# Synthesis and Characterization of the New Cellulose Derivative Films Based on the Hydroxyethyl Cellulose Prepared from ''Stipa Tenacissima'' Cellulose of Eastern Morocco. I. Solubility Study

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

[1]Laboratory of Applied Chemistry and Environment, Faculty of Sciences (Med I University), 60000 Oujda, Morocco
[2]Laboratory of Physical Chemistry of Natural Resources and Environment, National School of Applied Sciences, (Med I University), BP: 3, 32 003 Al Hoceima (Ajdir), Morocco
[3]Faculty of Sciences, Chemistry departement Rabat, Morocco

**ABSTRACT:** Hydroxyethyl cellulose Acetate (HECA) was prepared starting from hydroxyethyl cellulose (HEC), acetic anhydride and perchloric acid which was used as catalyst. The synthesized product was characterized by FTIR, ^{13}C NMR, and ^{1}H NMR. Substitution degree (DS) of HECA was determined using FTIR spectra taking a classical titration method as reference. The ^{1}H NMR spectroscopy was also used to confirm the results obtained by FTIR. The DS is substantially affected by the temperature, the time of reaction and especially the equivalent number (eq. nb.) of the acetic anhydride added. We have studied and discussed in the context of usage in modification reactions, the solubility of the HECA samples by varying their DS. This investigation was based on the determination of the Flory-Huggins interaction parameters ($\chi_{SP}$) using the partial Hansen solubility parameters (HSP). HSP of HEC and the HECA samples were calculated from the Van-Krevlen-Hoftyze (VKH) method and the T. Lindvig approximation. We have focused our work on predicting and controlling family solvents of HECA with various DS, to facilitate and to optimize the homogenous modification reaction conditions. From results on a range of HECA samples, it is conclude that their prediction solubility taking the value of DS into account is possible, and then the surface modification can relatively be easily realized. The thermal analysis study shows some differences in $T_g$ and thermal degradation between HEC and HECA, moreover these thermal temperatures are influenced by DS values. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2952–2965, 2011

**Key words:** synthesis; films; acetylating; substitution degree; solubility

## INTRODUCTION

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

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

A number of cellulose derivatives are currently prepared under heterogeneous conditions. Cellulose esters are generally synthesized employing an anhydride with a catalyst or an acid chloride in the presence of a tertiary base.[18] However, problems arise

such as poor uniformly of substitution; low yields and extensive by product formation, consequently there is much interest in developing new acetylating methods to provide products with novel characteristics.[19] For a maximum conversion of cellulose to its derivatives, it is advisable to carry out the reaction in a homogeneous medium, requiring a suitable solvent system.[20–22] The search for new systems and process is important on environmental grounds, because problems tend to be focused around optimization and ecological issues.

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

In this work, we describe the synthesis of a new cellulose derivative compound (HECA) soluble in most organic solvents such as THF, starting from Hydroxyethyl cellulose (HEC) prepared from "Stipa Tenacissima" cellulose of Eastern Morocco and acetic anhydride.[27] The resulted product (HECA) will combine, at the same time, the properties of the both most successful industrial biopolymers: Cellulose acetate (CA) and hydroxyethyl cellulose (HEC).

We studied also the effect of the temperature (T), the time of reaction (t), and equivalent numbers (eq. nb.) of acetic anhydride added on DS variations. It is known that the dissolution mechanisms of cellulose derivatives fibers are strongly dependent on the solvent quality and biopolymer structure respectively. The aim of this study was to better understand the dissolution mechanisms of HECA fibers in organic solvent systems and to better identify the influence of different DS values on dissolution capacities. The Hansen Solubility Parameters (HSP) determined by indirect measurements using the Van-Krevelen-Hoftyzer (VKH) method and the T. Lindvig approximation,[28] have been employed to develop a method capable of predicting and controlling dissolution of cellulose derivatives (HEC; HECA) in different solvent conditions, taking into account DS values. Solubility can be improved greatly, and then the fabrication of functionalized material can relatively be easily carried out.

## Theoretical background

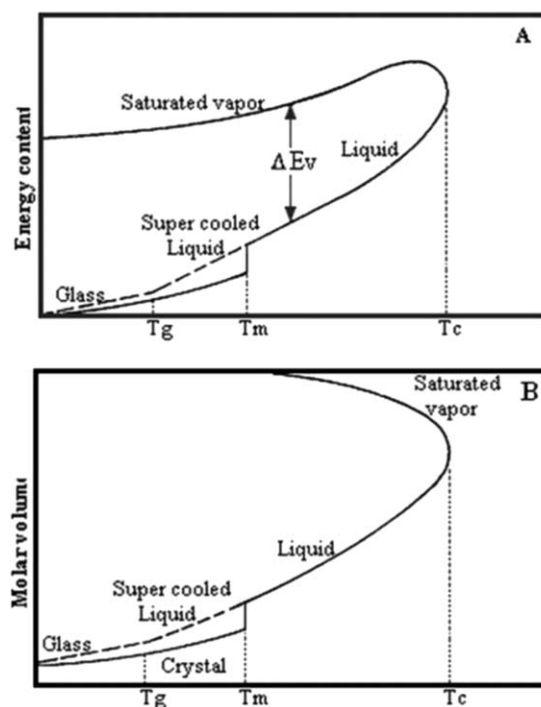An appreciation of the meaning of the solubility parameter in physical terms can be obtained from



**Figure 1** Dependence of energy content (A) and molar volume (B) on temperature.[45]

a study of Figure 1. Parts A and B, in a schematic fashion, the basic assumption in the solubility parameter concept is that there is a correlation between the cohesive energy density (CED) (potential energy per unit volume) and mutual solubility. The CED is the energy of vaporization ($\Delta E_i^v$) per cm³. The solubility parameter has been defined as the square root of the CED and describes the attractive strength between molecules of the material.[29]

$$\delta_i = \left(\frac{\Delta E_i^V}{V_i}\right)^{1/2} = (CED)^{1/2} \qquad (1)$$

The Hildebrand parameter defined by eq. (1) has proved useful for regular solutions i.e., solutions without molecular polarity or specific interactions, and good estimates of excess Gibbs energy (and consequently activity coefficients, etc.) It is still used for various purposes in nonregular solutions, but to some extent has been superseded by multicomponent solubility parameters.[30–33]

According to the Hansen solubility parameter theory,[34] the energy of vaporization can be divided into contributions of nonpolar (dispersion) forces (d), polar forces (p), and hydrogen-bonding (h) eq. (2):

$$\Delta E_V = \Delta E_{coh} = \Delta E_d + \Delta E_p + \Delta E_h \qquad (2)$$

The Hildebrand solubility parameter can be expressed in terms of the three Hansen solubility parameters related to each contribution[35]:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{3}$$

The corresponding equation for the mixing enthalpy can be calculated by

$$\Delta H_m = \varnothing_S \varnothing_P (\delta_S - \delta_P)^2 \tag{4}$$

where $\Delta H_m$ is enthalpy of mixing per unit volume, $\delta_S$ and $\delta_P$ are solubility parameters of solvent and polymer respectively.[36] Equation (4) predicts that $\Delta H_m = 0$ if $\delta_S = \delta_P$, so that two substances with equal solubility parameters should be mutually soluble due to the negative entropy factor (eq. 5), this is in accordance with the general rule that chemical and structural similarity favors solubility. As the difference between $\delta_S$ and $\delta_P$ increases, the tendency towards dissolution decreases.[36]

$$\Delta G = \Delta H - T\Delta S \tag{5}$$

By using eqs. (3) and (4) $\Delta H_m$ becomes:

$$\Delta H = \varnothing_S \varnothing_P \left[ (\delta_{dS} - \delta_{dP})^2 + (\delta_{pS} - \delta_{pP})^2 + (\delta_{hS} - \delta_{hP})^2 \right] \tag{6}$$

A solvent, therefore, with given values of $\delta_{p,S}$, $\delta_{d,S}$, and $\delta_{h,S}$ is represented as a point in space, and $\delta_t$ is the vector from the origin to this point. Furthermore, it has been found on a purely empirical basis that if $\delta_{dP}$ is plotted on a scale twice the size as that used for $\delta_{pP}$ and $\delta_{hP}$, then all solvents that dissolve the polymer fall within a sphere of radius R surrounding the point ($\delta_{p,P}$, $\delta_{d,P}$, and $\delta_{h,P}$).[37] The Hansen theory may, therefore, be considered a graphical quantification of the old "like dissolves like" concept of solubility (Fig. 2).

