

RSC Advances

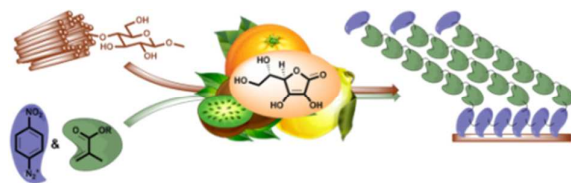


This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Table of contents entry

Cellulose sheets were grafted with several acrylic polymers, first globally through a dipping procedure and then locally by inkjet printing.

Keywords

Cellulose; Diazonium salts; Vitamin C; Graft polymerization; Inkjet printing; Eco-friendly.

ARTICLE

One-step and eco-friendly modification of cellulose membranes by polymer grafting

Cite this: DOI: 10.1039/x0xx00000x

Julie Credou, Rita Faddoul and Thomas Berthelot*,

Received 00th July 2014,
Accepted 00th July 2014

DOI: 10.1039/x0xx00000x

pubs.acs.org/Biomac

The increasing environmental awareness has stimulated the use of bio-based materials and processes. As an affordable and sustainable biopolymer, cellulose is an ideal engineering material. Beyond paper, cellulose finds applications in many areas such as composites, electronics and drug delivery. To fulfil these new functions, cellulose needs to acquire new properties, what is commonly done by graft polymerization of acrylic compounds. While cellulose modification is usually performed through complex and expensive procedures, the diazonium-based polymer grafting procedure presented here was performed in water, at room temperature, in a short single step. Cellulose sheets have been successfully grafted with several acrylic polymers, first globally through a dipping procedure and then locally by inkjet printing. The process developed herein is simple, eco-friendly and mostly time and cost-saving. More generally, it is a powerful tool for easy, robust and patterned graft copolymerization of cellulose sheets with various acrylic monomers and even bio-based monomers.

1. Introduction

The increasing environmental awareness and the growing will for sustainable technologic development have stimulated the use of biosourced materials and the development of bio-based processes worldwide. Besides, the current economic global issues have incited the search for cost-saving approaches^{1,2}. As the main material of plant cell walls, cellulose is the largest form of worldwide biomass (about 1.5×10^{12} tons per year)³. This biopolymer is therefore the most abundant organic raw material on earth¹. In addition to its large bioavailability, good biodegradability and biocompatibility, its high functionality and relatively high chain stiffness make cellulose an extremely interesting polymer⁴⁻⁸. Moreover, it is insoluble in most usual organic solvents and therefore is considered an ideal structural engineering material⁷. It swells but does not dissolve in water, hence enabling aqueous fluids and their contained components to penetrate within the fibers matrix and to wick by capillarity with no need for any external power source. In addition, cellulose sheets are available in a broad range of thicknesses and well-defined pore sizes, easy to store and handle, and lastly safely disposable⁹⁻¹¹. Furthermore, the recent impetus given to paper-based microfluidics by American, Canadian and Finnish research teams¹²⁻¹⁴ has resulted in the development of new paper-based devices for diagnostics, microfluidics, and electronics^{7,15}.

Beyond paper and cardboard, cellulose thus finds applications in many diverse areas such as composite materials, textiles, drug delivery systems and personal care products². In order to

increase its functionality and the scope of its use, modifications of cellulose biofibers are required. By introducing lots of new functional moieties in one reaction, graft polymerization enables to rapidly alter the physical and chemical properties of cellulose and increase its functionality without destroying its many appealing intrinsic properties². Many properties can be improved or added to cellulose by polymer grafting including hydrophobicity, oil repellency, antimicrobial activity, heat resistance and electrical properties, dimension stability, resistance to abrasion and wear, wrinkle recovery. As an example, polyacrylic acid may be grafted to cellulose in order to complex metal cations. If silver cation is chelated, its reduction will result in paper decorated with silver nanoparticles which will endow the membrane with antibacterial activity. All these potential additional features allow cellulose to be used for advanced material applications⁴. Cellulose graft copolymerization is usually performed by free radical polymerization of vinylic compounds in heterogeneous conditions, *i.e.* on a solid cellulose substrate with the monomer being in solution. Grafted side chains are initiated by radical formation on the cellulose backbone. This radical may originate from the homolytic bond cleavage within the glucose unit caused by high-energy irradiation for example, from the decomposition of a functional group such as peroxide, or from a radical transfer reaction initiated by a radical formed outside the cellulose backbone during a redox reaction^{2,16}. There are three kinds of approaches to covalent attachment of polymers to surfaces: (i) the “grafting-to” method, where a polymer is coupled with the functional moieties from cellulose backbone,

(ii) the “grafting-from” method, where copolymer chains grow from initiating sites on the cellulose backbone, and (iii) the “grafting-through” method, where the cellulose bears a polymerizable group, and hence acts as a macromonomer with which a smaller monomer copolymerizes. Among these three methodologies, the “grafting-from” approach is the most commonly used procedure^{2,4}. Consequently, the work presented here focuses on the widely employed “grafting-from” free radical graft copolymerization of cellulose with acrylic compounds.

Many studies have reported cellulose graft copolymerization with acrylic compounds^{17–23}. Cellulose modifications have usually been performed under harsh conditions, in organic solvent or with highly toxic compounds so far^{17–19,21}. Besides graft polymerization most often implements long-lasting, complex and / or expensive procedures such as ATRP (Atom Transfer Radical Polymerization)¹⁷, RAFT (Reversible Addition-Fragmentation chain Transfer polymerization)²⁰ and gamma irradiation initiation step^{18,20,21}. To the best of our knowledge, no cellulose modification has been done in a rather short one-step reaction and under soft conditions, *i.e.* in water and at room temperature.

Herein, a simple, fast, low-cost and eco-friendly way for graft copolymerization of cellulose sheets under soft and biocompatible conditions is presented. The cellulose modifications were performed in a single step, in water and at room temperature, in one hour or less. The cellulose modification pathway consisted in an aryldiazonium-based polymerization of acrylic monomers (GraftFastTM)^{24–26}. Two different dispensing methods were employed to impregnate cellulose sheets with copolymerization reaction mixture. Firstly, dipping was performed. Though ecologically friendly, the process produced lots of matter wastage and was therefore not economically friendly. Thus, inkjet printing was further implemented to reduce this wastage by localizing the polymerization mixture onto specific areas of the substrate. Moreover, this versatile dispensing method is considered as a competitive method for patterning flexible or rigid substrates. It is a fast, cost-effective, additive, biocompatible and environmentally friendly method for depositing thin or thick films (0.8 - 20.0 μm) according to complex patterns²⁷. Cellulose paper sheets have been successfully copolymerized (or printed and copolymerized) without damaging their intrinsic properties or even their visual aspect. Several acrylic monomers were compared. Furthermore, the inkjet printing process previously described²⁸ was proved to be an efficient method allowing the patterning of cellulose tapes with grafted polymers.

