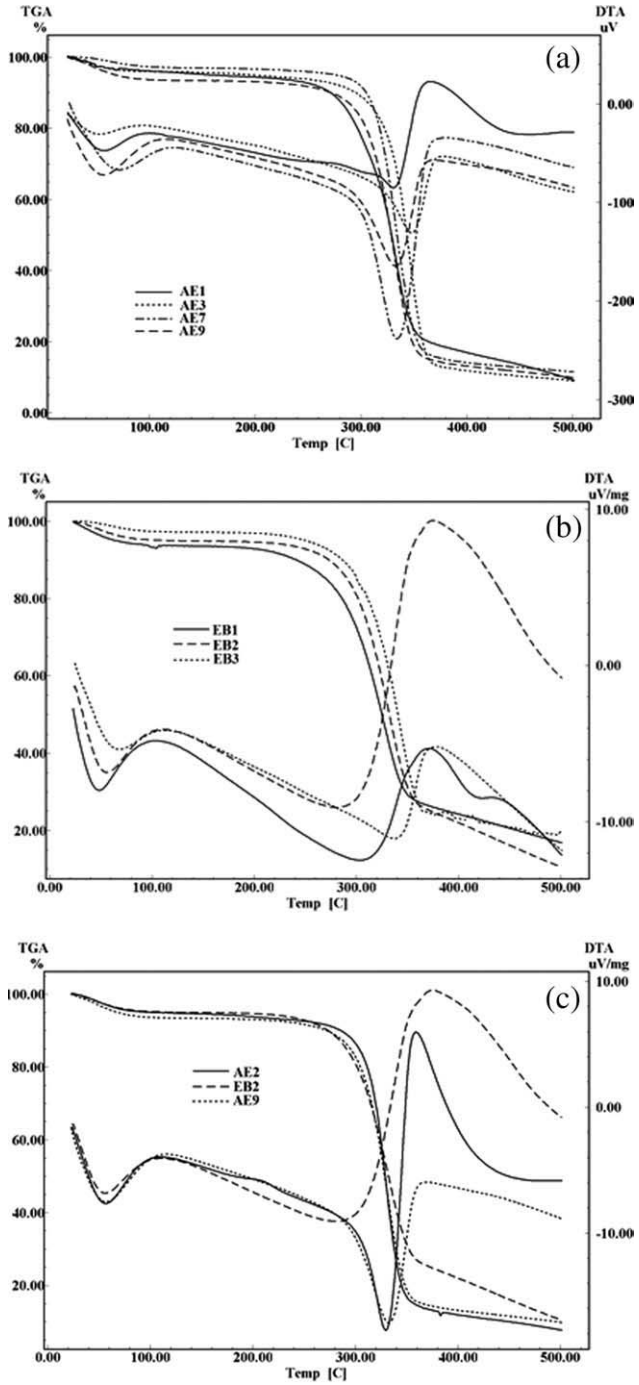

Figure 9. (a) Thermograms of cellulose samples extracted in acid medium; AE1, AE3, AE7, and AE9. (b) Thermograms of cellulose samples extracted in alkaline medium; EB1, EB2, and EB3. (c) Thermograms of cellulose samples; EA2, EA9, and EB2.

decreases with increases in the catalytic amount. At 50% weight loss the decomposition temperature raises from 328°C for AE1 to 342°C in the case of EA3, this diminution due to the elimination residual contaminants (hemicelluloses and lignin).

The glass transition temperature is not observed for all the cellulosic samples. It is well known that T_g detection for cellulose is very difficult and only with particular scan conditions it is possible to determine it with DSC.[56] This result confirms the high degree of crystallinity in this type of cellulose. By comparing the raw materials, an endothermic peak corresponding to the water vaporization appears about 60–100°C. In oxidized cellulose, the water content increases with decreasing the degree of crystallinity, this fact is explained by considering that, the oxidation being a degradative reaction, enhances the amorphous content in the cellulose.

For alkaline extraction [Figure 9(b)], we have not observed the same behavior as in the case of the extraction in acid medium. The decomposition temperature (T_d) starts at 280°C for EB1 and increases to reach 291°C for EB2. This last sample shows a moderate gain in thermal stability resulting from the elimination of residues of lignin and hemicelluloses. We have also observed a slight difference between T_d of EB2 and T_d of EB3 (293°C), and we can take the value of 292°C as the T_d of this pure cellulose extracted from Eastern Morocco's Esparto. Similarly, the decomposition temperature at 50% weight loss increases and takes place at 324°C for EB1, 332°C for EB2 and 340°C for EB3.

On the thermogram 10c, a small difference between EB2 and EA2 decomposition temperature is noted and may be due to the presence of acetyl groups grafted on the EA2 sample cellulosic chains and to the difference in index crystallinity contained in EB2 and EA2 samples respectively. The differential thermal analysis have illustrated three major areas, an initial shoulder peak appears between 254 and 295°C particularly for EA1, and is due to a mass loss (~10%) of the residual hemicelluloses. The major second decomposition peak is related to the thermal depolymerization of cellulose at about 295–346°C. The third stage of weight loss ranging from 346 to 500°C is attributed to the further degradation of cellulose and inorganic compounds. At 500°C, the cellulosic samples had a residual weight of about 7.5–15%. In an inert atmosphere, the cellulosic end products are carbonaceous residues.[57]

Water Absorption Test

Many polymers are susceptible to degradation due to the effect of water, particularly under favorable conditions. Factors that influence the susceptibility of a given polymer to hydrolysis include water permeability and solubility which in turn are influenced by the chemical structure of polymer and its physical state. The water absorption test is quite often used to indicate the tendency of polymers to undergo hydrolytic degradation.[58,59] The polymers can absorb water, swell, undergo hydrolysis and subsequently will deteriorate in the environment. Higher tendency to absorb water may indicate higher hydrolytic degradation behavior.

