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Synthesis of *graft*-copolymers from palm cellulose and solketal acrylate and their characterization

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ABSTRACT

The use of partially biobased monomers to functionalize palm cellulose via *graft*-copolymerization was explored. The aim of this work is to recycle a waste, the leaves of palm trees, which are abundant in North African countries in order to obtain novel cellulose derivatives having interesting physico-chemical properties. Furthermore, the monomer that was used for the *graft*-copolymerization was synthesized from a biobased synthon, glycerol. The synthesis of *graft*-copolymers from cellulose and (2,2-dimethyl-1,3-dioxolan-4-yl)methyl acrylate (solketal acrylate, DMDMA) was studied to determine the optimal conditions for grafting. The maximum grafting weight gain was 27% obtained after 72 min of reaction at 65 °C with 6.4 mmol KPS/eq OH and 1.51 mol DMDMA/eq OH. THF, used as dispersion solvent, hinders the homopolymerization side-reaction by creation of terminating radicals. FTIR spectroscopy confirmed the grafting of monomers to cellulose and X-ray diffraction revealed an organized structure of the side-chains. Thermogravimetry showed that the grafting could not confer a higher thermal stability to cellulose (loss of 35 °C in the decomposition temperature). Even though partial melting was observed when thermopressed, DSC analysis could not show a neat glass transition temperature but rather multiple exothermal peaks attributed to side-chains reorganization. Thermopressed grafted samples showed improved mechanical properties compared to palm cellulose.

1. Introduction

Interest in the chemical modification of cellulose has never decreased, with a view to enlarging the field of applications of this inexpensive and abundant biopolymer. The *graft*-copolymerization of monomers onto cellulose is one way to link two entities with different physicochemical properties within the same macromolecule. The result is a branched polymer in which the principal chain consists of cellulose and the lateral chains are formed from another oligomer or polymer, the length of the latter depends on the reaction conditions.

Grafting can be used to improve certain physicochemical properties of cellulose (Roy et al., 2009; Kang et al., 2013, 2015). Thermoplasticity or solubility is expected to be attained due to the diminution of hydrogen bonding during grafting, but at the same time, these properties largely depend on the nature and size of the side-chains and their statistical distribution along the backbone chain. To the best of our knowledge, there is no model to predict the resulting properties of the *graft*-polymer.

In this context, graft polymerization has been envisaged to create new materials with improved chemical and physical properties and to match various specifications. For example, self-assembled micelles can be obtained from cellulose graft copolymers and be used as carriers for drug and gene controllable delivery (Xu et al., 2010). The surface graft modification of cellulosic materials has also been envisaged using various monomers to produce adsorbents for removal of toxic ions (O'Connell et al., 2008; Wojnárovits et al., 2010; Tian et al., 2011), antibacterial surfaces (Roy et al., 2008) and additives to reinforce composites (Cao et al., 2009).

In this work we selected a partially-biobased vinyl monomer to react with cellulose: (2,2-dimethyl-1,3-dioxolan-4-yl)methyl

Abbreviations: DMDMA, 2,2-dimethyl-1,3-dioxolan-4-yl methyl acrylate; GP, grafting percentage; KPS, potassium persulfate; THF, tetrahydrofuran; TEA, triethylamine; NMR, nuclear magnetic resonance; FTIR, Fourier transform infrared; XRD, X-ray diffraction; TGA, thermogravimetric analysis; SEM, scanning electron microscopy.

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Table 1
ADF-NDF composition of cellulosic raw materials.

	Raw palm leaves (ground)	Extracted cellulose from palm leaves
Dry matter (%)	91.8	93.5
Cellulose (%)	49.6	87.4
Lignin (%)	23.2	2.1
Hemicellulose (%)	17.1	0.0

acrylate (solketal acrylate, DMDMA), a derivative of glycerol and acrylic acid that never has been used, to our knowledge, for *graft*-polymerization on cellulose. Recent studies have reported the use of other types of vinyl monomers for radical polymerization processes for cellulose (or other polysaccharides) grafting (Tosh and Routray, 2014). These monomers include acrylic acid (Hajeeth et al., 2013; Halib et al., 2014), ethyl acrylate (Thakur et al., 2013d; Zampano et al., 2009), methyl methacrylate (Wan et al., 2011), methyl acrylate (Thakur et al., 2013b), glycidyl methacrylate (Anirudhan et al., 2009), butyl acrylate (Thakur et al., 2013a,c), acrylonitrile mixed to styrene and to butanediene (Ma et al., 2015), acrylonitrile (Lv et al., 2009), acrylamide (Ye and Yang, 2015), 4-vinylpyridine (Dhiman et al., 2008) and *N*-vinylpyrrolidone (Gupta and Sahoo, 2001; Ibrahim et al., 2002).

Another important choice in this work was the cellulose source. *Graft*-polymerization studies have been carried out on cellulose of different origins such as bacterial (Mohd Cairul et al., 2012), nanocrystalline (Ma et al., 2015) or microcrystalline cellulose (Tao et al., 2009) as well as cellulose fibers from wood (Zampano et al., 2009) or cotton (Amatjan et al., 2014). In the present work we chose cellulose extracted from a natural resource cultivated abundantly in North Africa: palm tree. Chehma and Longo (2001) estimated the number of date palm trees to 10 millions in Algeria. Boudjelal and Nancib (2001) reported that 60 thousand tons per season of date palm fruits waste are available. This gives an idea of the potential availability of palm tree leaves rich in cellulose (almost 50%).

The accessibility of hydroxyl groups is one of the main concerns when a cellulose source is to be selected. In some cases, the cellulose is subjected to pretreatment before the reaction such as solvent-exchange (McCormick and Dawsey, 1990). Another approach is starting from a functional derivative such as cellulose acetate or carboxymethylcellulose, in which the accessibility of the hydroxyl groups is higher (Toledano-Thompson et al., 2005).