Skaarup and Hansen[38,39] have developed an equation for the solubility parameter "distance," $D_{SP}$, between two materials (solvent–polymer) based on their respective partial solubility parameter components.

$$D_{SP} = \left[ 4(\delta_{dS} - \delta_{dP})^2 + (\delta_{pS} - \delta_{pP})^2 + (\delta_{hS} - \delta_{hP})^2 \right]^{1/2} \tag{7}$$

A region of solubility has been characterized by the distance between solvent and polymer coordinates.[40,41] Each polymer, $P$, was characterized by a set of Hansen parameters defining the center of the solubility sphere and an interaction radius $^PR$
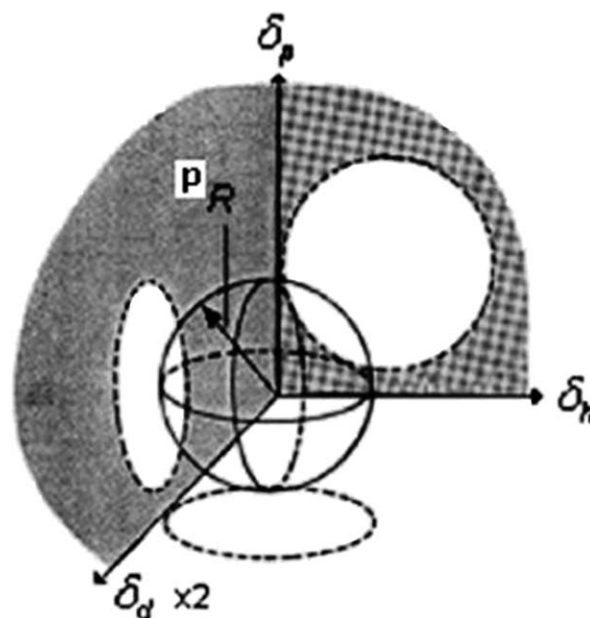
**Figure 2** Representation of a Hansen parameter solubility sphere and its projections on three axial planes (adopted from Beerbower and Dickey, http://www.dbe.dupont.com).

(Fig. 2). To predict the solubility, the distance $D_{SP}$ between the position ($\delta_{dS}$, $\delta_{pS}$, $\delta_{hS}$) and the center of the sphere of solubility ($\delta_{dP}$, $\delta_{pP}$, $\delta_{hP}$) must be less than the interaction radius $^PR$.

If the distance between the solvent and the polymer position exceeds $^PR$, the two components are not soluble, or swelling is less than expected.

The doubling of the $\delta_d$ scale, leading to the factor '4' in the first term, was intended to make the "volume of solubility" approximately spherical.[42] This factor is theoretically predicted by Prigogine[43] when the geometric mean is used to estimate the interaction in mixtures of dissimilar molecules.

## Methods for determination of solubility parameters

Hildebrand parameters cannot be calculated directly for polymers from heat of vaporization data because of their no volatility. However, it is calculated using the indirect correlation or atomic contribution group method.

### Indirect methods

The determination techniques for polymer solubility parameters have been widely described in literature, solvency testing (screening procedure),[44] osmotic pressure,[45] swelling values [44,46,47] turbidimetric titration,[48,49] specific volume,[50] intrinsic viscosity[51–53] inverse gas chromatography[54,55] and Matrix Assisted Laser Desorption Ionization, MALDI.[56]

## Correlation methods

Some of the techniques based on the correlation methods are dipole moment,[57] refractive index,[57,58] H-bonding parameter,[59] surface tension,[60] dielectric constant,[61] Flory-Huggins interaction parameter.[62] The simplest technique for the determination of polymers solubility parameters is the group contribution method, based on the assumption of different functional groups contribution.[63]

## Atomic group contribution methods

The previous methods have been used to estimate the solubility parameter.[45,64–68] VKH,[69] Fedors,[45] and Barton[70] have reviewed these methods and tables of group values had been given. The molar volume of solvents and polymers can also be estimated by group contribution techniques.

## Van Krevelen and Hoftyzer method

To determine the total polymers solubility parameters, using these calculations, VKH used the molar volumes and molar attraction constants of the repeating unit so as to calculate the partial solubility parameter of the polymer. The solubility parameter components may be predicted from group contributions, using the following equations (VKH)[36,71–73]

$$\delta_d = \frac{\sum F_{di}}{\sum V_i} \tag{8}$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{\sum V_i} \tag{9}$$

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{\sum V_i}} \tag{10}$$

The dispersive Hansen parameter treats the molar attraction constants as additive. The polar Hansen parameters also are additive, unless more than one polar group is present. The molar attraction constant is not applied to the H-bonding Hansen parameter. Rather, an H-bonding energy, $E_{hi}$, is used.[40]

## Calculation of the Flory parameter

According to the regular solution theory, the relationship between the Flory-Huggins interaction parameter and the solubility parameters is[74]:

$$\chi_{SP} = \frac{V_S}{RT}(\delta_S - \delta_P)^2 \tag{11}$$

Peppas et al.[75] have calculated Flory interaction parameters on the basis of the following procedure[52]

using the corresponding solubility parameters of two components. In general, the interaction parameters, $\chi$ is defined as

$$\chi_{SP} = \frac{zX_S\Delta w_{SP}}{kT} = \chi_H + \chi_S \tag{12}$$

where $z$ is the lattice coordination number, $X$ is the number of polymer segments relative to solvent, $\Delta w$ is the interaction energy. The term $\chi_S$ is the entropic contribution of $\sim 0.34$. The term $\chi_H$ is the enthalpy contribution and can be calculated from solubility parameters as shown by Mikos et al.[76]:

$$\chi_H = \frac{V_S}{RT}[(\delta_S - \delta_P)^2 + 2I_{SP}\delta_S\delta_P] \tag{13}$$

In which $I_{SP}$ and Vs are a binary interaction parameter and molar volume of solvent respectively. For the system consisting of two components with a similar chemical structure, $I_{SP} = 0$. The following equation is obtained:

$$\chi_{SP} = 0.34 + \frac{V_S}{RT}(\delta_S - \delta_P)^2 \tag{14}$$

For the estimation of Flory-Huggins interaction parameters Hansen[77] has used the following equation with $\alpha = 1$:

$$\chi_{SP} = \alpha\frac{V_S}{RT}\left[(\delta_{dS} - \delta_{dP})^2 + 0.25(\delta_{pS} - \delta_{pP})^2 \right.$$
$$\left. + 0.25(\delta_{hS} - \delta_{hP})^2\right] \tag{15}$$

Lindvig et al.[28] have estimated Flory-Huggins interaction parameters from the Hansen parameters with an optimum value of the correction constant $\alpha = 0.6$. As mentioned, the correction constant was different for different species pairs. According to the Flory-Huggins model a polymer and solvent are completely miscible if $\chi_{SP} \langle 0.5 \left(1 + \left(\frac{VmS}{VmP}\right)^{\frac{1}{2}}\right)^2$. In this work the relationships used for calculate the Flory-Huggins interaction parameter is the Lindvig correction, because it was optimized according to the structure of polymer synthesized; HECA (polar, H-bonding…).

## EXPERIMENTAL AND METHODS

### Material

Hydroxyethyl cellulose (HEC DS = 1.5) was prepared in NaOH/Urea aqueous solution[23] starting from cellulose extracted in basic medium as mentioned by A. El Idrissi et al.[27] using "Stipa Tenacissima" of Eastern Morocco. Acetic anhydride and perchloric acid were purchased from Aldrich

Chemical Company. All other chemicals were of analytical grade and are used without further purification and purchased also from Aldrich.

