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Graft copolymerization of hydroxyethyl cellulose with solketal acrylate: Preparation and characterization for moisture absorption application

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ABSTRACT

In this work, we reported the preparation of a novel biomaterial, by *graft*-polymerization of 2-2-dimethyl-1-3-dioxolan-4-yl methyl acrylate (solketalacrylate, DMDMA) on hydroxyethyl cellulose (HEC) using KPS as initiator. Several experiments were performed to find the optimum conditions for the preparation of this biopolymer, by varying the time of the reaction as well as the initiator and the monomer ratio. Results showed that the highest grafting yield was 25%, obtained after 72 minutes at 65 °C, using THF as solvent. The structure of the grafted copolymer was confirmed by X-ray diffraction patterns which showed, besides the characteristic peaks of HEC at $2\theta = 31.74^\circ$ and 44.63° a new peak at $2\theta = 30.72^\circ$ related to an organized structure of the grafted polymer on the HEC backbone. The DSC analysis showed a single glass transition temperature T_g , intermediate between the corresponding values for HEC and neat poly(solketal acrylate). Moreover, the grafted biomaterial presented two-fold more moisture absorption ability by comparison with HEC, making this new synthetic biomaterial highly promising for dryness applications. In our knowledge, the synthesized monomer: 2-2-dimethyl-1-3-dioxolan-4-yl methyl acrylate, (solketal acrylate, DMDMA), has never been grafted on the HEC backbones before that is what makes the novelty of the present work.

KEYWORDS

Bio based acrylate; graft copolymerization; hydroxyethylcellulose; synthetic biomaterials

Introduction

Hydroxyl ethylcellulose, HEC, is a nonionic cellulosic derivative, with linear structure and high solubility either in aqueous or in several organic solvents. Moreover, HEC is used in particular applications as thickening, gelation, emulsifier, or lubricant agent, due to its specific properties suitable for paints, textiles, and cosmetics.^[1,2] During the last decades, there has been a huge interest to the chemical modification of HEC to improve their bio-compatibility and expand the field of their applications. Grafting monomers on HEC remains a specific way to connect two different entities in a single macromolecule, with HEC as the main backbone and the side-chains consisting of oligomers that grow according to the synthesis conditions. The grafting method,

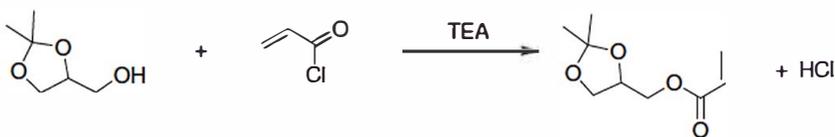


Figure 1. Synthesis of DMDMA.^[16]

either in homogeneous solution or in solid-liquid heterogeneous medium, leads to specific characteristics.^[3]

The HEC modification with acrylic monomers has been the subject of several works.^[3-5] Fekete et al.^[6] reported the hydrogel synthesis of hydroxyethyl-cellulose/acrylic acid that presents super-absorbent properties whereas pure or modified sodium alginate films with hydroxyethyl cellulose and poly-glycerol, prepared by Russo et al.^[7] showed an improvement in the thermal and mechanical properties of the HEC and an improvement in its water absorption properties. In the literature, various initiators have been employed to initiate the cellulose grafting process with vinyl or acrylic monomers. Even if they have not been used specifically for HEC, we considered interesting to report them as they were used on cellulosic molecules. For example, the ceric ammonium nitrate was used to carry out the graft polymerization of glycidylmethacrylate, ethyl acrylate, methylmethacrylate, butyl acrylate, and 2-hydroxyethylmethacrylate. Ceric ammonium sulfate and cobalt (III) acetylacetonate were also used with *N*-vinylpyrrolidone.^[8,9] Hydrogen peroxide^[10] and ammonium persulfate were used with acrylic acid to synthesize hydrogel composites with carboxymethyl-cellulose.^[11] Furthermore, azo-bis-isobutyronitrile,^[12] and potassium permanganate with acrylonitrile were used to develop antimicrobial graft cellulosic materials.^[13] Also, benzoyl peroxide was performed to initiate the polymerization of glycidylmethacrylate grafted on cellulose. The obtained materials were selected for the removal of chromium(VI), from water waste solutions.^[14,15]

In our previous work,^[16] we reported a successful method to graft the polymerization of 2,2-dimethyl-1,3-dioxolan-4-yl methyl acrylate (DMDMA, also called solketal acrylate), a derivative of glycerol and acrylic acid, on cellulose fibers. In this work, we grafted the same monomer DMDMA on the HEC fibers to improve the moisture adsorption properties, using the potassium persulfate (KPS) as initiator. The latter was chosen for its high efficiency,^[17] and its high water solubility.^[18] The obtained bio-copolymers, polyDMDMA-*graft*-HEC, were synthesized by varying several synthesis parameters, such as the initiator and the monomer concentrations and the duration of the reaction. The morphological properties were examined using SEM. The structural characterization was carried out by FTIR and DRX spectroscopies. The thermal properties were examined using TGA and DSC.