Summing up, the grafting and its distribution depend on the type of cellulosic raw material used, the nature of the monomer and the initiator used. For the grafting of DMDMA onto palm cellulose, we selected potassium persulfate (KPS) as initiator, as it has been reported to be efficient (Liu and Sun, 2008), soluble in water (Ghosh and Das, 2000), readily available and inexpensive. No transition metal catalysts were deliberately used.

The monomer was thus reacted onto cellulose in a heterogeneous environment, as in most previous reports. The monomers were expected to be preferentially attached to amorphous regions of cellulose, whereas the crystalline regions should be less modified due to the hydrogen bonds between the hydroxyl groups.

The effects of reaction time and reactant amounts on grafting rates were studied. The synthesized molecules were analyzed: the structure of the monomer was determined by NMR and FTIR spectroscopy. The extracted cellulose and its grafted copolymers were characterized by FTIR spectroscopy, X-Ray Diffraction, SEM Microscopy and thermal analyses.

2. Experimental

2.1. Materials and methods

1,2-*O*-Isopropylidene glycerol (solketal, 98% [100-79-8]), acryloyl chloride, potassium persulfate (99%), magnesium sulfate (97%), dichloromethane (99.8%), tetrahydrofurane (inhibitor-free) (99.9%) and hydrogen peroxide (30%) were supplied by Sigma-Aldrich. Triethylamine (99%) and sodium bicarbonate (99%) were supplied by Acros Organics. Sodium hydroxide (97%) was supplied by Carlo Erba. Ethanol (99.9%) was supplied by VWR. Toluene (99.9%) was supplied by Fluka. All reagents were used directly, without prior purification.

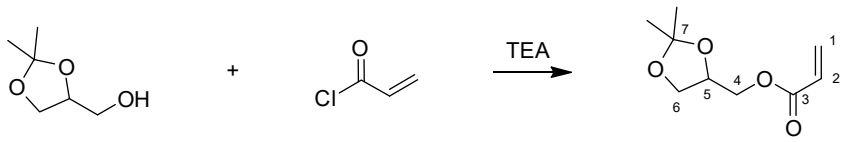
2.2. Cellulose extraction

The cellulose was obtained by chemical treatment of palm leaves collected from *Washingtonia filifera* palm trees cultivated in Algeria using different organic solvents. These treatments are intended to remove any other components present in this plant.

Thus at first, the palm leaves were ground and washed several times with distilled water and dried at 80 °C for 12 h, thereafter fat was removed by Soxhlet extraction with a mixture of ethanol and toluene (1/2, v/v), (Moran et al., 2008). Palm leaves were treated subsequently with an aqueous sodium hydroxide solution at different concentrations (18%, 10%, and 2%). Finally, the cellulose fibers were obtained after a bleaching treatment using a hydrogen peroxide solution (5%) at 60 °C for 4 h (Jiang et al., 2011) then washed with distilled water and dried at 40 °C for 12 h. The Van Soest and Wine (1967)'s ADF-NDF analysis of the raw palm leaves and palm extracted cellulose revealed the compositions shown in Table 1.

2.3. Synthesis of (2,2-dimethyl-1,3-dioxolan-4-yl)methyl acrylate (DMDMA, [13188-82-4])

A 250 mL round-bottom flask equipped with a magnetic stirrer and a dropping funnel was charged with 5.0 g (37.9 mmol) of solketal (racemic mixture), 4.6 g (45.5 mmol) of triethylamine and 80 mL of CH_2Cl_2. The reaction mixture was cooled to 0 °C. A solution of 4.1 g (45.5 mmol) of acryloyl chloride in 20 mL of CH_2Cl_2 was added dropwise, via the dropping funnel, over a period of 2 h. The reaction mixture was stirred continuously, with the magnetic stirrer, for 16 h, at room temperature. Triethylamine chlorhydrate salts were eliminated from the solution by filtration and the filtrate was washed with a 10% (w/w) aqueous solution of $NaHCO_3$. The organic phase was then dried with magnesium sulfate and filtered. The solvent was eliminated by rotary evaporation. The DMDMA was then purified by vacuum distillation (at 12 mbar). DMDMA was obtained with a yield of 90%, as a colorless oil. NMR spectra were acquired on a Fourier 300 (300 MHz) spectrometer from Bruker Corporation (Karlsruhe, Germany): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45 (dd, J = 17.3, 1.5 Hz, 1H, H-1), 6.16 (dd, J = 17.3, 10.4 Hz, 1H, H-2), 5.86 (dd,



Scheme 1. Synthesis of the DMDMA monomer (Sousa et al., 2011; Moity et al., 2015).

J = 10.4, 1.5 Hz, 1H, H-1), 4.40-4.32 (m, 1H, H-5), 4.26 (dd, J = 11.5, 4.6 Hz, 1H, H-4 or H-6), 4.18 (dd, J = 11.5, 5.9 Hz, 1H, H-4 or H-6), 4.10 (dd, J = 8.5, 6.4 Hz, 1H, H-4 or H-6), 3.78 (dd, J = 8.5, 6.1 Hz, 1H, H-4 or H-6), 1.44 (s, 3H, CH_3), 1.38 (s, 3H, CH_3) (Scheme 1). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1 (C-3), 131.5 (C-1), 128.1 (C-2), 110.0 (C-7), 73.8 (C-5), 66.5 (C-4/6), 64.9 (C-4/6), 26.8 (CH_3), 25.6 (CH_3).