## Hydroxyethyl cellulose acetylating

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

## Heca characterization

### Casting

The films with thickness of 1mm were prepared by casting HECA solution on Teflon plates. One gram of the HECA samples were dissolved in 30 mL of (DMF for DS $\leq$ 1.5, THF for DS $\geq$ 1.5 or water for DS = 0); to reach complete dissolution of the sample, the solvent was chosen depending on the DS value. Each solvent was eliminated by evaporation process under vacuum.

### DS determination

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

$$DS_{ref} = \frac{(M_{HEC} \cdot \Delta n_{KOH})}{(m_{sample} \cdot \Delta n_{KOH} \cdot M_{acl})} = 2.6 \quad (16)$$

where $DS_{ref}$ = substitution degree of the reference sample (sampl.8), $M_{HEC}$ = HEC monomer molar weight = 228.22 g mol$^{-1}$, $\Delta n_{KOH}$ = molar number vari-

ation of KOH before and after saponification, $M_{acl}$ = acetic liberated group molar weight = 42.04 g mol$^{-1}$.

Equation 16 was used to determine the DS value of the reference sample. The DS value of other HECA samples were calculated by taking into account the absorption band area of the functions existing in their chemical structure (C=O and O—H), using FTIR spectra. The following eq. (17) was obtained.

$$DS_{sample} = DS_{ref} \cdot \left( \frac{\left(\frac{S(CO)}{S(OH)}\right)_{sample}}{\left(\frac{S(CO)}{S(OH)}\right)_{ref}} \right) \quad (17)$$

where S(OH) and S(CO) are the integrated absorption bands area for hydroxyl and carboxyl functions respectively.

*NMR method.* The NMR spectra were performed on HECA samples dissolved in DMSO-d6. The different signals can be classified in three categories: 15 HEC main chain protons are located between 3.2 ppm and 5.6 ppm and $H_4$ HEC proton hidden by water protons at 3 ppm (Fig. 5), and methyl protons situated on ester group appeared at 2 ppm (Fig. 5). $^1$H-NMR spectroscopy can be also used as tool to calculate the DS of cellulose derivatives using integrated peak area of different functions. The resulted eq. (18) obtained may be used to deduct the DS value of HECA samples.

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

$$DS = \frac{15 I_{CH_3}}{3 I_{HEC} + I_{CH_3}} \quad (18)$$

where $I_{CH_3}$ and $I_{HEC}$ are the integrated peak area of methyl protons and 15 HEC protons, respectively.

## Spectroscopic measurements

The chemical structure of HECA samples were evaluated by FTIR, $^{13}$C NMR and $^1$H NMR spectroscopy techniques. FTIR analysis was conducted to study the functional groups present in HEC before and after chemical modification. FTIR experiments were performed using a Shimadzu Fourier transform infrared spectrometer FTIR-8400S using a KBr disc containing 2% finely ground samples. Twenty scans were taken of each sample recorded from 4000 to 400 cm$^{-1}$. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 200 MHz spectrometer at 360°K by Technical scientific research national center at Rabat-Morocco, using TMS as internal standard and DMSO-d$_6$ as solvent respectively.
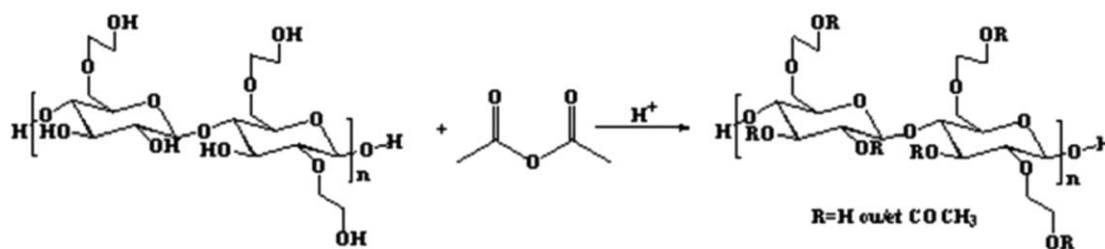
**Figure 3** HEC acylation reaction.

## Thermal analysis

Thermal study of HECA samples with various DS was performed using thermogravimetric 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$^{-1}$ under nitrogen flow.

## Solubility study

Some dissolution tests were performed to confirm the theoretical study. We carried out a comparative study of dissolving power of some solvents toward a series of HECA samples with various DS. Solutions of HECA were prepared by the following procedure. Powder samples were placed in a small weighting bottle and dried in vacuum oven at 70°C to constant mass. The dried samples were then placed in a bottle with an adequate solvent, keeping the mixture under stirring until the crystals disappeared (visual monitoring) and transparent solution was obtained. The mixture was kept at room temperature.

## RESULTS AND DISCUSSION

### The HEC modification

Figure 3 presents the acetylating reaction of HEC using acetic anhydride as reagent. The most important aspects to be considered when developing methods for the chemical modification of natural products are their simplicity and the time required for this process. This reaction was conducted at various molar ratio of HEC to acetic anhydride for different times and temperatures.

### FT-IR spectra

Figure 4, shows the FTIR spectra of unmodified HEC and Hydroxyethyl cellulose acetate samples (HECA) with different substitution degree [DS = 0.72; 1.27 and 2.4]. When the acetylating reaction takes place between acetic anhydride and HEC, the modification may be proved by the carbonyl ester

band apparition at 1739 cm$^{-1}$ and the decrease of OH broad band intensity assigned to alcohol group at 3480 cm$^{-1}$. The peaks located at $\sim$ 2948 cm$^{-1}$and $\sim$ 2885 cm$^{-1}$are attributed to $\nu$(C—H) and $\nu$(C—H$_2$) groups respectively,.[78] The band located also at 1647 cm$^{-1}$ corresponds to the bending mode of the naturally absorbed water.[79] The absorbance at 1375 cm$^{-1}$ arises from the C—CH$_3$ vibration, moreover the peak at 1242 cm$^{-1}$ is originated from $\nu$(C—O)$_{ester}$ vibration.

The effect of acetic anhydride equivalent numbers added to the solution mixture is illustrated by comparing the FTIR spectra presented in Figure 4. Using the experimental data, we have noted that with
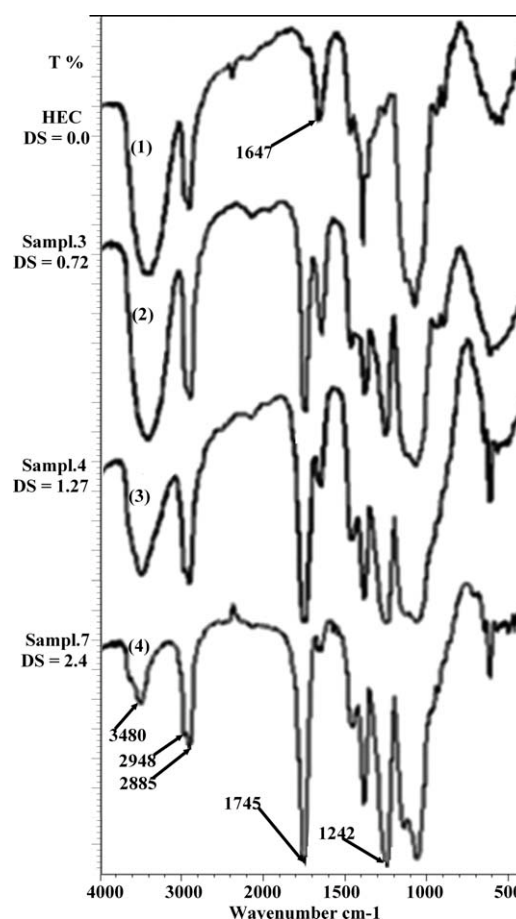


**Figure 4** FT-IR spectra of unmodified HEC (1) and HECA with DS = 0.72, (2) DS = 1.27 (3) and DS = 2.4 (4).

TABLE I
Results and Conditions of the HEC Acetylation

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

a, acetylation without catalyst; X, nonsoluble; O, soluble; b, 1 eq; a mount to acetylat one hydroxyl group; c, determined by volumetric method (ref).

increasing fraction of acetic anhydride in the mixture, the absorption band surface change, and the ratio between $\nu(C{=}O)$ and $\nu$ (O—H) areas increases. The experiments based on FTIR spectra show that the DS increases with increasing acetic anhydride amounts added. The eq. (16) was proposed to determine the (DS) values and the results obtained are grouped in Table I.