2. Experimental

2.1. Reagents and reaction materials

4-nitrobenzenediazonium tetrafluoroborate, acrylic acid (AA), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), poly(ethylene glycol) dimethacrylate (PEGDMA), L-

ascorbic acid (Vitamin C), tris(bipyridine)ruthenium(II) chloride ($[\text{Ru}(\text{bpy})_3]\text{Cl}_2$) and polyacrylic acid ($M_w = 130\,000\text{ g mol}^{-1}$) were purchased from Sigma-Aldrich (St Louis, MO, USA) and used as received. Water used in all experiments was purified by the Milli-Q system (Millipore, Brussels, Belgium). CF1 cellulose paper was from Whatman (Maidstone, Kent, UK). In the first set of experiments, substrates were dipped into polymerization solutions. In the second one, the polymerization solution was printed onto substrates using a laboratory piezoelectric drop-on-demand inkjet printer Dimatix Materials Printer DMP-2831 (Fujifilm, Santa Clara, CA, USA) with 10 pL nominal drop volume cartridge. Irradiations were carried at 453 nm at room temperature with a Golden Dragon Plus, deep blue LED (OSRAM Opto Semiconductors, Sunnyvale, CA, USA).

2.2. Characterization materials

Infrared (IR) spectra of the various substrates were recorded on a Vertex 70 FT-IR spectrometer (Bruker, Billerica, MA, USA) controlled by OPUS software (Bruker, Billerica, MA, USA) and fitted with MIRacleTM ATR (Attenuated Total Reflectance) sampling accessory (PIKE Technologies, Madison, WI, USA). The ATR crystal type was single reflection diamond/ZnSe crystal plate. The FT-IR detector was MCT working at liquid nitrogen temperature. Acquisitions were obtained at 2 cm^{-1} resolution after 256 scans.

Microstructure and surface morphology of samples were examined by a JSM-5510LV (JEOL, Tokyo, Japan) scanning electron microscope (SEM) after gold coating (K575X Turbo Sputter Coater (Quorum Technologies Ltd, Ashford, Kent, UK), working at 15 mA for 20 seconds). The images were acquired at various magnifications ranging from 100 \times to 3 000 \times . The acceleration voltage and working distance were 4 kV and 17 mm, respectively. Images were acquired applying the secondary electron detector.

Surface roughness, R_a , of pristine and copolymerized cellulose substrates was measured with an AlphaStep[®] D-120 Stylus Profiler (KLA-Tencor, Milpitas, CA, USA). Measurements were performed along a line of 1 mm long, with a stylus force of 1 mg and at a speed of 0.05 mm s^{-1} . The same profiler was used to measure printed polyacrylic acid films thickness and roughness.

Ink viscosity was measured with a MCR 102 Rheometer (Anton Paar, Ashland, VA, USA). Cone-plane geometry was used at a shear rate varying from 100 to 5 000 s^{-1} and at a 24 $^\circ\text{C}$ temperature. Gap distance was equal to 101 μm . Geometry diameter and angle were equal to 5 cm and 1 $^\circ$, respectively.

X-ray powder diffraction (XRPD) patterns were measured using a high-throughput Bruker D8 Advance diffractometer (Bruker, Billerica, MA, USA) working on transmission mode and equipped with a focusing Göbel mirror producing CuK_α radiation ($\lambda = 1.5418\text{ \AA}$) and a LYNXEYE detector. Data were collected at room temperature (RT), in the 2θ range 3–60 $^\circ$, with a 0.02 $^\circ$ step width.

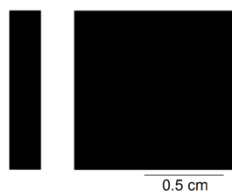


Figure 1. Scheme of the printed pattern.

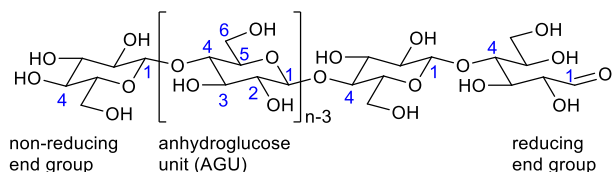


Figure 2. Cellulose molecular structure.

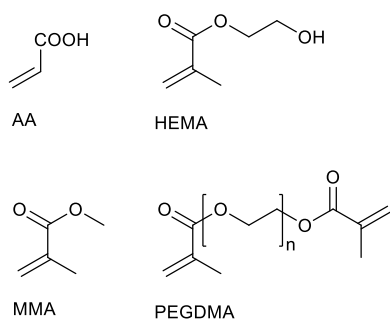


Figure 3. Molecular formulae of the monomers

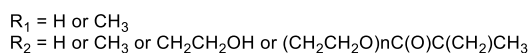
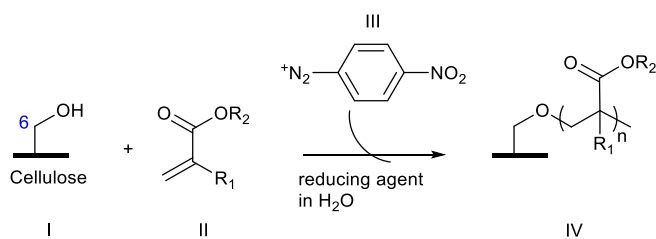


Figure 4. Cellulose graft copolymerization with acrylic monomers. Aryldiazonium (III) is reduced and reacts with cellulose (I) in an aqueous medium to initiate the grafting and polymerization of the monomer (II) and give a polymer-grafted cellulose membrane (IV).

2.3. Cellulose graft copolymerization

2.3.1. DIPPING PROCEDURE

Cellulose modification was performed in water, at open air and room temperature. The 2-mL aqueous reaction mixture contained 0.10 mmol of diazonium salt (23.69 mg; 1.0 eq.), 2 mmol of monomer (20 eq.) and 0.01 mmol of L-ascorbic acid (1.76 mg; 0.1 eq.). Components were first separately dissolved in water and then mixed under stirring in the following order: (i) monomer, (ii) diazonium salt, and (iii) L-ascorbic acid. A CF1 paper sheet (4 cm²) was dipped into this freshly prepared mixture and left to incubate for one hour in a plastic box. The

membrane obtained was rinsed and submitted to ultrasonic treatment in order to discard any ungrafted matter. A first wash was made with water, a second with ethanol. It was finally dried for 15 minutes at 60°C in an air oven. Several acrylic polymers were thus grafted to cellulose paper. The corresponding monomers were acrylic acid (AA), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA) and poly(ethylene glycol) dimethacrylate (PEGDMA). All the so functionalized papers were then analyzed using infrared spectroscopy in order to point out the carbonyl moieties brought by the polymerization. Their microstructure was pictured by SEM imaging. Their surface roughness was measured with a profiler.

2.3.2. PRINTING PROCEDURE

2.3.2.1. Ink formulation

Ink formulation was inspired from our previous work for flexible electronic interconnects²⁸. First of all, an aqueous mixture of acrylic acid (AA) monomer and polyacrylic acid (PAA) (13 wt. % of the 14.6 M commercial stock solution and 2.5 wt. % of a 1 wt. % aqueous stock solution, respectively) was prepared. Afterwards, 0.8 wt. % of solid 4-nitrobenzenediazonium tetrafluoroborate (NBD) was added to the previous solution. Finally, tris(bipyridine)ruthenium(II) chloride ([Ru(bpy)₃]Cl₂) (1.3 wt. % of a 0.02 M aqueous stock solution) was added to the ink. Hence, the final ink composition was: 2 M of AA, traces of PAA, 0.03 M of NBD and to 2.5 × 10⁻⁴ M of [Ru(bpy)₃]Cl₂.