2.4. Synthesis of poly-DMDMA (PDMDMA homopolymer)

A 100 mL triple-neck round-bottom flask equipped with a nitrogen line, a magnetic stirrer, a cooler and a dropping flask was charged with 6.5 g (35 mmol) of DMDMA. The flask was then immersed in a water bath maintained at 65 °C with a thermostat. 4 mL of an aqueous solution (0.4% w/w) of KPS were added dropwise whilst bubbling nitrogen through the mixture. After 2 h at 65 °C, the reaction mixture was cooled to 0 °C. The purified homopolymer was then obtained after several washes with THF and oven-drying at 50 °C for 14 h. Comparison of the FTIR spectra of the DMDMA monomer and the prepared homopolymer clearly showed a disappearance of the bands corresponding to the elongation vibration and deformation of the carbon–carbon double bond (1643 cm^{-1} and 1417 cm^{-1}, respectively) indicating lack of unreacted monomer (Fig. 1).

The homopolymer, PDMDMA, was then characterized by differential scanning calorimetry (DSC). The thermogram showed a glass-transition temperature of 11 °C. The flexible nature of the polymer observed at room temperature comforted this measurement. Surprisingly, the obtained homopolymer was not soluble in any of the common organic solvents, indicating probably a very high molecular weight, which could not be quantified due to insolubility.

2.5. Graft-copolymerization of DMDMA onto cellulose

A 50 mL triple-neck round-bottom flask equipped with a nitrogen line, a cooler and a dropping flask was charged with 500 mg (9.3 meq OH) of extracted cellulose in 20 mL of THF. The resulting mixture was stirred at room temperature for 3 h.

The flask was then immersed in a water bath maintained at 65 °C with a thermostat. 4 mL of an aqueous solution of KPS and then the DMDMA were added to the reaction mixture. In our experiments, the added amount of KPS was varied from 0.8 to 12.8 mmol/eq OH, and the amount of monomer, from 1 to 5 mL (0.75–3.77 mol/eq OH). Nitrogen was bubbled through the resulting reaction mixture for 2 h. The reaction mixture was then cooled on ice. The *graft*-copolymer (Scheme 2) was recovered by filtration followed by several washes with THF. It was then dried at 50 °C for 14 h.

The grafting percentage (GP) was calculated as Dhiman et al. (2008) and Lin et al. (2013) suggest:

$$GP\,(\%) = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 and W_1 are the weights of the cellulosic polymers before and after *graft*-copolymerization, respectively.

2.6. Characterization of the monomer, the homopolymer and the graft-cellulose

2.6.1. Nuclear magnetic resonance (NMR) spectroscopy

NMR spectra were acquired on a Fourier 300 (300 MHz) spectrometer from Bruker Corporation (Karlsruhe, Germany). Samples were dissolved in $CDCl_3$. Chemical shifts were relative to tetramethylsilane at 0 ppm. Standard pulse sequences were used for ^{1}H

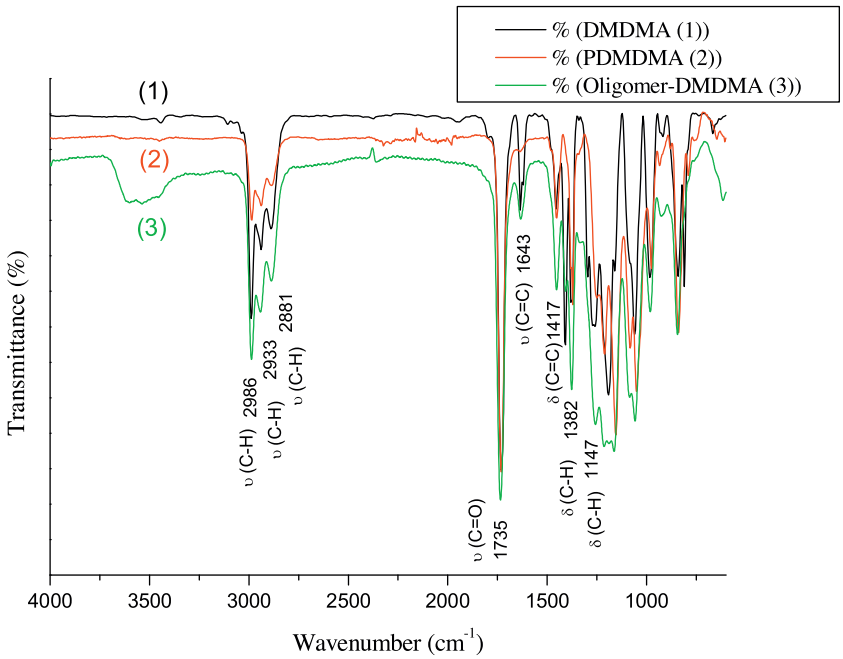
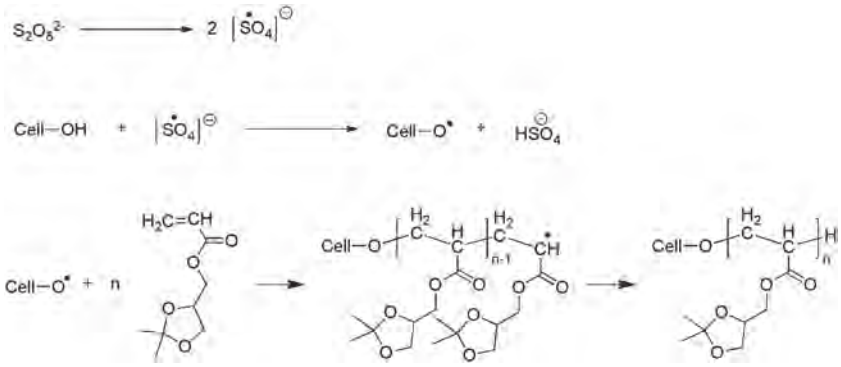


Fig. 1. FTIR spectra of DMDMA (1, monomer), PDMDMA (2, homopolymer) and a mixture of oligomer and DMDMA (3).