## NMR study

First, it must be noted that the sample must be purified. The spectra represented on Figure 5 shows the peak attributed to the water at $\sim$ 3 ppm. The HEC methylene proton signals between $\sim$ 3.5 ppm and $\sim$ 3.6 ppm were overlapped with the broad ring proton signals (2.8 $\sim$ 5.6 ppm) of the cellulose skeleton. HECA synthesis was successfully proved by the presence of a novel signals at 2.0 ppm and at 4.11 ppm which are attributed respectively, to the acetyl protons and to the methylene in $\alpha$ to the ester.

The DS values of HECA samples were also estimated using ^{1}H-NMR technique from the acetyl protons to the total HEC proton integrations as mentioned in section 3.3.2 (eq. 18), and the results are summarized in Table I.

Figure 6, presents the ring carbon of HECA DS = 2.4 (sample 7), in DMSO-$d_6$ at 360°K. The signals at 21 ppm and $\sim$ 170 ppm in the ^{13}C NMR spectra indicate the presence of the acetyl group carbon and the carbonyl ester respectively. The assignments of the other peaks are, according to Qi Zhou et al.[23]

and Juli et al.,[24] attributed to the HEC carbon region (60–105 ppm).

The substitution degree (DS) in the HECA samples increases with increasing respectively, the acetic anhydride equivalent numbers, and the reaction time as shown in the Figure 7(a,b). At 80°C, the process runs at a higher rate and the HECA obtained have a higher degree of substitution than the samples obtained at room temperature (c). From above experiments, the non variation of the degree of substitution at low temperature from 0 to 20°C [Fig. 7(c)] was noted. The DS values increase exponentially with an increase in the reaction temperature.

## HECA solubility study

One of the main difficulties to the use of cellulose and cellulose derivatives, especially cellulose ethers in many applications is theirs poor solubility in organic solvents. Thus, to overcome this drawback, we have modified the HEC for the sake of synthesizing the HECA with different DS. Furthermore, we have studied the influence of DS values on properties of HECA samples in particular on its solubility. A survey of the published data on the solubility of natural polymers in various solvents shows that dissolving power depends on the polymer and solvent structures, respectively.

The group contribution method (GCM) has proved, that the solubility characteristics of HECA compounds depend greatly on the substitution degree. This approach may be extended to various
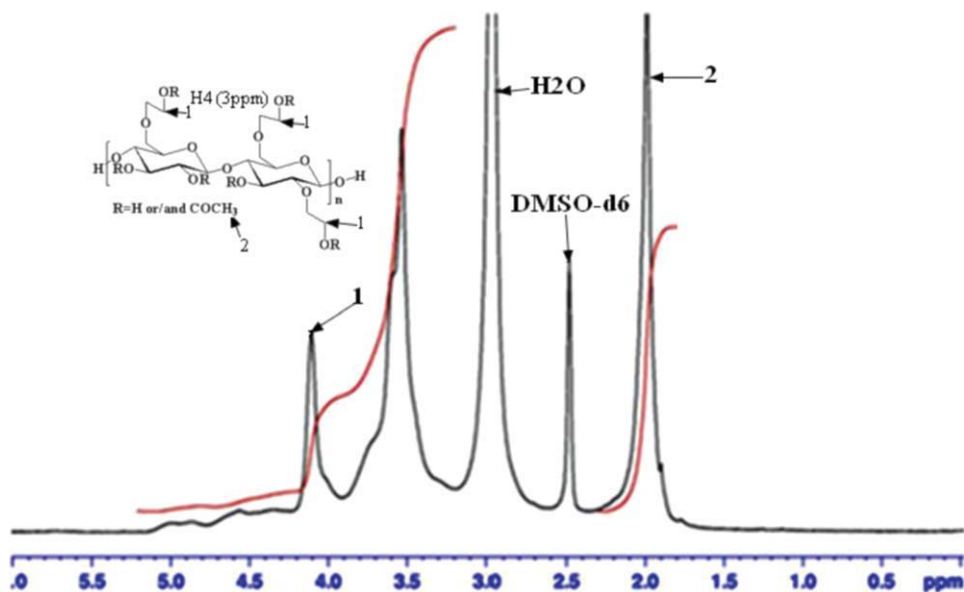
**Figure 5** $^1$H NMR Spectra of HECA DS = 2.4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cellulose ethers and other cellulose derivatives with a both various DS and nature of grafted groups. From the application of the VKH method using successively the eqs. (8), (9) and (10), and the contribution of each group is given in table II. The partial solubility parameters or the Hansen solubility parameters (HSP) were calculated and regrouped in Table III. Using these results, we have represented

on Figure 8 the Hansen solubility parameters [$\delta_t$, $\delta_d$, $\delta_p$, $\delta_h$, where $\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$] variation of HECA at different DS.

Figure 8, shows that the variation of total ($\delta_t = 33$–$21$ MP$^{1/2}$) and hydrogen bond solubility parameters ($\delta_h = 24$–$10$ MP$^{1/2}$) respectively, for DS situated between the values 0 and 3 is similar and decreases with increasing DS values. However, the polar ($\delta_p = 9.3$–$4.6$ MP$^{1/2}$)
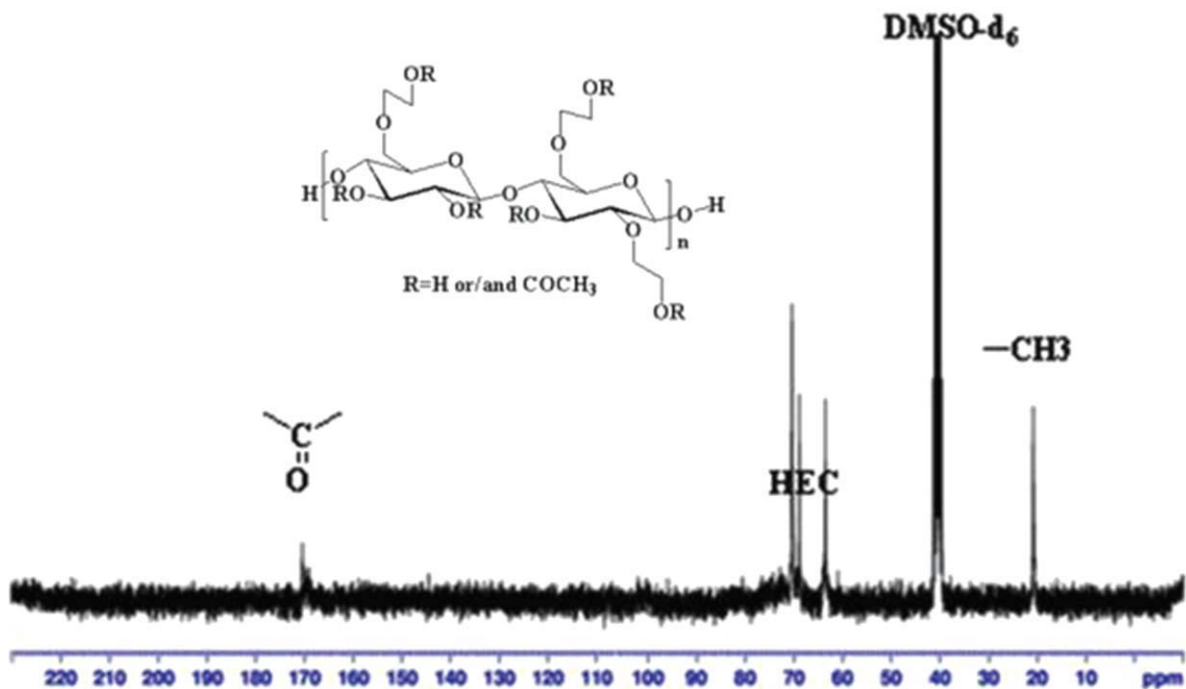