2.3.2.2. Inkjet printing and graft copolymerization

Acrylic acid aqueous solutions were printed onto cellulose substrates using the Dimatix inkjet printer. Nozzle diameter was 21.5 μm and nominal drop volume was 10 pL. Printing tests were performed at 30 V voltage with 15 μm drop spacing. The printed pattern (Figure 1) consisted of two solid forms of 1 cm × 1 cm and 1 cm × 0.2 cm dimensions. The pattern resolution was equal de 1693 dpi (dot per inch). Printings made of 1, 3 and 6 layers were compared. The patterned surfaces were irradiated at 453 nm (0.75 W cm⁻²) during 15 minutes (about 675 J cm⁻²) for inducing polymerization. After irradiation, printed substrates were dipped in distilled water during 5 hours to remove the physisorbed matter. They were finally dried for 60 minutes at 45°C in an air oven.

3. Results and discussion

3.1. One-step cellulose graft copolymerization

3.1.1. MOLECULAR LEVEL

Whatman CF1 paper was selected because it is a high quality paper, made of quite pure and clean cellulose (Figure 2), whose thickness and wicking properties are rather uniform (11 μm surface pore size and 176 μm thick). Cellulose is a natural biopolymer made up of glucose units (Figure 2). It is the simplest polysaccharide since it is composed of a unique monomer (glucose) which binds to its neighbors by a unique type of linkage (β-1,4 glycosidic bond resulting in acetal

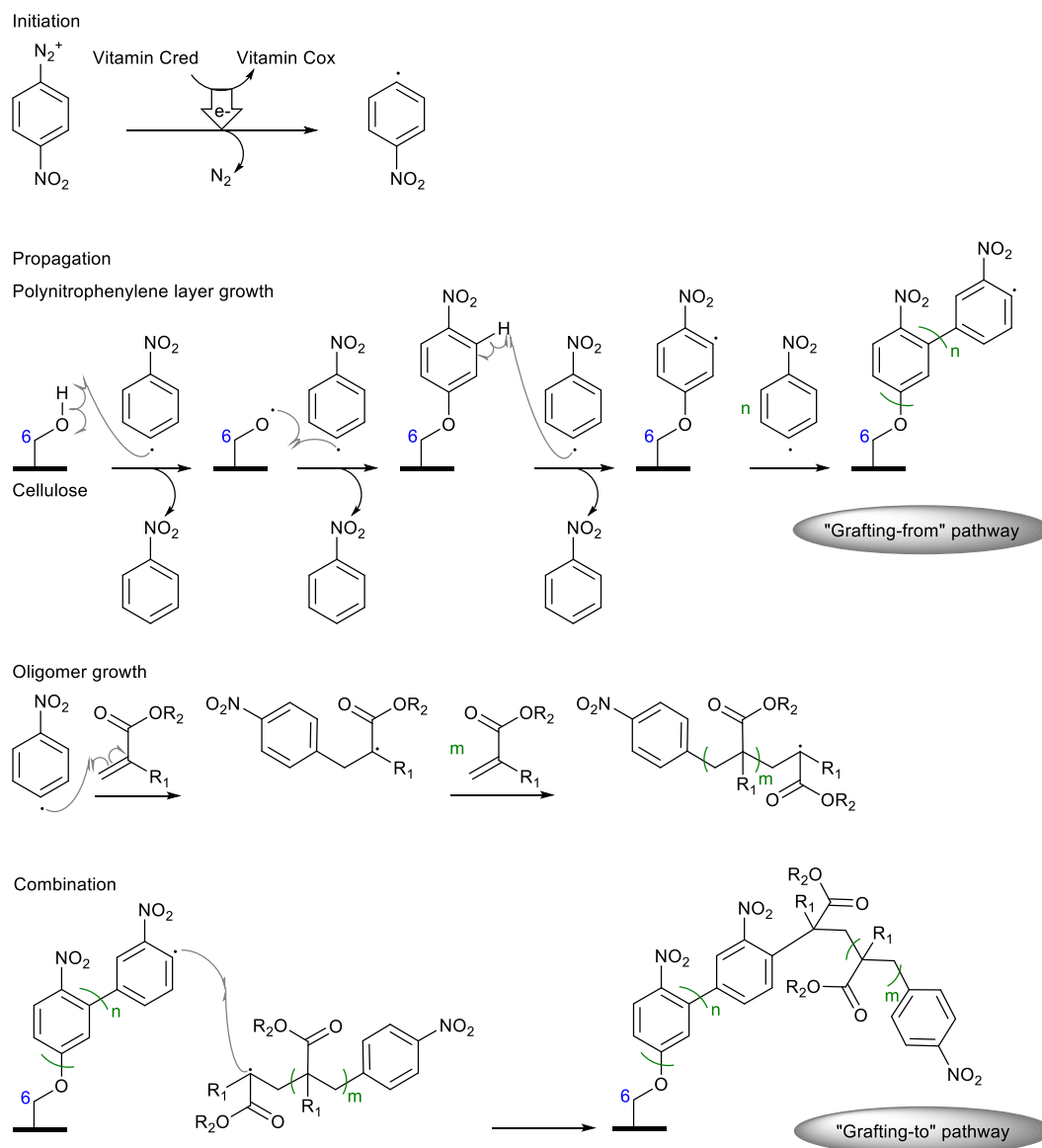


Figure 5. A proposed mechanism of free radical grafting of acrylic polymers onto cellulose.

function)¹. Hydroxyl groups in glucose units are responsible for cellulose chemical activity². Among the three hydroxyl groups in each glucose residue, the hydroxyl at 6-position (primary one) is the most reactive site^{1,2}.

Cellulose paper sheets have been copolymerized in soft conditions, in a single step and after only one hour incubation. Several acrylic polymers were grafted. The molecular structures of the corresponding monomers are shown in Figure 3. The graft polymerization pathway consisted in an aryldiazonium-based surface chemistry (Figure 4)^{24,26}. Diazonium salts are known to be free radical polymerization initiators²⁴. Acrylic graft copolymerization to the pre-existing polymeric cellulose backbone was therefore achieved by free radical graft copolymerization which was triggered by a reducing agent. According to the previously published work by Garcia *et al.*²⁸, both "grafting-from" and "grafting-to" polymerization pathway

are actually involved in the polymer grafting process. In light of the review of Roy *et al.* and works reported on it², we suggest the hypothesized mechanism depicted in Figure 5. Reaction took place in water at room temperature with a biological reducing agent (L-ascorbic acid, also known as vitamin C), thereby resulting in a biocompatible process. Cellulose sheets have been successfully grafted with the different polymers and characterized by several analytical techniques in order to assess the resulting surface chemical composition and morphological structure.