Experimental part

Materials and methods

Hydroxyethyl cellulose with 1.5 substitution degree, acryloyl chloride and 1,2-*o*-isopropylidene glycerol (solketal at 98% [100-79-8]), potassium persulfate (99%), magnesium sulfate (97%), dichloromethane (99.8%), and the tetrahydrofuran (with free-radical inhibitor at 99.9%), were supplied by Sigma-Aldrich. Tri-ethylamine and sodium bicarbonate (99%) were supplied by Acros Organics. All reagents were used straightly without prior purification.

DMDMA (2,2-dimethyl-1,3-dioxolan-4-yl methyl acrylate) was prepared by reacting solketal (racemic mixture) with acryloyl chloride and tri-ethylamine (Figure 1). The vinyl monomer obtained was purified by vacuum distillation as previously reported.^[16] In order to obtain neat homo-polymer for comparison purposes, DMDMA was radically polymerized (yielding

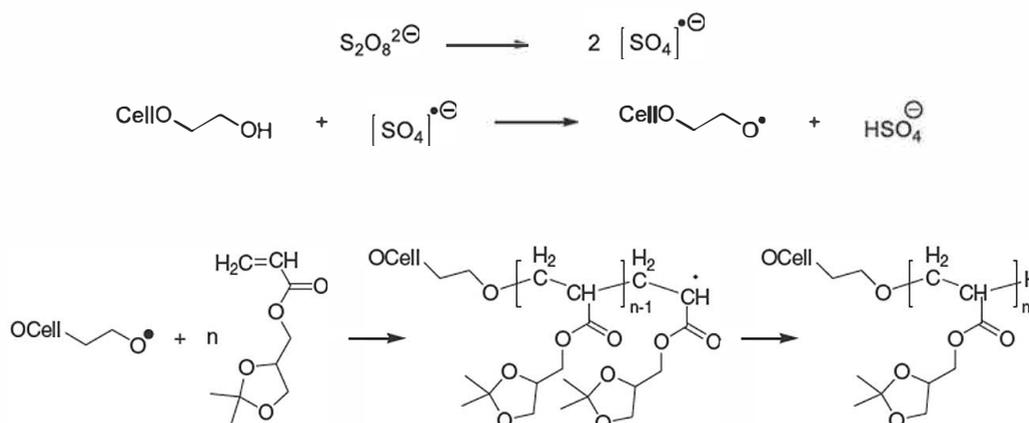


Figure 2. Synthetic mechanism of poly DMDMA graft HEC.

poly-DMDMA) using solid KPS, without THF whose free-radical inhibitor would have acted negatively.^[16] The polymerization mechanism is similar to the one described in Figure 2.

DMDMA graft-copolymerization on hydroxyethyl cellulose

The *graft*-copolymerization of DMDMA on HEC was performed as follows. A quantity of 500mg of HEC (7.9 meq OH), was dispersed in 20ml of THF, in a 50 ml triple-neck flash glass equipped with nitrogen flow. After 3 hours of magnetic stirring, KPS aqueous solution (25.2%) (amounts around 4ml to obtain between 0.94 and 15.01 meq of KPS), and adequate quantities of DMDMA (0.88 to 4.43 meq), have been added into the reaction vessel. The triple-neck flash glass was then introduced into a thermo-regulated that 65 °C. In these experiments, KPS and the monomer quantity varied between 0.94 and 15.01 mmol/eq OH and 1 to 5 ml (i.e. 0.88 to 4.43 mol/eq OH), respectively. The copolymerization time varied between 2 to 24 hours. The resulting mixture is kept under a nitrogen flow all over the copolymerization reaction. The termination step of the copolymerization was performed by cooling the reaction flask into an ice-bath. The resulting graft-copolymerization reaction followed the chemical mechanism led to the poly-DMDMA-*graft*-HEC, as shown in Figure 2. After a filtration and several washes with THF; the copolymer was dried at 50 °C for 12 hours and stored in desiccators until used.

In order to evaluate the grafting yield, we measured the weight gain (GP), defined as follows:

$$GP(\%) = \frac{W_1 - W_0}{W_0} \cdot 100 \quad (1)$$

where W_0 and W_1 are the cellulosic solid material weight before and after the grafting process, respectively.