**Figure 6** $^{13}$C NMR Spectra of HECA DS = 2.4 (Sample 7). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
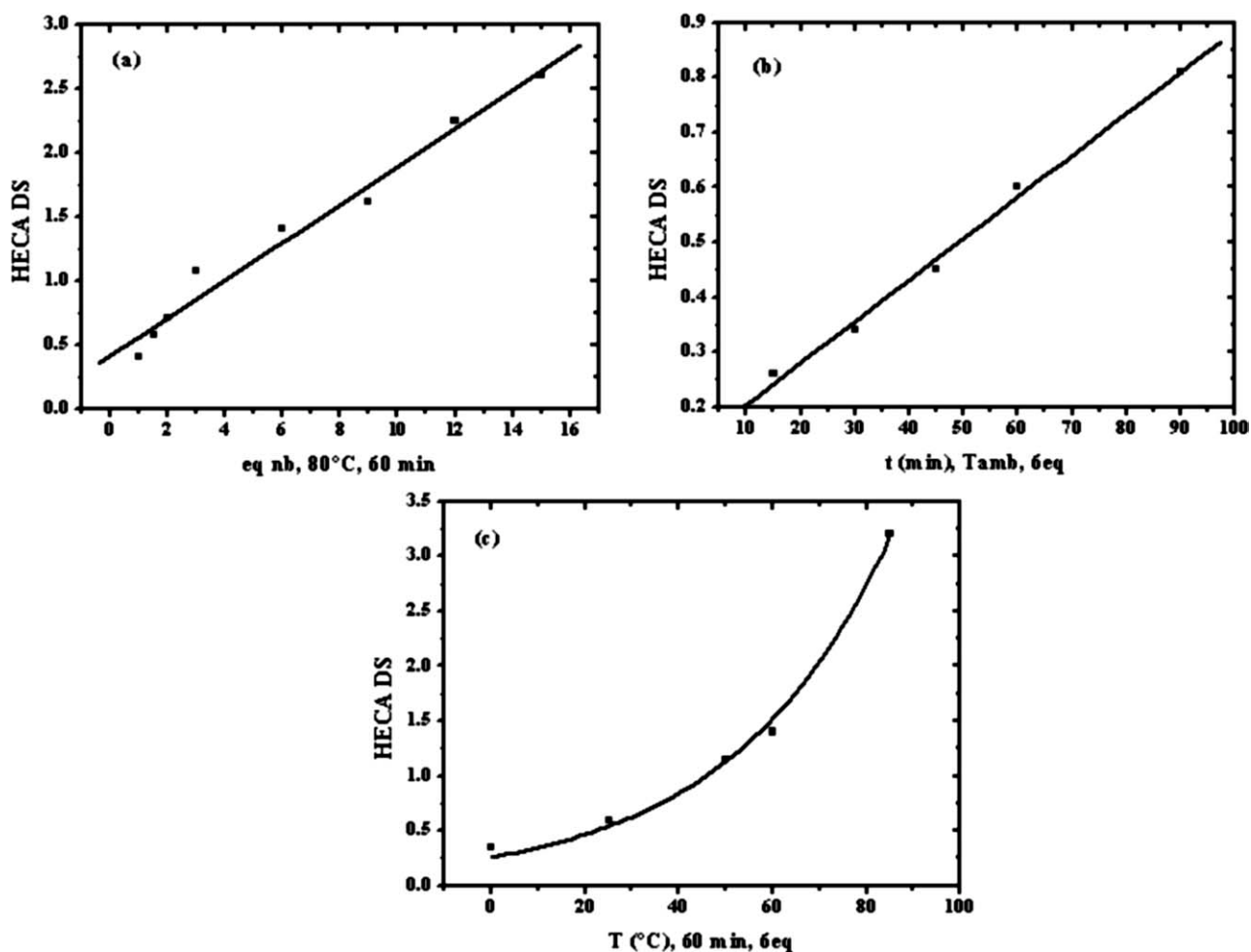
**Figure 7** (a) Acetic anhydride equivalent number, (b) time and (c) temperature reaction controlled acetylation of HEC.

and dispersion ($\delta_d = 21$–$18$ MP$^{1/2}$) components for DS situated in the range (0–3) have a slight variation with DS. From these results, we can conclude that the variation of the total solubility parameter ($\delta_t$) is imposed by the hydrogen bond component. According to the fundamental of the solubility theory "like dissolve like", we can predict, easily the best solvent of any polymer. As can be seen on the Figure 8, $\delta_t$ decreases when DS of HECA increases, moreover the solubility at low DS

begins in the protic solvent to the aprotic for the high DS.

The combination of the partial solubility parameters ($\delta_h$, $\delta_p$, $\delta_d$) variations in one graph has an important role to choose the appropriate solvent. The useful combinations cited in literature were; the Henry combination ($\delta_h - \delta_p$),[80] the Bagley et al. combination ($\delta_h - \delta_v$), [$\delta_v = (\delta_p^2 + \delta_d^2)^{1/2}$],[35] Hoernschemeyer combination ($\delta_h - \delta_t$) et ($\delta_a - \delta_t$) [$\delta_a = (\delta_p^2 + \delta_h^2)^{1/2}$].[82]

**TABLE II**
$F_d$, the Dispersion Component of Giving $\delta_d$, $F_p$, Polar Component; $E_h$, the Contribution of the Hydrogen Bond Forces to the Cohesive Energy of Group $i$ and the Number of Group $i$ Presented in the HECA Chemical Formula

| Group $i$ | $F_d$ J$^{1/2}$cm$^{3/2}$ mol$^{-1}$ | $F_p^2$ J cm$^3$ mol$^{-1}$ | $E_h$ J mol$^{-1}$ | Molar volumes (cm$^3$ mol$^{-1}$) | Repeat unit | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | DS = 0 | DS = 0.5 | DS = 1 | DS = 1.5 | DS = 2 | DS = 2.5 | DS = 3 |
| —COO— | 390 | 240100 | 5500 | 18 | 0 | 0.5 | 1 | 1.5 | 2 | 2.5 | 3 |
| —CH3 | 420 | 0 | 0 | 33.5 | 0 | 0.5 | 1 | 1.5 | 2 | 2.5 | 3 |
| —CH$_2$— | 270 | 0 | 0 | 16.1 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| >CH— | 80 | 0 | 0 | −0.1 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| —OH | 210 | 250000 | 20000 | 10 | 3 | 2.5 | 2 | 1.5 | 1 | 0.5 | 0 |
| —O— | 100 | 160000 | 3000 | 3.8 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 |
| Ring | 190 | 0 | 0 | 16 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

### TABLE III
### Hansen Solubility Parameters of HECA at DS = 0–3

| DS | $M_{RU}$ | $\delta_d$ ($j^{1/2}.cm^{-3/2}$) | $\delta_p$ ($j^{1/2}.cm^{-3/2}$) | $\delta_h$ ($j^{1/2}.cm^{-3/2}$) | $\delta_t$ ($j^{1/2}.cm^{-3/2}$) |
|----|----------|------------|------------|------------|------------|
| 0 | 228.22 | 21.51 | 9.29 | 23.92 | 33.48 |
| 0.5 | 249.24 | 20.49 | 7.94 | 20.96 | 30.37 |
| 1 | 270.26 | 19.73 | 6.92 | 18.44 | 27.88 |
| 1.5 | 291.27 | 19.14 | 6.14 | 16.21 | 25.83 |
| 2 | 312.29 | 18.67 | 5.51 | 14.19 | 24.09 |
| 2.5 | 333.31 | 18.28 | 4.99 | 12.28 | 22.59 |
| 3 | 354.33 | 17.96 | 4.57 | 10.44 | 21.27 |

The partial solubility parameters of some solvents were reported in the literature.[40] The distance $D_{SP}$ and the Flory-Huggins interaction parameter $\chi_{SP}$ between the solvent (S) and HECA (P) respectively, have been calculated using the eqs. (7) and (15), and the results are summarized in Table IV, where the molar volume is equal to $V_M = M/d$, (M is the molar weight and $d$ is the density of the solvent, respectively).