3.1.2. SURFACE CHEMICAL ANALYSIS

The outer surface layers of paper substrates were chemically analyzed by ATR-FTIR, thereby displaying the aforementioned bulk molecular structures. According to its layout, ATR-FTIR allows the identification of chemical bonds within 2 μm deep subsurface layers²⁹. All papers are mainly composed of a

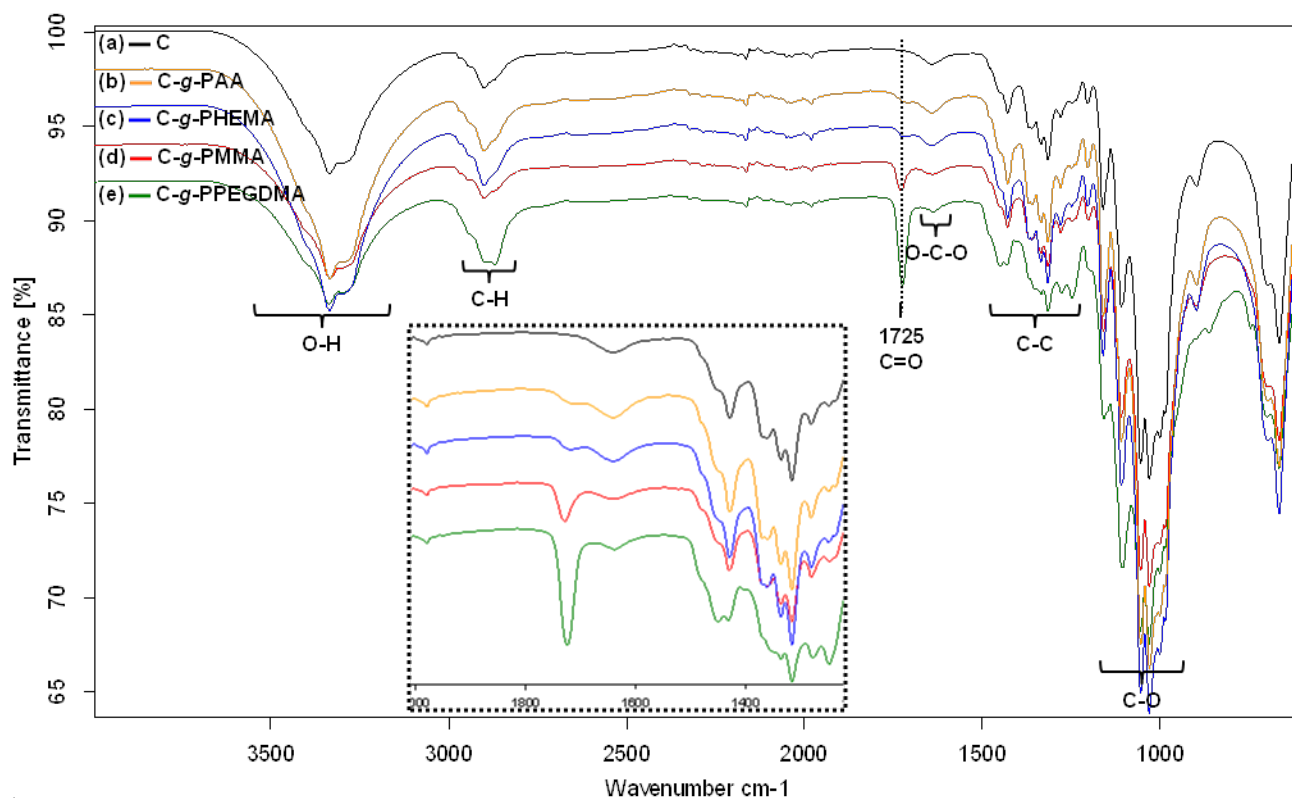


Figure 6. IR spectra of paper substrates after a 1-hour dipping. (a) is spectrum from pristine cellulose sheet, (b) from cellulose copolymerized with acrylic acid (AA) monomer, (c) with 2-hydroxyethyl methacrylate (HEMA), (d) with methyl methacrylate (MMA) and (e) with poly(ethylene glycol) dimethacrylate (PEGDMA). All spectra have several bands in common which correspond to O-H, C-H, C-C, C-O and O-C-O stretching vibrations. The C=O stretching vibrations specific to grafted polymers are labeled.

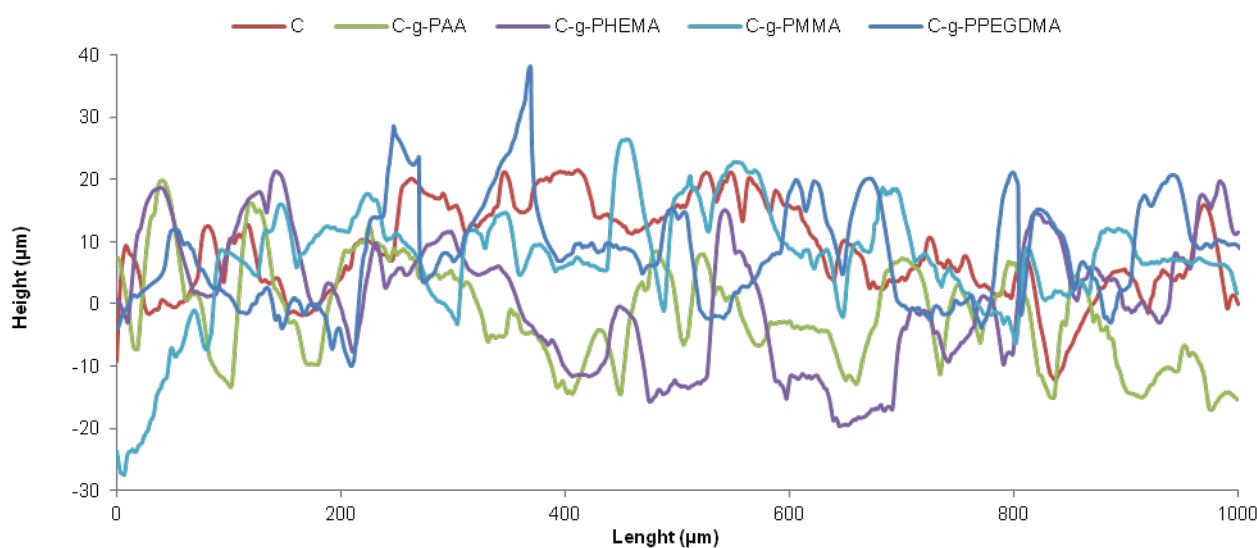


Figure 7. Line profiles of pristine cellulose (C) and polymer-grafted cellulose substrates (C-g-polymer).

cellulosic backbone and therefore the IR signals for its typical bond vibrations are shared by every spectrum shown. Figure 6 displays these common bands attributable to O-H, C-H, C-C, C-O and O-C-O stretching vibrations. As expected, polymer-grafted cellulose papers manifest additional peaks (1725 ± 5

cm^{-1}) attributable to C=O stretching vibrations from ester moieties of the grafted polymer. Their intensity depends on the monomer used and resulting grafted polymer. They stand in the following order: AA < HEMA < MMA < PEGDMA. On one hand, PEGDMA is predominant because it is a diacrylic

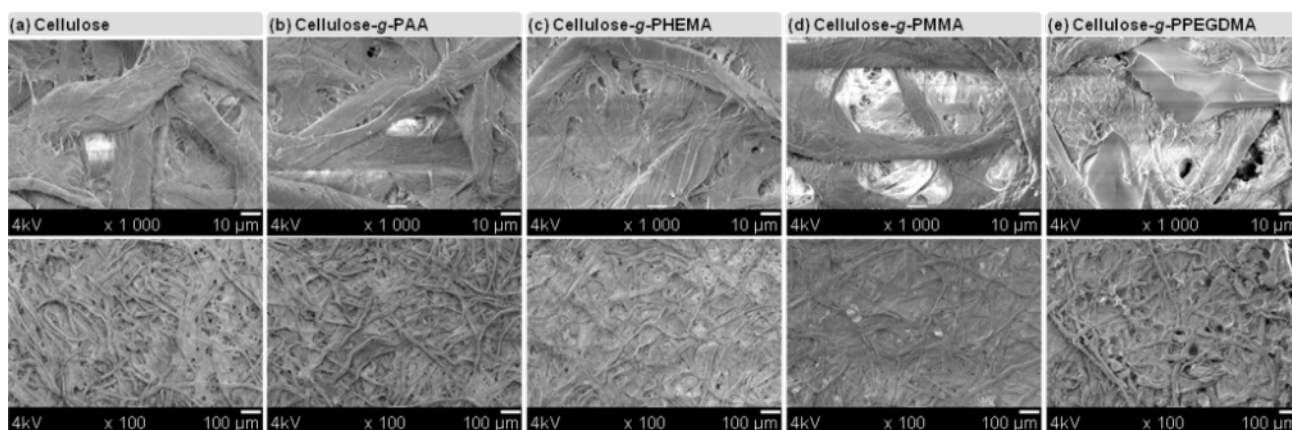


Figure 8. Surface SEM micrographs of (a) pristine cellulose sheet, (b) cellulose copolymerized with acrylic acid (AA), (c) with 2-hydroxyethyl methacrylate (HEMA), (d) with methyl methacrylate (MMA) and (e) with poly(ethylene glycol) dimethacrylate (PEGDMA).