Scheme 2. Simplified reaction mechanism for the synthesis of cellulose-*g*-PDMDMA.

and ^{13}C NMR. Signals were assigned on the basis of DEPT135, 2D COSY and HSQC data.

2.6.2. FTIR spectroscopy

The FTIR spectra were recorded in the 500–4000 cm^{-1} range, with a Perkin Elmer Spectrum 65 device. The dry powdered samples were mixed with KBr at a concentration of 7%.

2.6.3. Thermogravimetric analysis

Thermogravimetric analyses of the initial cellulose derivatives and graft copolymers were performed with a Mettler Toledo TGA (Stare system) between 30 and 600 °C, at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.6.4. Differential scanning calorimetry

Around 10 mg of sample for analysis was weighed and placed in an aluminum capsule, which was then sealed. Analyses were carried out on a Jade Perkin Elmer machine, between −40 and 300 °C, with a temperature ramp of 10 °C/min under a nitrogen atmosphere.

2.6.5. X-ray diffraction studies

The X-ray diffraction (XRD) curves of the initial cellulose and graft copolymers were recorded on a Rigakuminiflex II (Japan) X-ray diffractometer, with a Cu K target, at 30 kV and 15 mA. The diffraction angle ranged from 5° to 40° (0.05°/min).

2.6.6. Scanning electron microscopy

The samples were deposited on metal grids and covered with araldite epoxy resin. The product was well insulated, so the surfaces were rendered conductive by the deposition of a layer of silver several nanometers thick with an Edwards Scancoat SIX metallizing device. A morphological analysis of the samples was carried out under a LEO 435VP scanning electron microscope.

2.6.7. Mechanical properties

Palm cellulose and corresponding graft copolymers were thermopressed at 180 °C under 100 bar for 10 min. The thermopressed sheets were used to get six specimens sized 50 × 15 mm. A metal spacer was used to produce sheets of about 1 mm (Mangavel et al., 2004). The real thickness was measured at five points with a digital micrometer (model IDC-112B, Mitutoya Corp., Tokyo, Japan) and the mean value was recorded. After conditioning the sheets at 25 °C and 60% R.H. for one week, a TA-XT2 texture analyzer (RHEO Stable

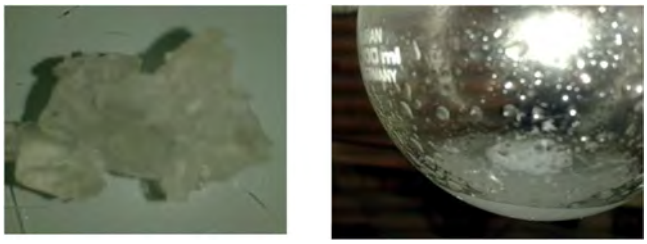


Fig. 2. (left) PDMDMA homopolymer obtained in solvent-free conditions, (right) viscous liquid obtained in the flask after synthesis in THF (magnetic stirring) and evaporation of the solvent.

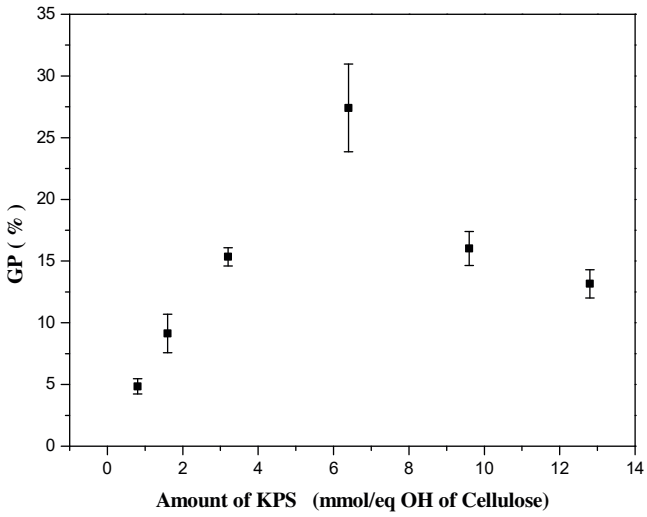
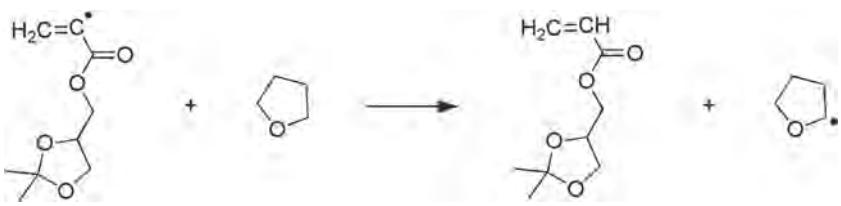


Fig. 3. Variation of grafting percentage with the molar amount of potassium persulfate.



Scheme 3. Competitive reactions during the polymerization reaction in the presence of THF.

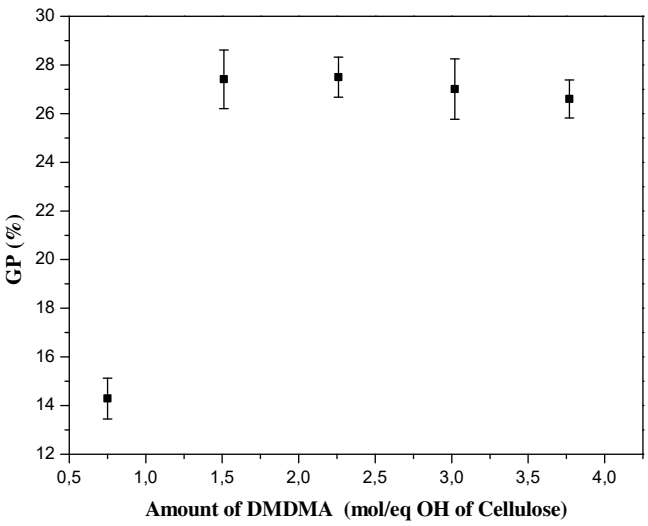


Fig. 4. Variation of grafting percentage with the molar amount of DMDMA.