Figure 9, presents the variation of $D_{SP}$ between solvents and the polymer (HECA) with different DS. The $D_{SP}$ decreases for all solvents except the following cases: methanol $D_{SP}$ (increase from DS ∼ 1), DMF, and DMSO show a constant $D_{SP}$ between (DS ∼ 1.5 and DS ∼ 3), in the case of ethanol $D_{SP}$ increases from DS ∼ 1.5 except of water. The same variations than $D_{SP}$ were observed for the $\chi_{SP}$.

According to the Flory-Huggins model, both polymer and solvent are completely miscible if $\chi_{SP} \langle 0.5 \left(1 + \left(\frac{VmS}{VmP}\right)^{\frac{1}{2}}\right)^2$ where $VmS$ and $VmP$ are respectively, the molar volume of the solvent and polymer. In the present work we suppose that $VmP \rangle\rangle\rangle VmS$, consequently the good miscibility of HECA and the solvent will be reached at $\chi_{SP} \leq 0.5$. A good correlation is noted between the theoretical (Fig. 10) and the experimental solubility studies (Table I). Dissolution tests were perfectly in agreement with the theoretical study based on Hansen solubility parameters; adequate and determined solvents were specified for each HECA sample. The factors determining the solubility of HECA were studied at different levels. At the supramolecular level the solubility of HECA in solvents depends on the total solubility parameter ($\delta_t$), in particular the hydrogen bond solubility parameters ($\delta_h$). Introduction of acetate group makes the macromolecules hydrophobic (molecular level) and insoluble in water. In summary, the experimental tests are in agreement with the predictions and anticipations of theoretical study.

### Thermal study

The effect of the acetylating on the thermal behavior of HEC was also studied by TGA and TDA in the temperature range from 35 to 500°C. Figure 11 Shows the TGA and TDA Thermograms of unmodified HEC (a), HECA with DS = 0.72 (b) and HECA with DS = 2.4 (c). From the above figure, it can be seen that the thermal degradation temperature of HECA increases with increasing DS values. The HEC starts to decompose at 280°C, while the acetylated HEC DS = 0.72 (b) and DS = 2.4 begin to decompose respectively, at 312°C and 327°C. At 50% weight loss, the decomposition temperature occurs at 330°C for unmodified HEC and 345°C for HECA (DS = 0.72) and at 355°C for HECA (DS = 2.4). This increasing in the decomposition temperature implied that the thermal stability of HECA is more important than that of HEC, and increases with the DS values. Similar results were also observed in the case of cellulose and cellulose acetate.[82]

The TDA Thermograms of unmodified HEC (a), HECA DS = 0.72 (b), and HECA DS = 2.4 (c) are presented also on Figure 12. The first endothermic phase transition may be attributed to the glass transition temperature ($T_g$). Then, $T_g$ of the unmodified HEC appeared at ∼ 62°C,[83] while, the $T_g$ values of HECA (DS = 0.72) and HECA (DS = 2.4) are higher than HEC value. It can be suggested that the acetyl group (CH$_3$) in the HECA samples influences the
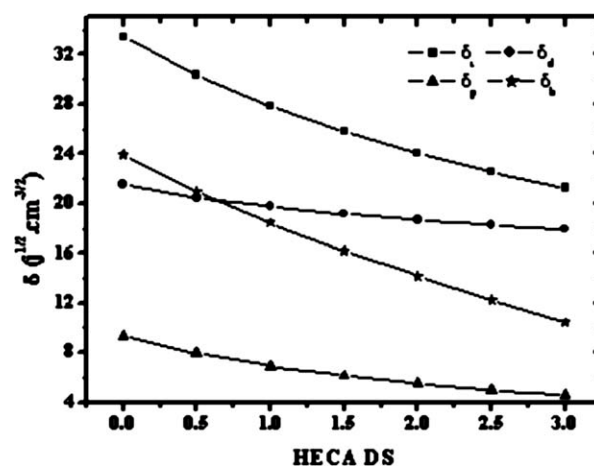


**Figure 8** The variation of the Hansen solubility parameters HECA at different DS.

**TABLE IV**
**Flory-Huggins Interaction Parameter ($\chi_{SP}$) and The Distance ($D_{SP}$) between The Solvent (S) and The HECA Plymer (P) at Various DS.**

| Solvent | $V_m$ | HECA DS = 0 | | HECA DS = 0.5 | | HECA DS = 1 | | HECA DS = 1.5 | | HECA DS = 2 | | HECA DS = 2.5 | | HECA DS = 3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\chi_{sp}$ | $D_{sp}$ | $\chi_{sp}$ | $D_{sp}$ | $\chi_{sp}$ | $D_{sp}$ | $\chi_{sp}$ | $D_{sp}$ | $\chi_{sp}$ | $D_{sp}$ | $\chi_{sp}$ | $D_{sp}$ | $\chi_{sp}$ | $D_{sp}$ |
| Toluene | 106.285 | 3.808 | 24.333 | 2.747 | 20.667 | 2.011 | 17.685 | 1.477 | 15.155 | 1.075 | 12.93 | 0.765 | 10.910 | 0.523 | 9.017 |
| chloroform | 80.162 | 2.063 | 20.625 | 1.384 | 16.891 | 0.931 | 13.851 | 0.616 | 11.268 | 0.392 | 8.992 | 0.232 | 6.921 | 0.120 | 4.974 |
| 1,1 Dichloromethane | 78.977 | 3.111 | 25.512 | 2.311 | 21.988 | 1.751 | 19.14 | 1.339 | 16.739 | 1.025 | 14.645 | 0.778 | 12.763 | 0.580 | 11.021 |
| Carbon Tetrachloride | 96.500 | 4.001 | 26.177 | 2.958 | 22.507 | 2.2251 | 19.522 | 1.682 | 16.97 | 1.273 | 14.764 | 0.948 | 12.745 | 0.688 | 10.854 |
| Tetrahydrofuran | 81.091 | 1.742 | 18.844 | 1.117 | 15.085 | 0.711 | 12.037 | 0.44 | 9.466 | 0.257 | 7.233 | 0.136 | 5.262 | 0.062 | 3.559 |
| 1,4 Dioxane | 85.299 | 1.829 | 18.822 | 1.190 | 15.182 | 0.776 | 12.258 | 0.498 | 9.827 | 0.311 | 7.762 | 0.186 | 6.01 | 0.109 | 4.603 |
| Ether diethyl | 103.900 | 3.719 | 24.323 | 2.644 | 20.509 | 1.900 | 17.426 | 1.384 | 14.839 | 0.999 | 12.608 | 0.713 | 10.646 | 0.499 | 8.907 |
| Acetone | 73.518 | 1.922 | 20.785 | 1.338 | 17.341 | 0.955 | 14.65 | 0.694 | 12.495 | 0.515 | 10.761 | 0.392 | 9.391 | 0.312 | 8.376 |
| Methyl ethyl ketone | 89.573 | 2.579 | 21.812 | 1.807 | 18.261 | 1.290 | 15.427 | 0.928 | 13.085 | 0.668 | 11.104 | 0.480 | 9.411 | 0.345 | 7.976 |
| Cyclohexanon | 103.31 | 2.615 | 20.451 | 1.771 | 16.831 | 1.208 | 13.902 | 0.817 | 11.434 | 0.539 | 9.286 | 0.339 | 7.367 | 0.198 | 5.624 |
| Ethyl acetate | 98.222 | 2.531 | 20.638 | 1.691 | 16.865 | 1.134 | 13.814 | 0.753 | 11.253 | 0.486 | 9.046 | 0.301 | 7.118 | 0.177 | 5.458 |
| Pyridine | 80.558 | 1.707 | 18.714 | 1.153 | 15.379 | 0.794 | 12.764 | 0.553 | 10.655 | 0.39 | 8.941 | 0.279 | 7.568 | 0.209 | 6.543 |
| Aniline | 91.149 | 1.264 | 15.138 | 0.734 | 11.532 | 0.414 | 8.66 | 0.220 | 6.320 | 0.109 | 4.452 | 0.056 | 3.193 | 0.048 | 2.951 |
| N-Methyl-2-pyrrolidone | 96.431 | 1.972 | 18.383 | 1.361 | 15.274 | 0.976 | 12.932 | 0.726 | 11.156 | 0.564 | 9.835 | 0.464 | 8.918 | 0.410 | 8.384 |
| N, N-Dimethylformamid | 77.430 | 1.154 | 15.694 | 0.772 | 12.839 | 0.556 | 10.893 | 0.438 | 9.669 | 0.384 | 9.05 | 0.374 | 8.938 | 0.400 | 9.242 |
| Dimethylsulfoxid | 70.774 | 1.188 | 16.659 | 0.878 | 14.317 | 0.705 | 12.837 | 0.615 | 11.988 | 0.577 | 11.611 | 0.576 | 11.596 | 0.603 | 11.866 |
| Methanol | 40.221 | 0.428 | 13.267 | 0.334 | 11.712 | 0.316 | 11.387 | 0.342 | 11.849 | 0.397 | 12.766 | 0.473 | 13.938 | 0.567 | 15.273 |
| Ethanol | 58.388 | 0.534 | 12.292 | 0.323 | 9.555 | 0.234 | 8.143 | 0.219 | 7.870 | 0.251 | 8.425 | 0.317 | 9.477 | 0.413 | 10.814 |
| Cyclohexanol | 104.115 | 1.28 | 14.252 | 0.685 | 10.424 | 0.341 | 7.358 | 0.149 | 4.864 | 0.056 | 2.986 | 0.034 | 2.328 | 0.068 | 3.295 |
| Water | 18.054 | 0.571 | 22.858 | 0.673 | 24.822 | 0.787 | 26.834 | 0.905 | 28.775 | 1.025 | 30.63 | 1.148 | 32.417 | 1.276 | 34.177 |
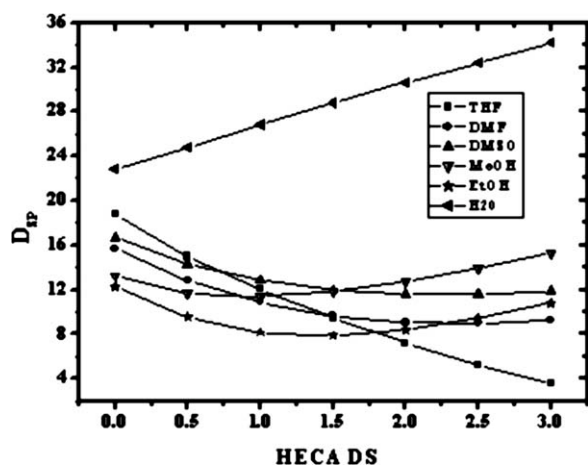
**Figure 9** $D_{SP}$ of solvents at various DS of HECA.