Characterization of the poly-DMDMA-graft-HEC

FTIR spectroscopy

The FTIR spectra of the poly-DMDMA-*graft*-HEC bio-materials were recorded between 500 and 4000 cm^{-1} using a Perkin Elmer Spectrum with a resolution of 2 cm^{-1} and 64 scans. Dry powdered samples were mixed with spectroscopic KBr at a concentration of 5%. A background spectrum without any sample was subtracted from all the spectra.

Differential scanning calorimetry (DSC)

The glass transition temperature (T_g) of the sample was measured with a TA Instrument 2010, DSC2 differential scanning calorimeter using a sample weight of 10 to 15 mg at a heating rate of 20 °C/min under nitrogen flow between 40 and 300 °C. The initial onset of the change of slope in the DSC trace during the second heating scan was identified with the T_g .

Thermo-gravimetric analyses (TGA)

Thermo-gravimetric measurements were performed using a Mettler Toledo TGA (Stare system). About 10 mg of sample was heated in a platinum crucible from ambient temperature to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

X-Ray diffraction investigation

The structure of the biopolymers was investigated by X-ray powder diffraction (XRD). XRD patterns were recorded by a X-ray diffractometer with graphite monochromatized CuK_α at scanning rate of 4°/min. The diffraction angle was ranged from 5° to 40° (0.05°/min).

Scanning electron microscopy (SEM)

SEM images were recorded using a LEO 435VP scanning electron microscope. For SEM measurement, a thin layer of the biopolymers were deposited on metal grids using an araldite epoxy resin. Surfaces were rendered conductive by silver layering of several nanometers thick with an Edwards Scanco SIX metalizing device.

Moisture adsorption measurements

Pristine HEC as well as the grafted materials were dried in an oven at 100 °C for about 12 h. Samples weighing 1 g, were placed into desiccators containing a sulfuric acid solution 18.5% v/v, introduced one day before at room temperature.^[19]

After one or two days respectively, the samples were removed and weighed again. The experiment was repeated three times at least. The moisture absorption ability ($\%M_{\text{abs}}$) was evaluated following the weight percentage equation:^[20]

$$\%M_{\text{abs}} = \frac{W_f - W_i}{W_i} \cdot 100 \quad (2)$$

where W_i and W_f are the samples weights before and after their input in the desiccators, respectively.

Results and discussion

In order to make clear the impact of each pertinent parameter on the graft-copolymerization of the DMDMA monomer onto HEC, a series of poly-DMDMA-*graft*-HEC copolymers were prepared varying the concentration of KPS between 0.94 and 15.01 mmol/eq OH (Figure 3).

The increasing of KPS increases the grafting rate, up to a maximum value of 25.2%, obtained when KPS = 7.51 mmol/eq OH. Higher amounts of KPS causes a fast decrease in the grafting rate. Such behavior can be explained by the fact that the increase in the KPS amount generates the creation of radicals also on the THF by radical transfer, at the expense of the graft reaction.^[16,21]

The next parameter was studied by keeping the KPS amount at its optimum value (7.51 mmol/eq OH). The influence of the ration of monomer to HEC was then studied.

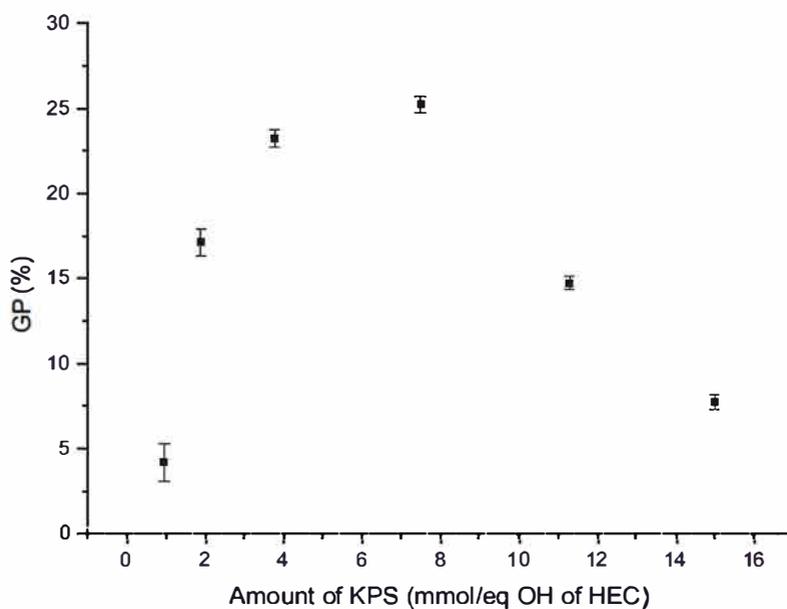


Figure 3. Grafting yield (expressed as weight gain) evolution with the amount of KPS.