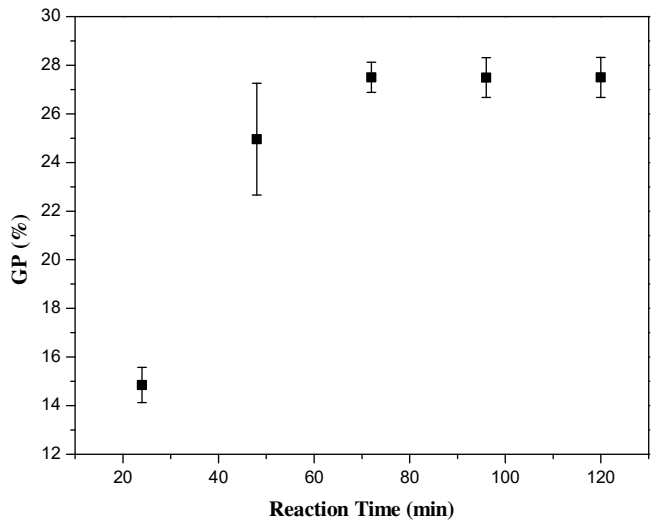


Fig. 5. Variation of grafting percentage with reaction time.

Micro Systems, London, UK) was used to assess their mechanical properties. Stress–strain measurements were carried out to determine tensile strength (σ_{max}) and elongation (ε_{max}) at break value. A speed of 1 mm s^{-1} was used, with an initial grip separation of 55 mm, as described in standards.

3. Results and discussion

The DMDMA was first prepared by reacting solketal with acryloyl chloride in the presence of triethylamine. This vinyl monomer was obtained in 90% yield after purification by vacuum distillation.

The PDMDMA homopolymer was then obtained by radical polymerization reaction with the use of KPS as initiator and in the absence of solvent. The obtained solid product (Fig. 2 left) was supple and elastic when hand-pulled.

Since *graft*-polymerization of cellulose uses THF as dispersion solvent, we attempted the synthesis of homopolymer under the same operation conditions (see Section 2.4) in the presence of THF (20 mL). After 2 h of reaction at 65 °C, and contrarily to the previous experiment, no solid product was obtained. The removal of THF with a rotary evaporator yielded a viscous liquid (Fig. 2 right). According to FTIR data shown in Fig. 1 (3), the liquid consisted of some oligomers (significant diminution of the C=C 1643 cm^{-1} band) solubilized in monomer.

DMDMA monomer polymerizes by a radical reaction by the association of radicals created by the initiator KPS (Scheme 2). However, in the presence of an important number of THF molecules, a competing reaction with a stable radical THF• comes into play to

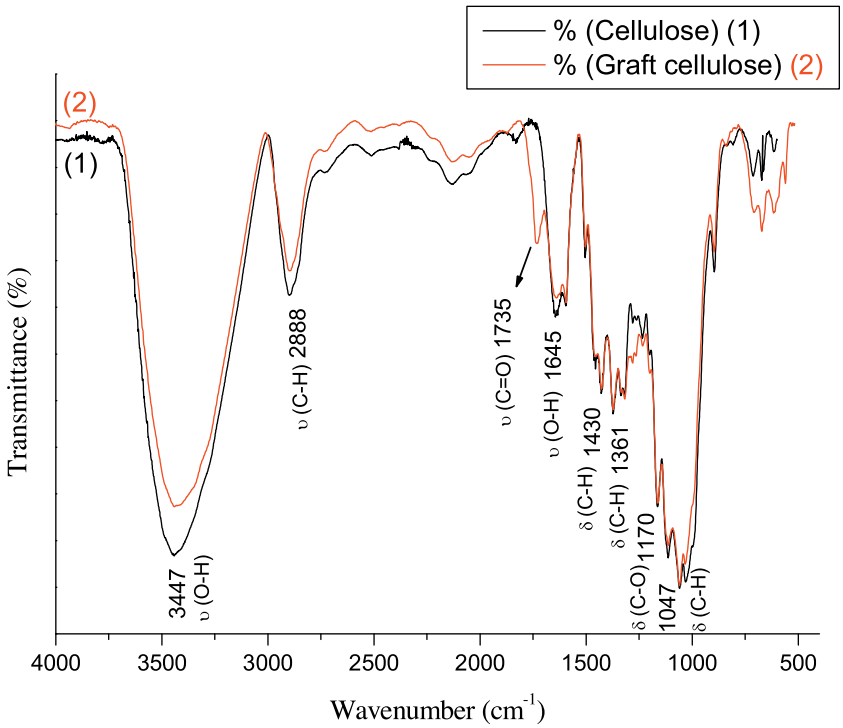


Fig. 6. FTIR spectra of palm cellulose before and after grafting of DMDMA.