**Figure 11** Thermograms of unmodified HEC (a), HECA DS = 0.72 (b), and HECA DS = 2.4 (c).

intermolecular interaction and a diminution in cross-link density.

The thermal degradation of HEC showed two peaks at 315°C 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 temperature at high DS could be explained by the disappearance of the hydrogen bonding and the ordered regions, though this suggestion will be correlated by the XRD data.

## CONCLUSIONS

Resuming the carried out investigation we can conclude the following:

- HECA samples with various DS were fabricated from HEC which was prepared from cellulose extracted in basic medium using "Stipa Tenacis-
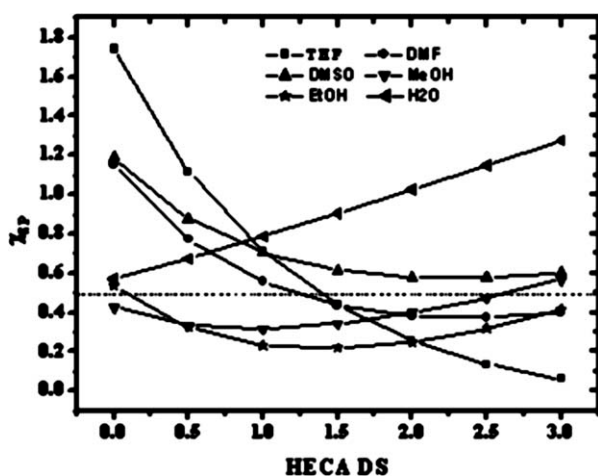


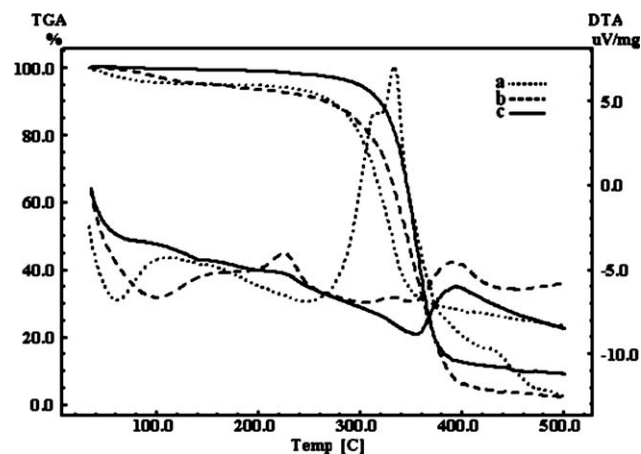**Figure 10** The interaction Flory parameter $\chi_{SP}$ between solvents and HECA.

sima" of Eastern Morocco. The resulted compounds were characterized by spectroscopy techniques (FTIR, NMR). The DS values were obtained from direct titration method, especially FTIR and NMR techniques respectively. The effect of acetic anhydride equivalent numbers (eq. nb.) added to the reaction mixture, the temperature and the time of reaction have respectively, a high influence on the DS value.

- The Flory-Huggins interaction parameters of HECA ($\chi_{SP}$) have been determined using the partial Hansen solubility parameters (HSP). HSP of HEC and HECA samples were calculated from the Van-Krevlen-Hoftyze (VKH) method and the T. Lindvig approximation. At the supramolecular level, it was found that the solubility of HECA in solvents depends on the total solubility parameter ($\delta_t$), in particular the hydrogen bond solubility parameters ($\delta_h$). We have identified in general, the influence of DS values on dissolution capacities in organic solvent systems. It was found that with increasing DS, the solubility phenomenon increases. The dissolving power depends on the polymer and solvent structures respectively. Furthermore, the HSP can be employed to develop a method capable of predicting and controlling dissolution of cellulose derivatives (HEC; HECA) in different solvent conditions taking into account their DP value. From these results the control of solubility is possible, and the fabrication of functionalized material can relatively be easily carried out.

- HECA samples thermal behaviors were investigated by thermogravimetric analysis (TGA) under nitrogen. The results indicated some differences in glass transition temperature ($T_g$) and thermal degradation of HEC and HECA, these thermal temperatures were influenced by the DS values. The HECA cellulose derivative

exhibited more heat resistant property compared with starting HEC; we can conclude that HECA is thermally more stable material than HEC and common cellulose. Specific focus should be placed on modification of the cellulose backbone as a means of enhancing solubility and stability.