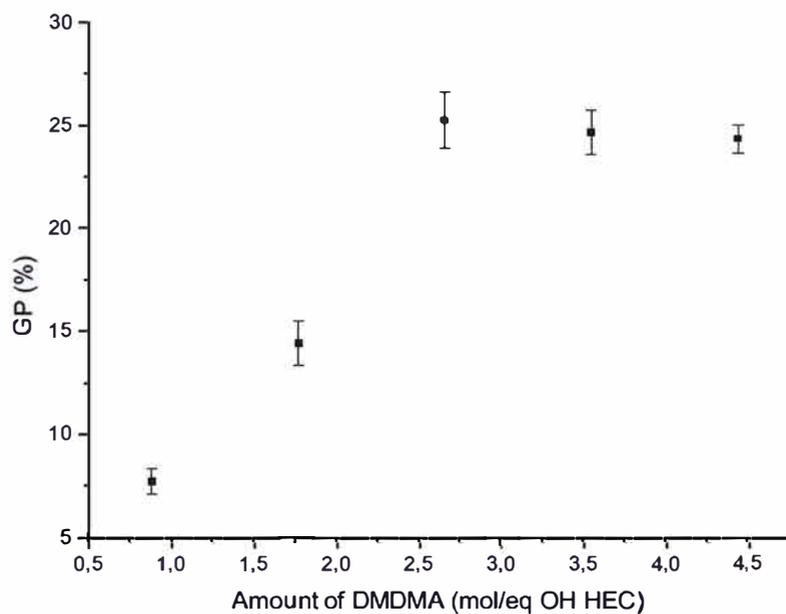


Figure 4. Grafting yield (expressed as weight gain) evolution with the molar amount of DMDMA.

Through this part, the amount of DMDMA was varied from 0.88 to 4.43 mol/eq OH (Figure 4).

Subsequently, a gradual increase in the grafting yield is observed as the DMDMA amount increases from 0.88 to 2.66 mol/eq OH reaching a weight gain of 25.2%. Beyond 2.66 mol/eq OH, the grafting yield barely changes.

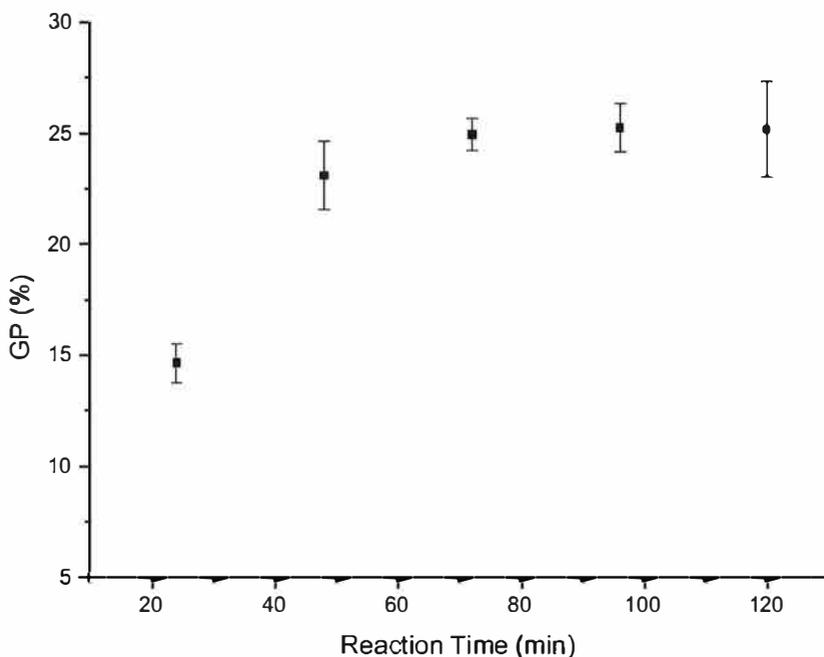


Figure 5. Grafting yield (expressed as weight gain) evolution with the reaction time.

The KPS and the DMDMA amounts were fixed at 7.51 mmol/eq (OH) and 2.66 mol/eq(OH) for the study of the reaction time. Five reactions conducted under identical conditions were carried out. They were stopped at different durations going from 24 to 120 minutes (Figure 5).

As shown in Figure 5, a gradual increase in the grafting rate is obtained as the reaction time increases. Beyond 72 minutes time, where the weight gain reaches 25.2%, the grafting yield reaches a plateau making fruitless the increasing of the reaction duration.

These experiments allowed us to conclude that an optimum grafting rate, equal to 25.2%, was obtained using a KPS concentration of 7.51 mmol/eq OH and 2.66 mol/eq OH of DMDMA monomer, during 72 minutes of reaction time.

The comparison between the FTIR spectra of the pristine HEC and the grafted HEC (Figure 6) showed a new peak at 1735 cm^{-1} , corresponding to the stretching vibration of the C=O bond, which is related to the ester group grafted on the HEC chains.