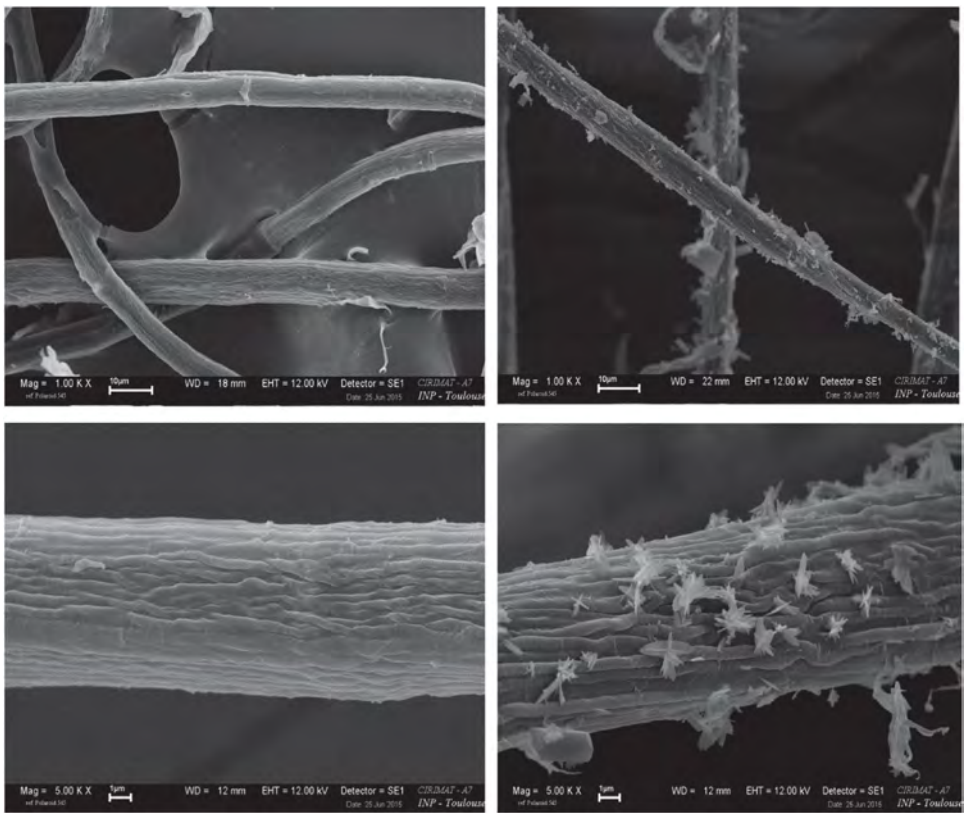


Fig. 7. SEM images of palm cellulose (left) and PALM cellulose-g-PDMDMA (right). Upper row: magnification ×1000, lower row: ×5000.

inhibit the homopolymerization reaction (Scheme 3), giving statistical priority to the formation of oligomers with a low molecular weight.

The question now is: how will the presence of THF affect the *graft*-polymerization? Grafting only a few monomers on the side-chains can be enough to modify the properties of the cellulose polymer. Thus, the DMDMA monomer was used for a *graft*-copolymerization reaction on cellulose, a reaction that has never, to the best of our knowledge, been studied before. A suspension of extracted cellulose in THF was stirred for 3 h at 65 °C. An aqueous solution of KPS as a radical initiator recently used for the *graft*-copolymerization of cellulose with acrylic acid (Toledano-Thompson et al., 2005), followed by 3 mL of the DMDMA monomer, were added dropwise to the flask, at 65 °C. The molar ratio of KPS/eq OH was varied to investigate the effect of this experimental parameter on the reaction and, in particular, on the rate of grafting of the DMDMA polymer onto cellulose (Fig. 3).

The experiments were duplicated and quite reproducible. The grafting rate appeared to increase with the amount of KPS, eventually reaching 27% for a ratio of 6.4 mmol KPS/eq OH. Beyond this value, the grafting rate decreased significantly, possibly due to the tendency of DMDMA to undergo preferential homo-oligomerization when monomer radicals become abundant as KPS renders them readily available.

In another series of reactions, we set the number of moles of KPS to 6.4 mmol/eq OH, which led to the highest rate of grafting and we varied the number of moles of DMDMA monomer from 0.77 to 3.77 mol/eq OH in the reaction medium. The curve illustrating the variation of grafting according to the amount of monomer is shown in Fig. 4. A gradual increase of grafting percentage was obtained, until arriving at the monomer amount of 1.51 mol/eq OH in the reaction medium, reaching 27% in GP. Beyond this value, the amount of monomer had no effect, and the grafting rate remained constant.

We analyzed the effect of reaction time on copolymerization, by fixing the amounts of KPS (6.4 mmol/eq OH) and monomer (1.51 mol/eq OH) at values favoring grafting onto cellulose and varying the reaction time from 24 to 120 min.

The effect of reaction time on grafting rate is clearly illustrated in Fig. 5. There was a progressive increase in yield for the first 72 min. Thereafter, the weight gain remained practically constant (27%).

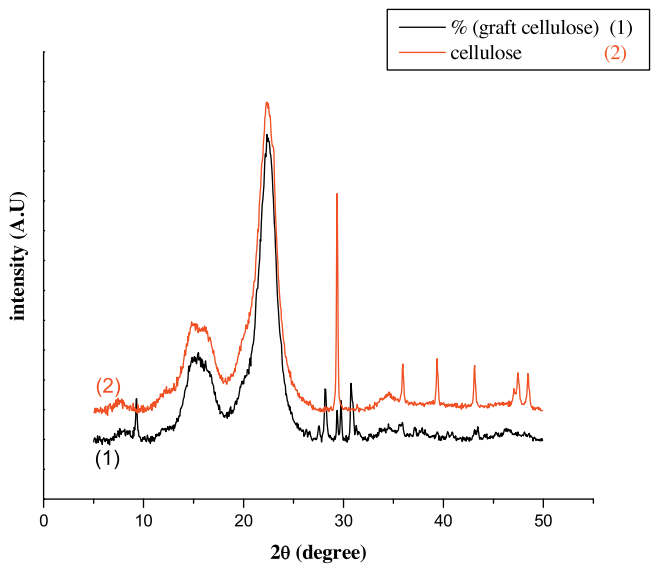


Fig. 8. X-ray diffraction spectra of palm cellulose before and after grafting.