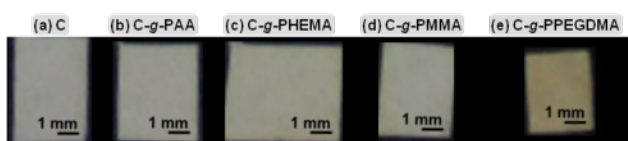


Figure 9. Photographs of (a) pristine cellulose sheet, (b) cellulose copolymerized with acrylic acid (AA), (c) with 2-hydroxyethyl methacrylate (HEMA), (d) with methyl methacrylate (MMA) and (e) with poly(ethylene glycol) dimethacrylate (PEGDMA).

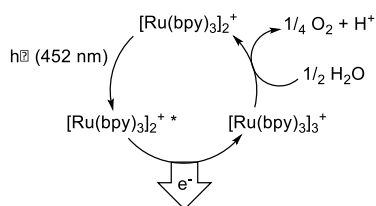


Figure 10. Photoactivated reducing behavior of $[\text{Ru}(\text{bpy})_3]^{2+}$.

monomer. On another hand, since cellulose is a porous material these intensities cannot be directly related to amount and thickness of grafted polymer. More investigations should be conducted in order to analyze surface morphological structure.

3.1.3. SURFACE MORPHOLOGICAL STRUCTURE

Beyond the chemical differences in molecular structure, the various grafted polymers introduced physical and morphological differences between the cellulose substrates. Thus, in order to quantify the variation in surface morphological structure, topological analysis was conducted by measuring substrates' roughness (Ra). Morphology and microstructure of the various polymer-grafted cellulose substrates was visualized by SEM imaging. Visual global evaluation was also performed.

Line profiles of pristine cellulose substrate and polymer-grafted cellulose substrates were quite similar (see Figure 7). Substrates were rather heterogeneous, rough, and displays numerous and wide pores. Surface roughness (Ra) values confirmed this high roughness and were also quite similar. Hence, the average value was $6.45 \pm 0.25 \mu\text{m}$.

Pores sizes and arrangement pictured by SEM imaging (Figure 8) were consistent with the previous statements. Pristine cellulose substrate and polymer-grafted cellulose substrates looked quite similar. They displayed numerous and wide surface pores. However, differences could be noticed between the various polymer-grafted cellulose substrates. Micrographs revealed that the grafted polymers filled cellulose surface pores, as expected. Progression of the filling extent matched the progression previously observed with IR peak intensities: $\text{AA} < \text{HEMA} < \text{MMA} < \text{PEGDMA}$. Therefore, these intensities could actually be related to an amount of grafted polymer.

Although the microstructures of the several cellulose substrates were different, the various substrates visually appeared quite similar. Except for cellulose-g-PPEGDMA which is slightly colored, grafted cellulose substrates were white and displayed no visual difference with pristine cellulose (Figure 9). Cellulose molecular, physical and micro-morphological properties can therefore be modified without impact on the visual aspect of paper.

3.2. Spatially controlled cellulose graft copolymerization

Though the aforementioned process was ecologically friendly, the dipping procedure implemented was not economically friendly. Indeed, a large part of the reaction mixture was not involved in the cellulose graft copolymerization but in the homopolymerization of the added monomer. In order to reduce this matter wastage, the polymerization was further localized onto selected specific areas of the substrate by means of inkjet printing. Printing is a versatile technique allowing the deposition of variable kinds of solutions (biomolecules, polymers, solvents, metals) onto different types of substrates (cellulose, polymer, glass, silicon) and according to any design desired^{30,31}. This is fast dispensing process enabling low-cost, high throughput fabrication³¹. Moreover it is regarded as an environmentally friendly process and therefore a very attractive approach regarding the economic and ecological goals. However, the previous reaction mixture was not printable as was. The polymerization trigger had to stay inactive as long as



Figure 11. Photographs of printed solid forms on cellulose substrates after irradiation and rinsing steps: (a) 1-pass printing, (b) 3-pass printing and (c) 6-pass printing.

Table 1. Raw cellulose substrate roughness and printed polyacrylic acid films roughness and thickness.

	Roughness (μm)		Thickness (μm)	
	Before rinsing	After rinsing	Before rinsing	After rinsing
Cellulose	7 \pm 1			
1-pass printed cellulose	9 \pm 1	7 \pm 1	9 \pm 3	
3-pass printed cellulose	9 \pm 1	8 \pm 2	15 \pm 4	4 \pm 2
6-pass printed cellulose	14 \pm 3	9 \pm 1	29 \pm 9	13 \pm 8

it was in cartridge otherwise homopolymerization would have taken place before printing. Thus, vitamin C was exchanged for a photoactivated reducing agent: $[\text{Ru}(\text{bpy})_3]^{2+}$. $[\text{Ru}(\text{bpy})_3]^{2+}$ strongly absorbs at 452 ± 3 nm in aqueous medium³². In presence of oxidative quenchers such as aryldiazonium salt, the excited $[\text{Ru}(\text{bpy})_3]^{2+*}$ relaxed to $[\text{Ru}(\text{bpy})_3]^{3+}$ while transferring an electron to the aryldiazonium, thereby triggering cellulose graft copolymerization. $[\text{Ru}(\text{bpy})_3]^{3+}$ is a powerful oxidant (1.29 V vs. SCE = Standard Calomel Electrode, in CH_3CN) and would therefore be able to spontaneously oxidize water and return to its original $[\text{Ru}(\text{bpy})_3]^{2+}$ form (Figure 10)^{33–35}.

Reaction was still performed in water at room temperature. Cellulose sheets were successfully printed with a photoactive ink containing acrylic acid. Cellulose was further copolymerized by irradiating the printed pattern. Resulting substrates were characterized by several analytical techniques in order to assess their surface chemical composition and morphological structure.

3.2.1. INK BEHAVIOR

Before printing, ink rheological behavior was analyzed in order to check the printability of the prepared solution. To be inkjet printable, a fluid should be Newtonian with a viscosity in the range of 1 to 10 mPa s³⁶. The formulated ink showed a Newtonian behavior with a constant viscosity of 3.2 mPa s at shear rates varying from 100 to 5 000 s⁻¹. Shear stress varied linearly, from 0.3 to 16.2 Pa, as a function of shear rate (100 to 5 000 s⁻¹). The temperature was maintained at 24°C during the whole measurements.