The detailed examination of the pristine HEC FTIR spectrum, showed a large band centered at 3434 cm^{-1} ; related to the stretching vibration of the associated hydroxyl bond OH. This band became sharper after grafting. The stretching vibration of methyne and methylene CH and CH_2 bonds appeared at 2933 cm^{-1} and 2881 cm^{-1} respectively. The band centered at 1648 cm^{-1} , is related to the water H_2O absorption distortion vibration. The two bands centered at 1462 cm^{-1} and 1351 cm^{-1} respectively are related to the distortion vibration CH_2 and the CH bonds.

The DSC thermo-grams of the studied materials were recorded and gathered on Figure 7. The glass transition temperature of the grafted HEC showed a single glass transition $T_g = 33^\circ\text{C}$, which is intermediate between the T_g values of the poly-DMDMA ($T_g = 14^\circ\text{C}$) and the pristine HEC ($T_g = 122^\circ\text{C}$), respectively. This finding confirmed the grafting process of the DMDMA on the HEC resulting in a homogeneous biopolymer. The T_g of the poly-DMDMA was found to be less than the ambient temperature. This result showed that this homo-polymer is supple and flexible.

The TGA thermo-grams of the homo-polymer poly-DMDMA and the HEC before and after the grafting process are presented in Figure 8. The decomposition temperatures of HEC and the homo-polymer were found to be 350°C and 400°C , respectively (Table 1). Their thermal

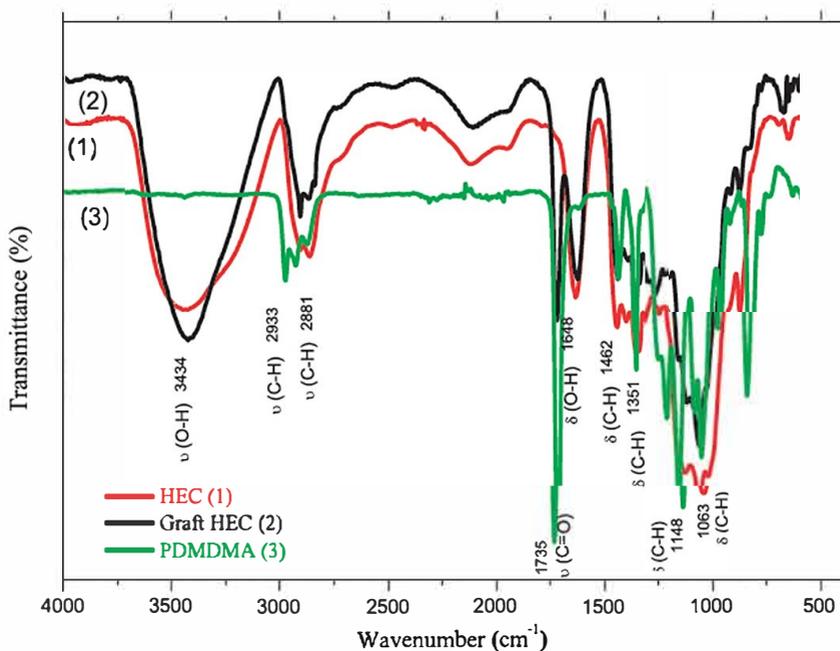


Figure 6. FTIR spectra of pristine HEC, grafted HEC and poly DMDMA.