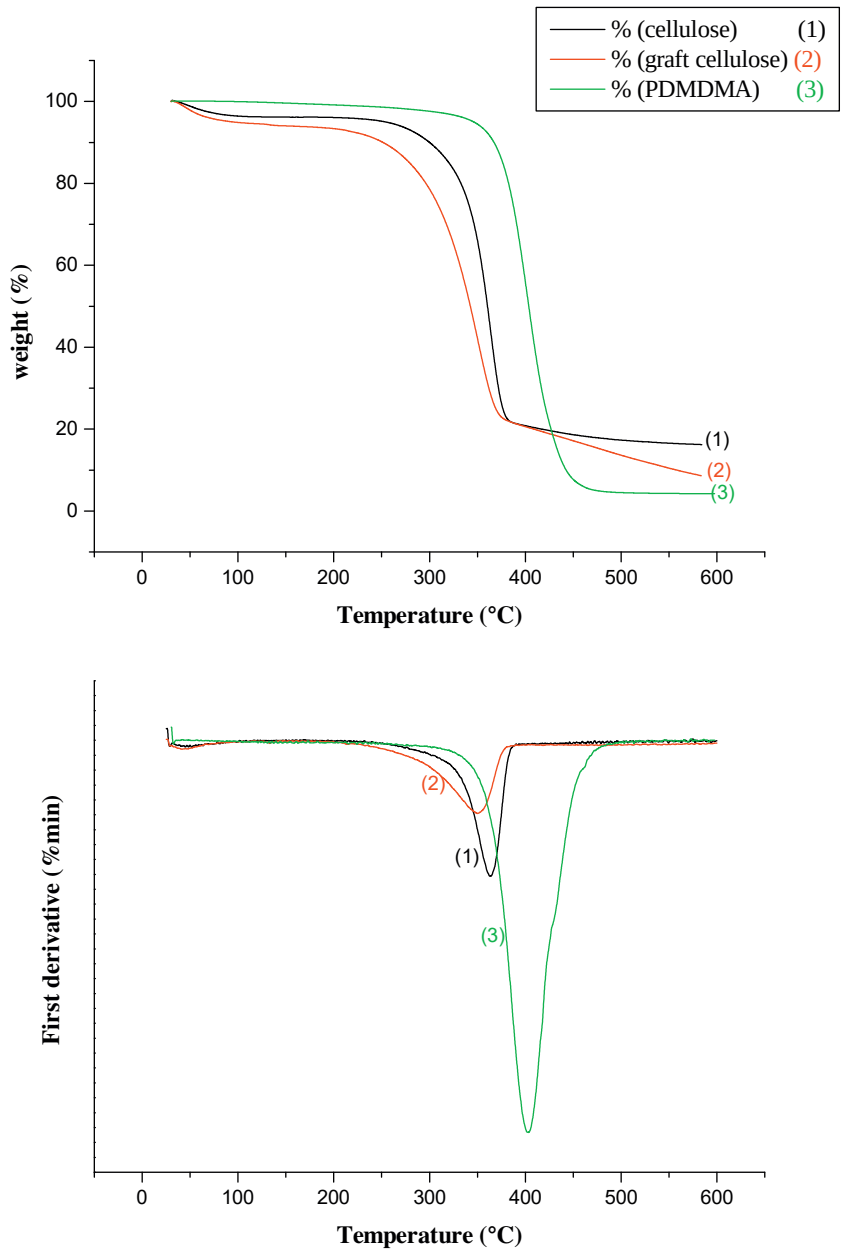


Fig. 9. TGA and DTG thermograms of samples of PDMDMA, cellulose and cellulose-*g*-PDMDMA.

We can therefore conclude that each of the three factors studied — the molar quantity of KPS, the molar quantity of monomer and the reaction time — have a direct effect on the grafting percentage. The tendencies for these parameters are difficult to predict.

The best grafting rates were obtained after a reaction time of 72 min in the presence of 6.4 mmol/eq (OH) of KPS and 1.51 mol/eq (OH) of monomer.

A comparison of the FTIR spectra of the palm cellulose, used as raw material, and the grafted cellulose (Fig. 6) revealed a new band at 1735 cm^{-1} in the grafted cellulose spectrum corresponding to the elongation vibration of the C=O bond of the ester group present in the moieties grafted onto the cellulose backbone. This band corresponded to that observed on the spectrum of the synthesized PDMDMA homopolymer. But as we showed above (Fig. 2), there is no significant homopolymer formation when reaction takes place in the presence of THF. The ester band corresponds therefore to the grafted side-chains.

Morphological features of the various obtained samples were then analyzed by scanning electron microscopy (SEM). The SEM images (Fig. 7) revealed a major difference between cellulose and grafted cellulose. The surface of the cellulose was smooth, ordered and appeared to be homogeneous. By contrast, the surface of the grafted cellulose appeared to be more heterogeneous and covered with clusters resulting from the grafts attached during the polymerization reaction.

The palm cellulose used as the starting material and the grafted cellulose were then characterized by X-ray diffraction XRD (Fig. 8).

In these two cases, we obtained diffraction lines for 2θ of about 16° and 22.4°. These lines correspond to the diffraction of cellulose designating planes ($1\bar{0}1$) and (002) of the cellulose (Kaushik and Singh, 2011). New diffraction lines of low intensity appeared at around 30° on the spectrum for grafted cellulose, suggesting a new organized structure attributed to the grafting of DMDMA side-chains to the cellulose backbone. Nevertheless, the grafted

Table 2
Decomposition temperature of cellulose, grafted cellulose, and PMDMA.