Then, inkjet printing was performed onto cellulose substrates. 1, 3 and 6 printing passes of acrylic acid aqueous ink were printed onto cellulose according to the pattern displayed in Figure 1. Patterned surfaces were further irradiated, rinsed and dried. Photographs of the resulting printed forms are shown

Figure 11. When only 1 (Figure 11a) and 3 (Figure 11b) printing passes are deposited, both solid forms are well defined. However, when 6 printing passes are performed (Figure 11c), the larger solid form is not homogeneous. This is probably due to the high ejected ink volume compared to the absorption capability of cellulose fibers³⁷.

3.2.2. SURFACE CHEMICAL ANALYSIS

Figure 12 shows IR spectra of raw cellulose and cellulose printed and copolymerized with acrylic acid. New peaks appeared on cellulose substrates at 1350, 1530 and 1710–1730 cm^{-1} after light induced polymerization of acrylic acid. Peaks around 1530 and 1350 cm^{-1} are attributable to stretching vibrations of nitrophenyl groups from NBD derivatives. Peaks around 1710 – 1730 cm^{-1} are related to the stretching vibrations of carboxylic groups (COOH). Peaks intensity was proportional to the number of passes. After rinsing in distilled water during 5 hours, peaks attributed to NBD could not be identified anymore. Furthermore, even though the carboxylic peaks (1728 cm^{-1}) were still easy to discern, their intensity had decreased. This phenomenon is partially caused by the COOH/COO⁻ equilibrium resulting from the sustained exposure to distilled water. No copolymer's peak was observed anymore on the spectra corresponding to 1-pass printing. This could be explained by an ejected ink volume too small to allow surface polymerization of acrylic acid.

3.2.3. SURFACE MORPHOLOGICAL STRUCTURE

Printing and graft copolymerization of cellulose with acrylic acid monomer resulted in the formation of a thin film of polyacrylic acid onto cellulose sheet surface. Those films' thicknesses and roughnesses are displayed in Table 1. Roughness values were compared to raw cellulose one. Thus, printing and graft copolymerization made roughness increase from 7 μm to 14 μm (6-pass printing). Grafted films thicknesses varied from 9 μm for 1-pass printing to 29 μm for 6-pass printing. Washing printed substrates with distilled water further allowed removing the physisorbed material, thereby inducing thickness and roughness decrease. Besides, the film resulting from 1-pass printing completely vanished after rinsing. In this case, film thickness could not be measured and the film roughness was equal to raw cellulose one. This might stem from the complete absorption of the small ejected volume of ink by cellulose fibers and pores, hence inhibiting light induced polymerization of acrylic acid onto cellulose surface. Indeed, the grafting efficiency depends, inter alia, on the photoinitiator and the monomer concentrations³⁸. Thus, the ejected volume could be a determining factor outlining the thickness of the grafted polymer as well as the polymerization efficiency.

In order to further investigate films morphology, scanning electron microscopy was performed. Surface micrographs of raw cellulose and printed plus copolymerized cellulose are shown in Figure 13. Firstly, raw cellulose and 1-pass printed cellulose looked almost identical. One may suggest that most of the ejected ink had been absorbed by the cellulose surface pores. Then, 3-pass printed and 6-pass printed cellulose appeared quite different from raw cellulose. Fewer pores are

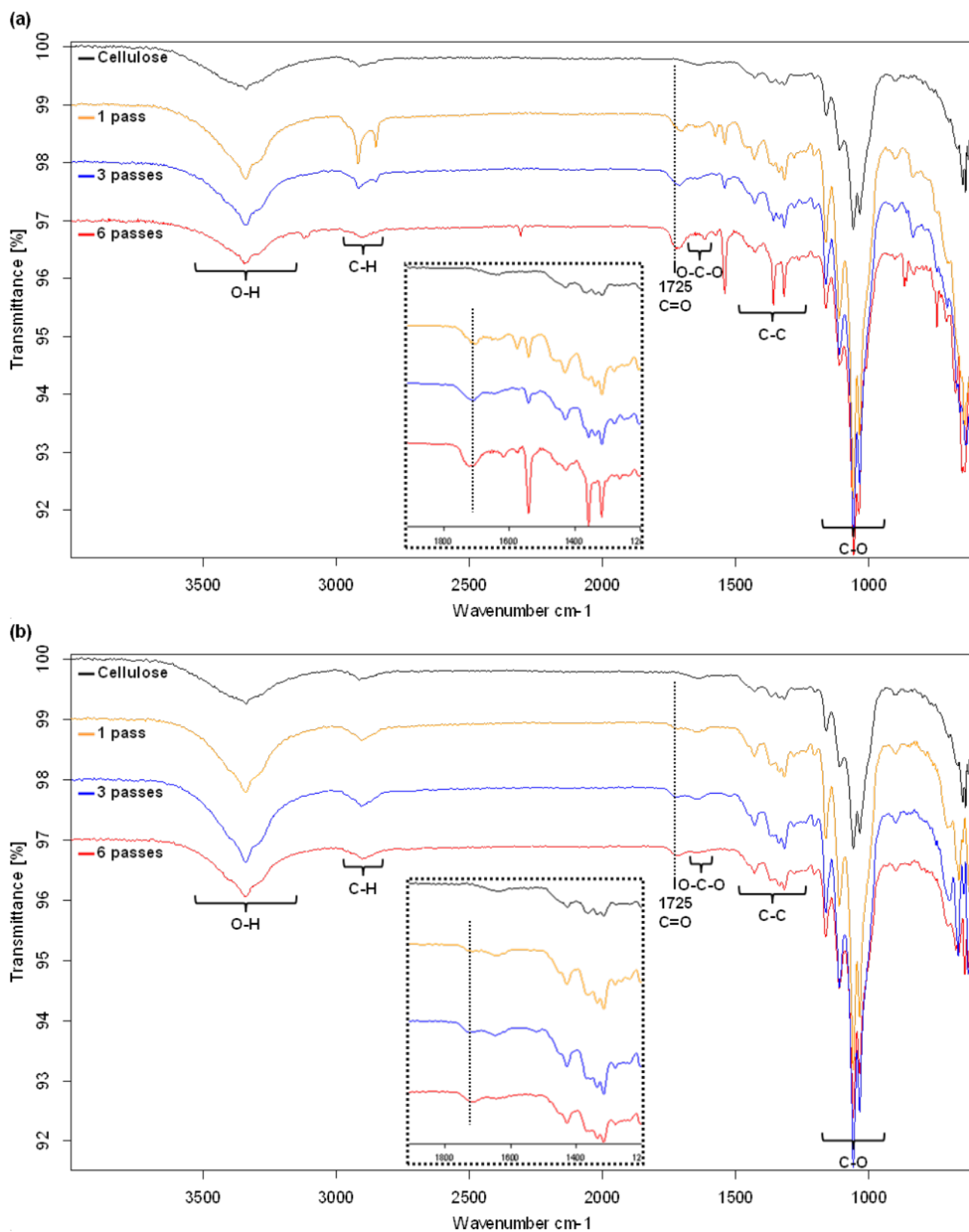


Figure 12. IR spectra of raw cellulose and cellulose printed and copolymerized with acrylic acid monomer. 1-pass printing, 3-pass printing and 6-pass printing were displayed. Spectra from the first set (a) were recorded before rinsing and those from the second (b) after rinsing.

