



# 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.

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## 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.

**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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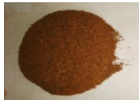

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Grafting can be used to improve certain physicochemical properties of cellulose (Roy et al., 2009; Kang et al., 2013, 2015). Thermoplasticity or solubility is expected to be attained due to the diminution of hydrogen bonding during grafting, but at 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

**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 butadiene (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. Chehema 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%), tetrahydrofuran (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<sub>2</sub>Cl<sub>2</sub>. 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<sub>2</sub>Cl<sub>2</sub> 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<sub>3</sub>. 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): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 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,

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