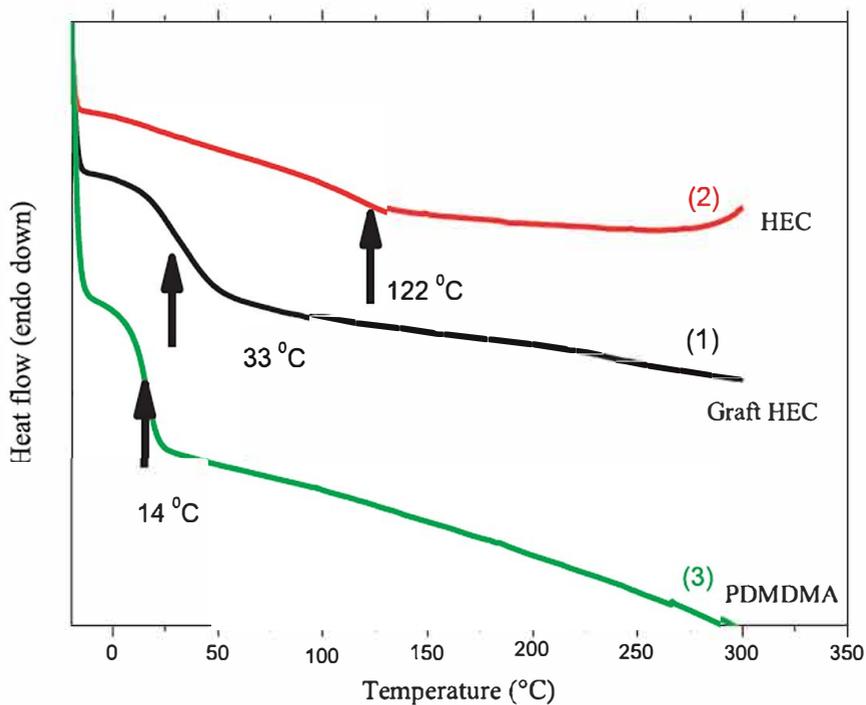


Figure 7. DSC thermo grams (2nd scan) of samples of HEC, grafted HEC and poly DMDMA.

degradation occurred in one stage. On the other side, the thermal decomposition of the grafted HEC occurred in two stages: the first one appears at 312 °C followed by the second and intense stage at 363 °C related to a random break of C–C bonds over the main chains. This second maximum temperature of total decomposition of the grafted HEC is greater than that of the pristine

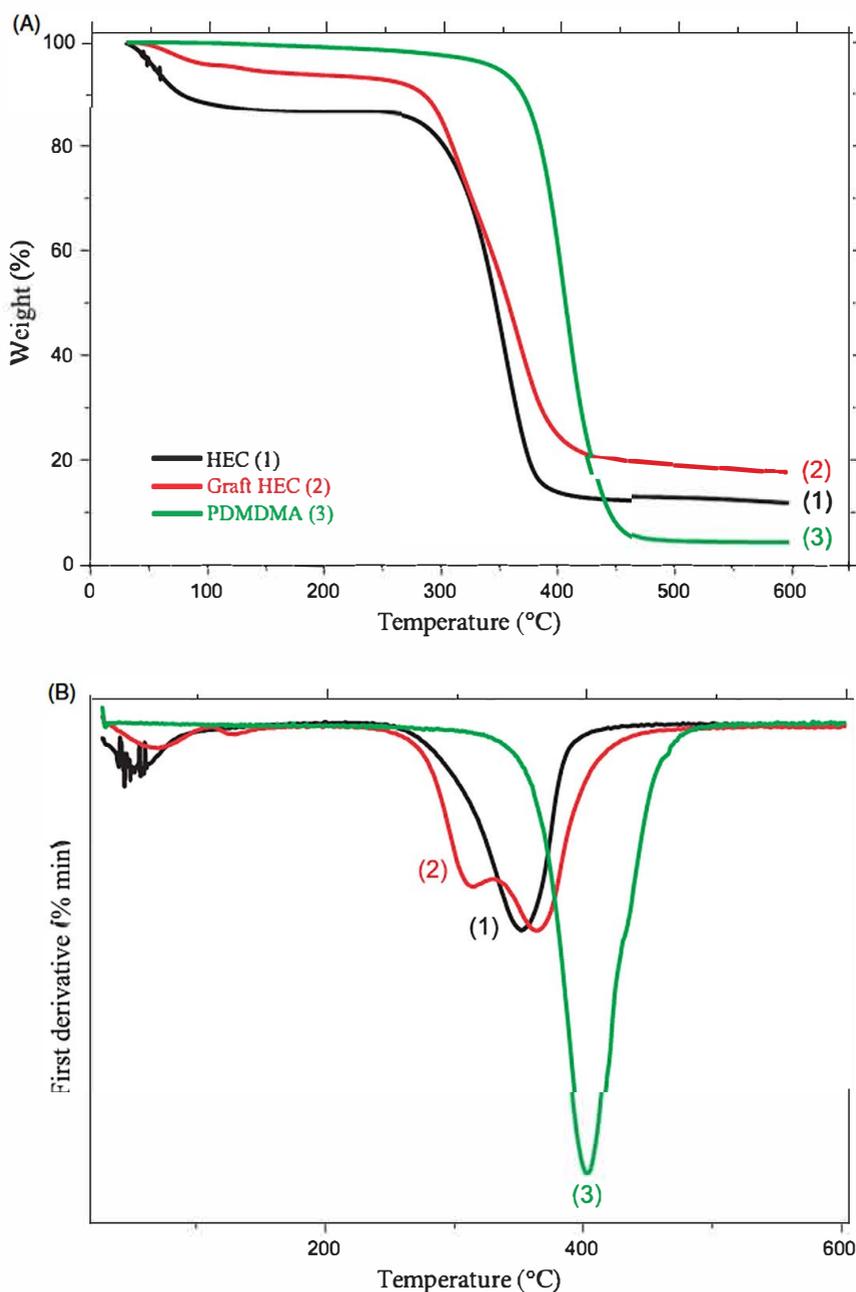


Figure 8. TGA (A) and DTG (B) thermograms of the HEC, the graft HEC and the PDMDMA.