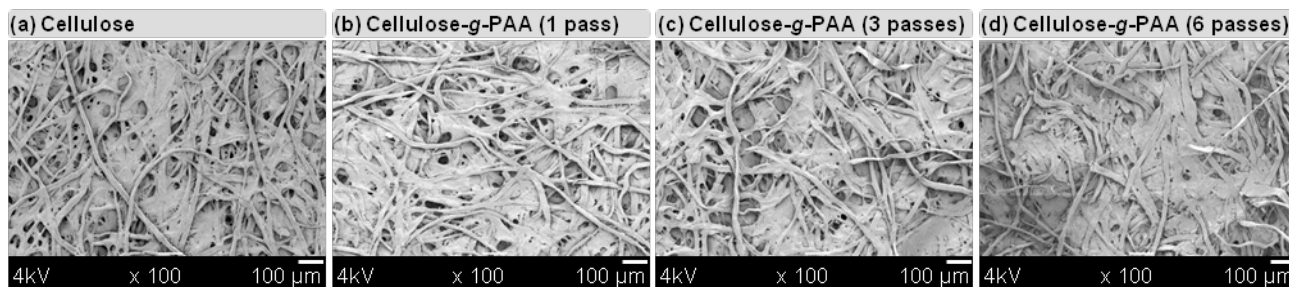


Figure 13. Surface SEM micrographs of raw cellulose (a) and cellulose printed and copolymerized after rising step: 1-pass printing (b), 3-pass printing (c) and 6-pass printing (d) are displayed.

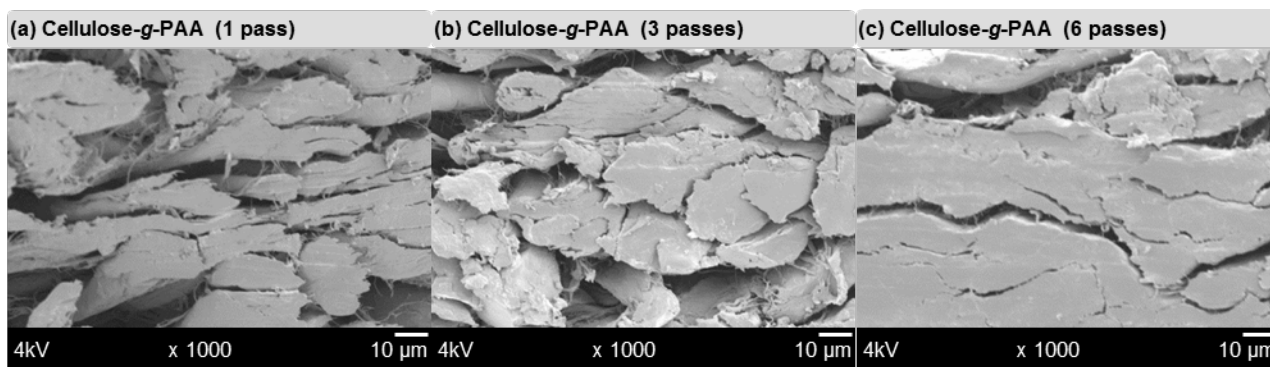


Figure 14. Cross-section SEM micrographs of printed and copolymerized cellulose after rising step: 1-pass printing (a), 3-pass printing (b) and 6-pass printing (c) are displayed.

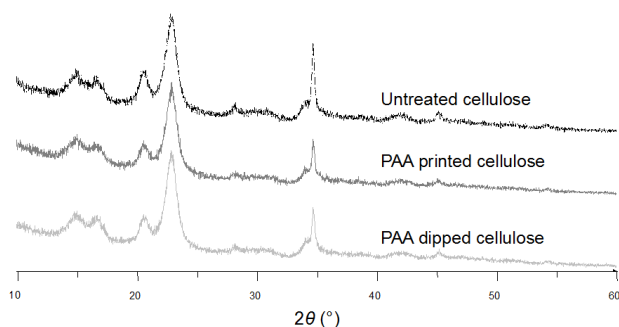


Figure 15. X-ray diffraction spectra of untreated, PAA printed and PAA dipped cellulose. The XRD Data were collected using $\text{CuK}\alpha$ radiation.

observed on the surface which seems more homogeneous, mainly after the 6-pass printing. This results are consistent with Määttänen *et al.* findings³⁹ which demonstrated that ink is quickly and completely absorbed into the depth of porous surfaces. Thus, in order to enhance ink deposit onto the substrate surface more passes should be performed.

Cross-section micrographs of printed and copolymerized cellulose are shown in Figure 14. According to these micrographs, structure changed as a function of the passes numbers. Fewer pores were observed when the number of printings increased from 1 to 6 passes. Furthermore, cellulose sheet depth appeared more packed with the increasing number of passes. This confirmed the fact that ink penetrated through the cellulose capillarity and pores.

3.3. Structural characterization

XRD analysis of the PAA printed and dipped cellulose was performed in order to investigate the behavior of cellulose crystallinity with the different grafting processes (Figure 15). Compared to untreated cellulose, the printing and dipping processes do not alter the structure of cellulose fibers.

3.4. Inkjet printing of complex patterns

As previously mentioned, one major advantage of inkjet printing dispensing method is the freedom in design of the printed pattern. This advantage was illustrated here by printing a copolymerization mixture according to the nature of the monomer and the resulting polymer grafted to cellulose.

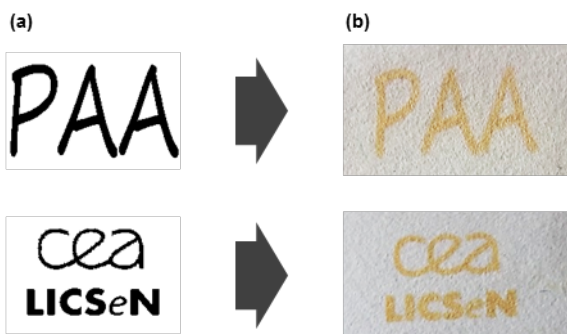


Figure 16. Printed pattern designs (a) and photographs of the solid forms actually printed on cellulose (b).

Therefore, acrylic acid aqueous ink was printed (6-pass printing) onto cellulose according to a pattern drawing the abbreviation PAA (Figure 16a). Patterned surface was further irradiated, rinsed and dried. Photograph of the resulting printed form is shown in Figure 16b. Visual aspect was consistent with previous results for a 6-pass printing (see section 3.2.1). As expected, the drawn pattern allowed direct reading of the grafted polymer. Afterwards, a smaller and thinner pattern was printed in order to assess the resolution of the actually grafted film. Pattern and photograph are shown in Figure 16a and Figure 16b, respectively. They confirmed that this process enables to precisely modulate properties of a cellulose surface according to complex patterns. Spatial control of surface properties is key asset of such a modification process. For instance, precise spatial control of electrical properties is particularly interesting in order to produce paper-based electronic circuit.

4. Conclusion

The work described herein offers a simple, fast, low-cost and eco-friendly way for cellulose surface graft copolymerization. This original approach, based on aryldiazonium salt chemistry, is achieved under soft aqueous conditions and through a one-step reaction. Cellulose sheets have been impregnated with copolymerization reaction mixture by means of two different dispensing methods. Firstly, dipping was performed and enabled to use a biological reducing agent: vitamin C. The process was thus ecologically friendly but not economically friendly. This is why inkjet printing was further implemented. This versatile and economically friendly dispensing method ensured reduction of the matter wastage by localizing the polymerization mixture onto specific areas of the substrate. However, this process modification required to exchange vitamin C for a photoactivated reducing agent: $[\text{Ru}(\text{bpy})_3]^{2+}$. Several acrylic polymers were grafted to cellulose. Results suggest that the chemical pathway followed here allows graft copolymerization of cellulose sheet with many different acrylic monomers.