## References

1. Pondy, A.; Coccal, C. R.; Nigam, P. Bioressor Technol 2000, 74, 69.
2. Richardson, S.; Grton, L. Anal Chim Acta 2003, 497, 27.
3. Focher, B.; Palma, M. L.; Conetti, M. Ind Crop Prod 2001, 13, 193.
4. Mohanty, A. K.; Misra, M.; Hinrichsen, G. Macromol Mater Eng 2000, 276, 1.
5. Mohanty, A. K.; Misra, M.; Drzol, L. T. J Polym Environ 2002, 10, 19.
6. Gamini, S.; Wolfgong, G. G. Carbohydr Polym 1993, 22, 979.
7. Buchanan, C. M.; Hyah, J. A.; Lowman, D. W. Macromolecules 1987, 20, 2750.
8. Stamin, A. J. Wood and Cellulose Science; Ronald Press: New York, 1964.
9. McCromick, C. L.; Callais, P. A. Polymer 1987, 28, 2317.
10. Phillip, H.; Schleicher, H.; Wagerknecht, X. Chem Tech 1977, 7, 702.
11. Turbak, A. F.; Hammer, R. B.; Davies, R. E.; Hergert, H. L. Chem Tech 1980, 10, 51.
12. Hudson, S. M.; Cuculo, J. A. J Macromol Sci 1980, 18, 1.
13. Tatiana, B.; Arnis, T. Carbohydr Polym 2002, 48, 23.
14. Heinze, T. Prog Polym Sci 2001, 26, 1689.
15. Rohn, K.; Diamantaglon, M.; Kleum, D.; Berghmous, H.; Heinze, T. Angew Makromol Chem 1996, 238, 143.
16. Liu, C. F.; Sun, R. C.; Zhang, A. P.; Ren, J. L.; Geng, Z. C. Polym Degrad Stab 2006, 91, 3040.
17. Potthost, A.; Posenau, T.; Sartori, J.; Sixta, H.; Kosma, P. Polymer 2003, 44, 7.
18. Shimizu, Y.; Nakayama, A.; Hayashi, J. Cellulose Chem Technol 1991, 25, 275.
19. Shimizu, Y.; Nakayama, A.; Hayashi, J. Transaction 1993, 49, 352.
20. El Kafrawy, A. J Appl Polym Sci 1982, 27, 2435.
21. Morgenstern, B.; Kemmer, H. W. Trends Polymer Sci 1996, 4, 87.
22. Striegel, A. M. Carbohydr Polym 1997, 34, 267.
23. Qi, Z.; Lina, Z.; Ming, L.; Xiaojun, W.; Gongzhen, C. J Polym Bull 2005, 53, 243.
24. Li, J.; Xie, W.; Cheng, H. N.; Nickol, R. G.; Wang, P. G. J Macromol 1999, 32, 2789.
25. Pourchez, J.; Grosseeau, P.; Guyonnet, R.; Ruot, B. J Cement Concrete Res 2006, 36, 1777.
26. Singh, N. K.; Mishra, P. C.; Singh, V. K.; Narang, K. K. J Cement Concrete Res 2003, 33, 1319.
27. El Barkany, S.; El Idrissi, A.; Ouslimane, S.; Amhamdi, H. Phys Chem News 2009, 46, 135.
28. Lindvig, T.; Michelsen, M. L.; Kontogeorgis, G. M. J Fluid Phase Equilibria 2002, 203, 247.
29. Mieczkowski, R. Eur Polym Mater 1990, 27, 377.
30. Barton, A. F. M. Chem Rev 1975, 75, 731.
31. Brandrup, J.; Immergut, E. H. Polymer Handbook, 3rd ed.; Wiley Interscience, New York, 1989.
32. Hildebrand, J. H.; Scott, R. L. The Solubility of Non-Electrolytes, 3rd ed.; New York: Reinhold, 1959.
33. Scatchard, G. Chem Rev 1949, 44, 7.
34. Hansen, C. M. J Paint Technol 1967, 39, 104.
35. Breitkreutz, J. J Pharmaceut Res 1998, 15, 1370.
36. van Krevelen, D. W. Properties of Polymers, Amsterdam: Elsevier Science, 1997.
37. Good, R. J. In Treatise on Adhesion and Adhesives; Patrick, R. L., Ed.; New York: Marcel Dekker, 1967.
38. Hansen, C.; Skaarup, K. J Paint Technol 1967, 39, 511.
39. Hansen, C. Hansen Solubility Parameters—A User's Handbook; CRC Press: Boca Raton, 1999.
40. Brandrup, J.; Immergut, E. H.; Grulke, E. A.; Abe, A.; Bloch, D. R. Polymer Handbook, 4th ed.; Wiley Interscience: New York, 2003.
41. Beerbower, A.; Dickey, J. R. Am Soc Lubric Eng Trans 1969, 12, 1.
42. Barton, A. F. M. CRC Handbook of Solubility Parameters and Other Cohesion parameters; 2nd ed.; CRC Press: Florida, USA, 1991.
43. Prigogine, I.; Bellemans, A.; Mathot, V. The Molecular Theory of Solutions. North-Holland Publ. Company: Amsterdam, 1957.
44. Gee, G. Trans Inst Rubber Ind 1943, 18, 266.
45. Fedors, R. F. Polym Eng Sci 1974, 14, 147.
46. Huglin, M. B.; Pass, D. J. J Appl Polym Sci 1968, 12, 473.
47. Hamurcu, E. E.; Baysal, B. M. J Polym Sci 1994, 32, 591.
48. Suh, K. W.; Clarke, D. H. J Polym Sci 1967, 5, 1671.
49. Marco, C.; Bello, A.; Faton, J. G.; Garza, J. Makromolek Chem 1986, 187, 177.
50. Liron, Z.; Cohen S. J Pharm Sci 1983, 72, 499.
51. Errede, L. A. Macromolecules 1986, 19, 1522.
52. Flory, P. J. Principles of Polymer Chemistry. Ithaca, New York: Cornell University Press, 1953.
53. Stockmayer, W. H.; Fixman, M. J Polym Sci 1963, 1, 137.
54. DipaolaBaranyi, G. Macromolecules 1982, 15, 622.
55. Ashworth, A. J.; Price, G. J. Macromolecules 1986, 19, 362.
56. Sperling, L. H. Introduction to Physical Polymer Science, 3th ed.; Wiley: United States of America, 2001.
57. Koenhen, D. M.; Smolders, C. A. J Appl Polym Sci 1975, 19, 1163.
58. Mandel, M.; Varkevisser, F. A.; Vantreslong, C. J. B. Macromolecules 1982, 15, 675.
59. Hansen, C.; Beerbower, A. In Encyclopedia of Chem Technology, 2nd ed.; Kirk-Orthmer, Standen, A., eds., Supp. vol., New York: Wiley-Interscience, 1971.
60. Thomos I. B. Sc, Applied Chemistry Dissertation, Toronto Polytechnique, 1975.
61. Darbye, J. R.; Touchette, N. W.; Sears, K. Polym Eng Sci 1967, 7, 295.
62. Shultz, A. R.; Glory, P. J. J Polym Sci 1955, 15, 231.
63. Ravindra, R. Carbohd Polym 1998, 36, 121.
64. Small, P. A. J Appl Chem 1953, 3, 71.
65. Dunkel, M. J Phys Chem 1928, 138, 42.
66. Bowden, S. T.; Jones, W. J. Phil Mag 1948, 39, 155.
67. Hoftyzer, P. J.; van Krevelen, D. W. Paper No.IIIs-15, presented at International Symposium on Macromolecules of IUPAC, Lyden, 1970.
68. Hoy, K. L. J Paint Technol 1970, 42, 76.
69. van Krevelen, D. W.; Hoftyzer, P. J. Properties of Polymers. Correlations with Chem Structure, New York: Elsevier, 1972.
70. Barton, A. F. M. CRC Handbook of Solubility Parameters and Other Cohesion Parameters; Boca Raton, FL: CRC Press, 1983.
71. van Krevelen, D. W. Fuel 1965, 44, 229.
72. van Krevelen, D. W.; Hoftyzer, P. J. J Appl Polym Sci 1967, 11, 2189.
73. van Krevelen, D. W.; Hoftyzer, P. J. Properties of Polymers. Correlation with Chem Structure; Amsterdam: Elsevier, 1976.

74. Lindvig, T.; Michelsen M. L.; Kontogeorgis, G. M. AIChE J 2001, 47, 2573.

75. Peppas N. A.; Brannon-Peppas, L. J Control Release 1996, 40, 245.

76. Mikos, A. G.; Peppas N. A. Biomaterials 1988, 9, 419.

77. Hansen, C. M. Hansen Solubility Parameters. A User's Handbook, CRC Press; Boca Raton, FL, 2000.

78. Garside, P.; Wyeth, P. Studies Conserv 2003, 48, 4.

79. Pastarova, I.; Botto, R. R.; Arisz, P. W.; Boon, J. J. Carbohydra Res 1994, 262, 27.

80. Henry, L. F. Polym Eng Sci 1974, 14, 167.

81. Hoernschemeyer, D. J Appl Polym Sci 1974, 18, 61.

82. Lieu, C. F. Polymer Degrad Stab 2006, 91, 3040.

83. Marianiava, D.; Lapcik, L. and Pisarcik, M., Study of The Dielectric Properties of Cellulose Derivatives, *Acta Polymerica* 1992, 34, 303.