HEC. Such difference in the thermal properties between pristine HEC and the grafted HEC confirms the chemical modification of the HEC backbone. Furthermore, the increasing in the weight loss at 600°C in the case of the grafted material (Table 1) might be attributed to the griffons' emergence on the HEC polymer.

The study of the crystallinity of the polymers was investigated by XRD analyses. Figure 9 gathers the XRD patterns of the PDMDMA and the HEC before and after the grafting process. The presence of a peak centered at 20.7° either in the HEC or in the grafted HEC was attributed to the crystallinity of both biopolymers. A new peak appeared on the grafted HEC pattern at 30.7°;

Table 1. Glass transition and decomposition temperatures of HEC, grafted HEC and poly DMDMA.

	$T_g(^{\circ}\text{C})^a$	Onset decomposition temperature ($^{\circ}\text{C})^b$	$T_{max}(^{\circ}\text{C})^c$		Residual Wt(%) ^d
HEC	122	249	350		12
Grafted HEC	33	247	312	363	18
PDMDMA	14	325	400		4

^aGlass transition temperatures obtained at the onset of the DSC thermo grams.

^bDegradation temperature of the first step of decomposition obtained by TGA analyses.

^cMaximum degradation temperature of the last step of decomposition obtained by TGA.

^dResidual weight loss at 600 $^{\circ}\text{C}$.

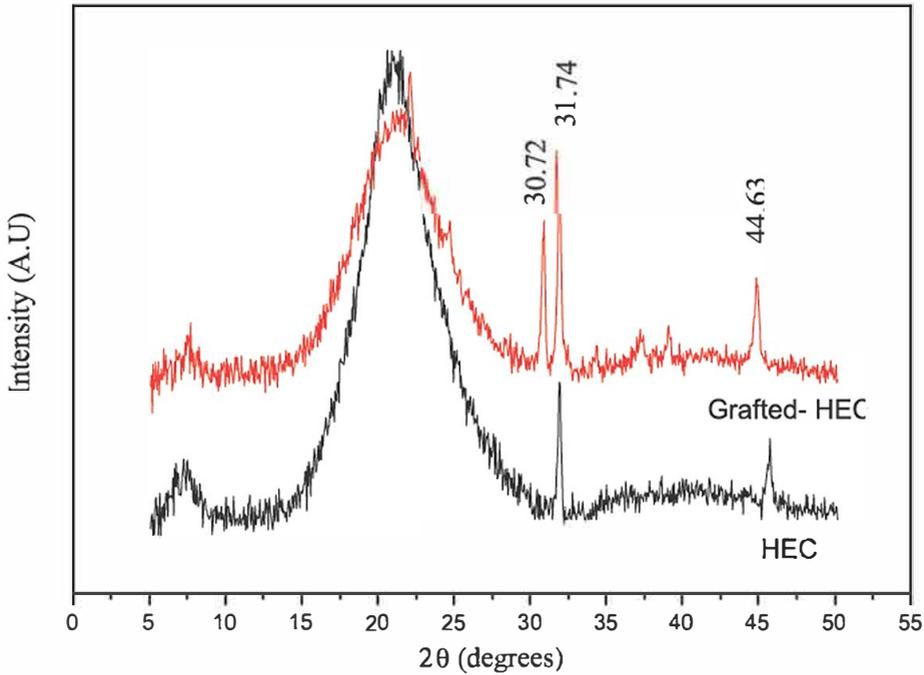


Figure 9. DRX of HEC and grafted HEC.

it might correspond to a new crystallinity induced by the presence of the side-chains of the poly-DMDMA on the HEC fibers.^[16] A reduction of 30% in the crystallinity index after grafting was determined by Eq. (3).^[22] Such results may confirm the crystal-structure modification of the HEC in the grafted HEC.

$$CI = \frac{I_{002} - I_{am}}{I_{002}} \cdot 100 \quad (3)$$

The examination of the SEM images, shown in Figure 10, proved a pronounced morphological variation between the two materials. The image of these group was completely different from the one represented by the grafted HEC. Such variety is due to the input of poly-DMDMA on the HEC surface. Consequently, SEM images showed clearly the morphological change before and after the grafting process.