This research was proposed to meet the need of paper-based technology for cost and time-saving methods allowing robust and sustainable graft copolymerization of cellulose sheets. In addition to the simplicity of a one-step reaction, inkjet printing dispensing of the reaction mixture allows to precisely localize the polymerization and to save expensive monomers. Therefore, the expounded process provides a powerful tool for easy and robust graft copolymerization of cellulose sheets with various polymer films and according to complex patterns.

Acknowledgements

This work was financially supported by the Commissariat à l'Energie Atomique et aux Energies Alternatives (France).

Notes and references

CEA Saclay, IRAMIS, NIMBE, LICSEN (Laboratory of Innovation in Surface Chemistry and Nanosciences), F-91191 Gif sur Yvette, France; E-mails: julie.credou@cea.fr; rita.faddoul@cea.fr; thomas.berthelot@cea.fr.

* Author to whom correspondence should be addressed; E-mail: thomas.berthelot@cea.fr; Tel.: +33 169086588; Fax: +33 169084044.

- J. Credou and T. Berthelot, *J. Mater. Chem. B*, 2014, **2**, 4767–4788.
- D. Roy, M. Semsarilar, J. T. Guthrie, and S. Perrier, *Chem. Soc. Rev.*, 2009, **38**, 2046–2064.
- R. L. Crawford, *Lignin biodegradation and transformation*, John Wiley & Sons Inc, New York, NY, USA, 1981.
- E. Malmström and A. Carlmark, *Polym. Chem.*, 2012, **3**, 1702–1713.
- J. S. Han and J. S. Rowell, in *Paper and composites from agro-based resources*, eds. R. M. Rowell, R. A. Young, and J. K. Rowell, CRC Press, 1996, pp. 83–134.
- D. Klemm, B. Heublein, H.-P. Fink, and A. Bohn, *Angew. Chem. Int. Ed. Engl.*, 2005, **44**, 3358–3393.
- S. Kalia, B. S. Kaith, and I. Kaur, *Cellulose Fibers: Bio- and Nano-Polymer Composites*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2011.
- D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, and A. Dorris, *Angew. Chem. Int. Ed. Engl.*, 2011, **50**, 5438–5466.
- R. Pelton, *Trends Anal. Chem.*, 2009, **28**, 925–942.
- A. W. Martinez, S. T. Phillips, G. M. Whitesides, and E. Carrilho, *Anal. Chem.*, 2010, **82**, 3–10.
- J. Credou, H. Volland, J. Dano, and T. Berthelot, *J. Mater. Chem. B*, 2013, **1**, 3277–3286.
- A. W. Martinez, S. T. Phillips, and G. M. Whitesides, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 19606–19611.
- SENTINEL: Bioactive Paper Network <http://www.bioactivepaper.ca/index.php?module=page&id=4000> (accessed Jan 31, 2014).
- S. Aikio, S. Grönqvist, L. Hakola, E. Hurme, S. Jussila, O.-V. Kaukonen, H. Kopola, M. Käsäkoski, M. Leinonen, S. Lippo, R. Mahlberg, S. Peltonen, P. Qvintus-Leino, T. Rajamäki, A.-C. Ritschkoff, M. Smolander, J. Vartiainen, L. Viikari, and M. Vilkinan, *Bioactive paper and fibre products: Patent and literary survey*, Oulu, Finland, 2006.
- Materials Research Society, *MRS Bull.*, 2013, **38**, 294–352.
- D. Klemm, B. Philipp, T. Heinze, U. Heinze, and W. Wagenknecht, *Comprehensive Cellulose Chemistry Volume 2 Functionalization of Cellulose*, WILEY-VCH, Weinheim, 1998, vol. 2.
- J.-F. Zhong, X.-S. Chai, and S.-Y. Fu, *Carbohydr. Polym.*, 2012, **87**, 1869–1873.
- E. Takács, L. Wojnárovits, É. Koczog Horváth, T. Fekete, and J. Borsa, *Radiat. Phys. Chem.*, 2012, **81**, 1389–1392.
- R. Bongiovanni, S. Marchi, E. Zeno, A. Pollicino, and R. R. Thomas, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2013, **418**, 52–59.
- Y. Kodama, M. Barsbay, and O. Güven, *Radiat. Phys. Chem.*, 2014, **94**, 98–104.
- E. Takács, L. Wojnárovits, J. Borsa, and I. Rácz, *Radiat. Phys. Chem.*, 2010, **79**, 467–470.

22. W. Dahou, D. Ghemati, A. Oudia, and D. Aliouche, *Biochem. Eng. J.*, 2010, **48**, 187–194.
23. K. Littunen, U. Hippi, L.-S. Johansson, M. Österberg, T. Tammelin, J. Laine, and J. Seppälä, *Carbohydr. Polym.*, 2011, **84**, 1039–1047.
24. V. Mévellec, S. Roussel, L. Tessier, J. Chancolon, M. Mayne-L’Hermite, G. Deniau, P. Viel, and S. Palacin, *Chem. Mater.*, 2007, **19**, 6323–6330.
25. T. Berthelot, A. Garcia, X. T. Le, J. El Morsli, P. Jégou, S. Palacin, and P. Viel, *Appl. Surf. Sci.*, 2011, **257**, 3538–3546.
26. V. Mévellec, S. Roussel, S. Palacin, T. Berthelot, C. Baudin, A. Trenggono, and G. Deniau, 2006. WO 2008/078052.
27. R. Faddoul, N. Reverdy-Bruas, and A. Blayo, *Mater. Sci. Eng. B*, 2012, **177**, 1053–1066.
28. A. Garcia, N. Hanifi, B. Jousseme, P. Jégou, S. Palacin, P. Viel, and T. Berthelot, *Adv. Funct. Mater.*, 2013, **23**, 3668–3674.
29. PIKE Technologies, *MIRacle ATR; Product Data Sheet*, Madison, WI, USA, 2014.
30. D. Gamota, P. Brazis, K. Kalyanasundaram, and J. Zhang, Eds., *Printed Organic and Molecular Electronics*, Springer US, Boston, MA, 2004.
31. J. Birkenshaw, *Printed Electronics (Pira on printing)*, Leatherhead, Surrey, UK, 2004.
32. X. Zhou, D. Zhu, Y. Liao, W. Liu, H. Liu, Z. Ma, and D. Xing, *Nat. Protoc.*, 2014, **9**, 1146–1159.
33. M. Hara, C. C. Waraksa, J. T. Lean, B. A. Lewis, and T. E. Mallouk, *J. Phys. Chem. A*, 2000, **104**, 5275–5280.
34. J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev.*, 2011, **40**, 102–113.
35. F. Teplý, *Collect. Czechoslov. Chem. Commun.*, 2011, **76**, 859–917.
36. R. Leach and R. Pierce, *The Printing Ink Manual*, Springer US, Boston, MA, 1993.
37. M. Bergh, Chalmers University of Technology, Göteborg, Sweden, 2011.
38. A. Bhattacharya and B. N. Misra, *Prog. Polym. Sci.*, 2004, **29**, 767–814.
39. A. Määttänen, P. Ihalainen, R. Bollström, M. Toivakka, and J. Peltonen, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2010, **367**, 76–84.