The most serious handicap to the use of cellulosic fibers in several utilizations is their extreme sensitivity to water, which reduces their mechanical properties in a damp atmosphere. The evolution of water absorption as a function of the immersion time and as a functional of temperature is shown in Figure 10(a,b), respectively. In the present investigation it is observed that the cellulosic fibers have considerable capacity of water absorption. The water absorption increased with the immersion time and the immersion temperature and reached the

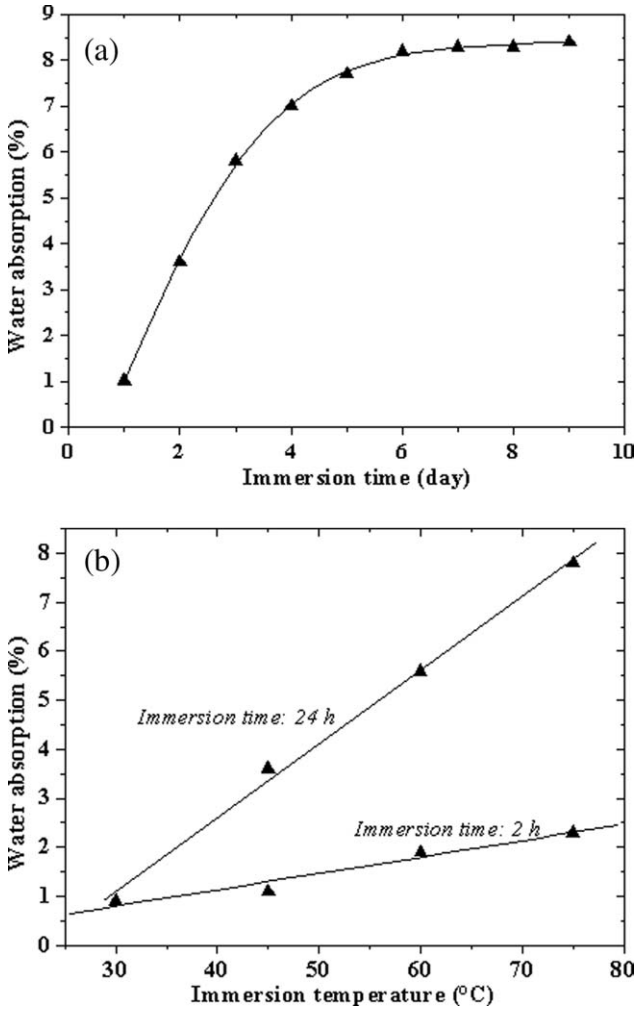

Figure 10. (a) The evolution of water absorption as a function of the immersion time. (b) The evolution of water absorption as a function of the immersion temperature.

equilibrium value after 6 days at a temperature of 25°C, while this value is reached in 24 h for temperature equal to 75°C. Water molecules interact directly with the hydrophilic groups of cellulose chains and penetrate in the pores of fibers only in the amorphous region; a low moisture regain value in the sample means a high crystallinity degree of the material.[60] Thus, the equilibrium water uptake depended on the treatment process and the resulted fibers absorbed about 8.3% of the water. However, The Esparto's cellulosic fibers can be modified in order to enhance their hydrophobicity and the range of their applications became wider.

CONCLUSIONS

For the first time, we have obtained natural cellulosic fibers from Esparto plant with structure and performance properties that would make them appropriate for various high quality fibrous applications. Fibers here refer to a bundle of individual cells held together by hemicelluloses, lignin, and other noncellulosic substances. In addition, the process of fibers extraction from this plant requires relatively lesser energy and is also environmentally friendly. We have proved that the extraction using an acetic acid solution was very successful by adding 2% in volume of nitric acid (HNO_3), furthermore the use of an alkaline solution (NaOH, 1*M*) is preferable because it gives cellulosic fibers with high purity also, the absence of acetylating reactions and the non degradation of the resulted fibers are noted. However, as mentioned earlier, the quality and the yield of fibers are dependent on the treatment conditions such as alkaline and acid concentrations, time and temperature. The chemical treatment under conditions specified above produces high quality fibers with the required fineness, length, etc., without hydrolyzing the fibers into individual cells. The resulted cellulosic fibers were characterized by different techniques in order to examine the chemical composition and the structure of the fibers in comparison to other natural cellulosic fibers and can be useful in evaluating the utility of the Esparto's fibers. Therefore, this plant shows greater promise in providing large quantities of natural cellulosic fibers with significant economic benefits than any other agricultural plants. However, these benefits cannot be realized unless these fibers are suitable for industrial applications, especially for biodegradable goods. We believe we have finally found such a fiber source in Esparto.

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