Finally, the moisture absorption properties of HEC and the grafted HEC materials were investigated and the corresponding values were gathered in Figure 11. As we can see, no significant difference in moisture absorption of HEC showed after 24 h and 48 h (i.e., 9.8% and 10.5% respectively). On the other hand, the grafted HEC moisture absorption was 18.4% and 25% after 24 h and 48 h. Such behavior can be explained by the fact that water molecules were accessible to

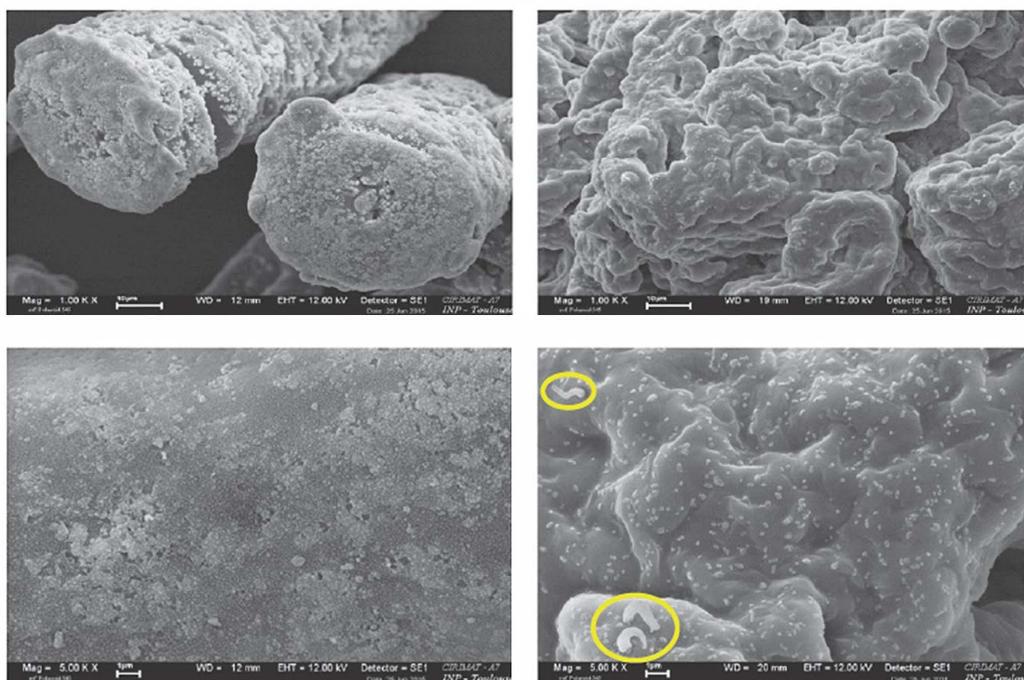


Figure 10. MEB images of HEC (left) and HEC graft PDMDMA (right). Upper row: magnification $\times 1000$; lower row: $\times 5000$.

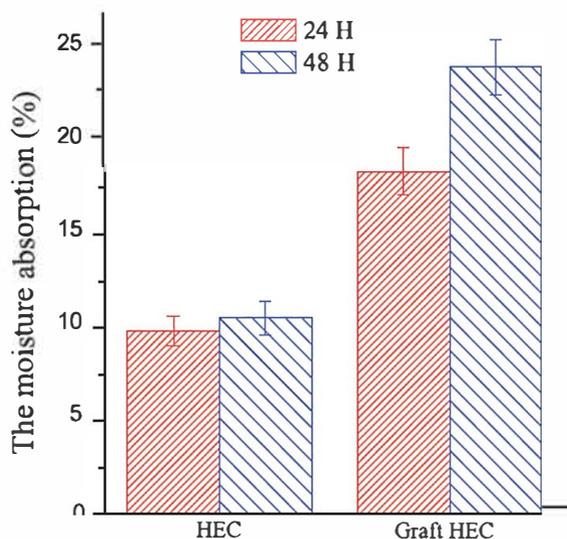


Figure 11. Moisture absorption of HEC and grafted HEC.

the surface of the cellulose and readily developed hydrogen bond interactions^[20] which increased two-fold the values of the moisture absorption in the grafted HEC by comparison to the initial HEC.

Conclusions

In this paper, we reported the grafting polymerization of 2,2-dimethyl-1,3-dioxolan-4-yl methyl acrylate on hydroxyethyl-cellulose by radical polymerization reaction using potassium persulfate

as initiator. The experimental protocol allowed us to conclude that in the optimum conditions the grafting rate was equal to 25.2%, using 7.51 mmol/eq OH of KPS and 2.66 mol/eq OH of the monomer DMDMA, during 72 minutes at 65 °C in the presence of THF. The SEM pictures showed a morphological modification of the HEC fibers. The obtained copolymer structure modification was confirmed by FTIR and X-Ray diffraction (XRD) analyses. Furthermore, the water adsorption tests showed that the grafted HEC has increased hydrophilic characteristics. Furthermore, results showed the grafted biomaterial presented two-fold more moisture absorption ability by comparison with HEC, making this new synthetic biomaterial highly promising for dryness applications.

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