	Onset decomposition temperature (°C)	Temperature of maximum rate of mass change (°C)
Cellulose	250	360
Grafted cellulose	220	349
PDMDMA	325	400

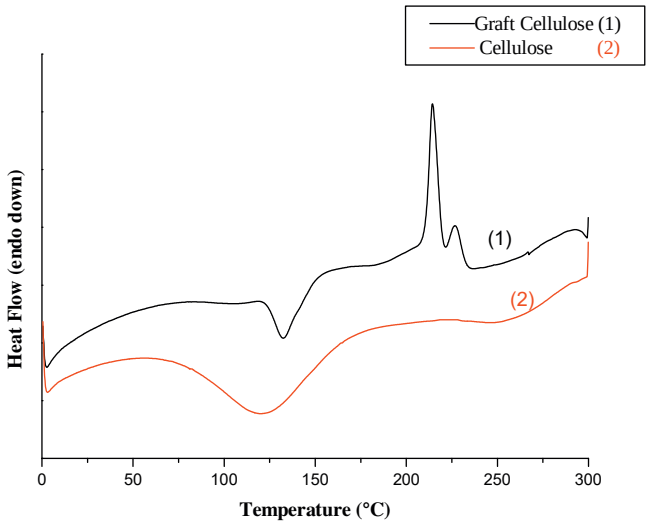


Fig. 10. DSC thermograms (2nd run) of samples of cellulose and cellulose-*g*-PDMDMA.

cellulose had a lower thermal stability than cellulose (Fig. 9). It began to break down at a lower temperature (220 °C, Table 2) than cellulose (360 °C). These results were compared with those obtained for PDMDMA. The thermal decomposition of PDMDMA occurs at 325 °C, but when DMDMA is grafted to cellulose, the thermal resistance is not increased. It becomes evident that the grafted side-chains are too short to improve the thermal resistance of cellulose and consequently, the organized segments observed by X-ray spectroscopy can correspond to the stacking of the pending groups (solketal ester moiety) in two or more neighboring DMDMA grafted monomers (Scheme 2).

Differential scanning calorimetry was conducted with rising temperature from 0 to 100 °C, then cooled and heated again from 0 to 300 °C at 10 °C/min. In the second run we could not observe a distinguishable glass transition for the *graft*-cellulose (Fig. 10). Instead, a first endothermal peak at around 130 °C and two exothermal peaks between 210 and 230 °C were observed, that is, quite below its decomposition temperature. These three peaks were absent in the homopolymer DSC diagram (not shown), which showed only a glass transition at 11 °C. The 130 °C peak could be attributed to melting. However, the complex statistical structure of the *graft*-copolymer can be subjected to internal rearrangements of the lateral side-chains revealed by the exothermal peaks.

When the sample of grafted palm cellulose was subjected to thermopressing, partial melting, observable by the naked eye, occurred (Fig. 11). The mechanical properties of the obtained thermopressed sheets are shown in Table 3.

Even though the mechanical resistance is roughly twenty times lower than other cellulose derivatives such as cellulose acetate (Gedon and Fengi, 2000), the grafting of side-chains led to a significant increase in the elastic modulus accompanied by a slight increase of the tensile strength. In turn, there was also a decrease of the elongation at break, but this is a common phenomenon with the increase of the other two properties. Such low properties can be

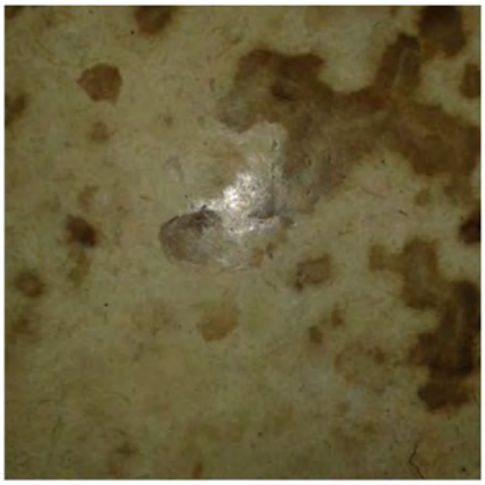


Fig. 11. Thermopressed sheet of cellulose-*g*-PDMDMA.

Table 3
Mechanical properties (tensile) of palm cellulose and grafted palm cellulose (average and standard deviation on six specimens).

	Young modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Palm cellulose	48.3 ± 20.5	1.5 ± 0.7	5.4 ± 2.1
Grafted cellulose	256.8 ± 35.5	3.1 ± 0.9	1.7 ± 0.6

explained by the partial melting leading to heterogeneous samples and a big standard deviation on six specimens.

4. Conclusion

This work was focused on the radical polymerization reaction between palm cellulose and 2,2-dimethyl-1,3-dioxolan-4-yl methyl acrylate (DMDMA) in the presence of potassium persulfate (KPS).

The maximum grafting weight gain was 27% obtained after 72 min of reaction at 65 °C with 6.4 mmol KPS/eq OH and 1.51 mol DMDMA/eq OH. If THF is used as dispersion solvent, the homopolymerization side-reactions are reduced. FTIR and TGA analyses excluded the hypothesis of a final product consisting of a mixture of homopolymer and cellulose. Organized sub-structures of the side-chains were revealed by a new peak in XRD spectroscopy and by two new exothermal peaks in DSC. The obtained adduct is partially thermoplastic and shows improved mechanical properties (modulus 5 times higher and strength 2 times higher compared to palm cellulose, but around twenty times lower than cellulose acetate). It does not possess a well-defined glass transition and its decomposition temperature is 35 °C lower than that of cellulose.

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