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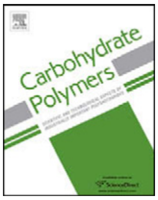

Short communication

Starch–cellulose crosslinking—Towards a new material

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ABSTRACT

This work describes a simple method for direct cross-linking of modified polysaccharides. Azide cellulose and alkyne starch were synthesized using classical methods. The two components were cross-linked in the presence of Cu(I) catalyst, a type of Huisgen's 1,3-dipolar azide-alkyne cycloaddition which is also defined as a "click chemistry" reaction, leading to the formation of starch crosslinked to cellulose. The modified polysaccharides were characterized by NMR, FTIR and X-ray photoelectron spectroscopies and the resulting material was analyzed using scanning electron microscopy (SEM).

1. Introduction

Starch use in papermaking dates back to the invention of paper 2000 years ago, when it was applied to obtain a stronger and smoother writing surface. Starch contributes to paper manufacturing because it serves as a binding agent which can enhance the mechanical properties of paper and improve paper manufacturing by increasing paper pulp retention on the paper machine (Hubbe, 2006). Starch was also chemically modified into cationic forms to further improve interconnections between fibers, increasing thus the paper strength (Alince, Lebreton, & St-Amour, 1990; Formento, Maximino, Mina, Srayh, & Martinez, 1994; Ghosh, 1994; Greif & Gaspar, 1980; Hofreiter, 1981; Howard & Jowsey, 1989; Moeller, 1966). Modified starch may also be blended to form new "green" biocomposites (CEN/TR, 2010; Mohanty, Misra, & Drzal, 2005; Vilaplana, Strömberg, & Karlsson, 2010). Non-covalent binding of starch and fiber in biocomposites were created using a polymer suspension either by, for example, drying or hot-pressing (Duanmu, Gamstedt, Pranovich, & Rosling, 2010; Kumar & Singh, 2008; Song, Zhao, Dong, & Deng, 2009).

In this paper, starch was grafted on microcrystalline cellulose using CuAAC (Copper Catalyzed Azide-Alkyne Cycloaddition) in order to create a three-dimensional network without using traditional crosslinking agents (Huisgen, Knorr, Mobius, & Szeimmies, 1965; Kolb, Finn, & Sharpless, 2001; Krouit, Bras, & Belgacem, 2008; Lucas, Zerrouki, Granet, Krausz, & Champavier, 2008; Rostovtsev, Green, Fokin, & Scharpless, 2002; Tornoe & Meldal, 2001; Tornoe, Christensen, & Medal, 2002). This crosslinked network could be used in new biocomposite materials. These materials are expected to have high strength. Furthermore the incorporation of a variable percentage of this material might greatly enhance properties of paper. Contrary to the existing use of starch in paper industry, we developed here an oriented and covalent network. That's why some physical studies are underway. Based on this finding, alkyne and azide groups were introduced to both starch and cellulose polysaccharides, respectively. The two components were linked in the presence of Cu(I) catalyst, a type of Huisgen's 1,3-dipolar azide-alkyne cycloaddition which is also defined as a "click" chemistry reaction. This chemical pathway led *in situ* to the new material formation (Scheme 1). Morphology of the starch-grafted cellulose was finally revealed by scanning electron microscopy (SEM).

2. Materials and methods

2.1. Materials

All solvents and chemicals were commercially available, and unless otherwise stated, were used as received. Potato starch powder, DMAc, LiCl, NaOH and $CuSO_4$ were purchased from Acros Organics. Propargyl bromide, p-toluenesulfonyl chloride and sodium azide were purchased from Alfa Aesar. Microcrystalline cellulose, DMF, sodium ascorbate and triethylamine were purchased from Sigma–Aldrich.

2.2. Methods

Example of substitution degree (DS) calculation for tosylation from XPS data:

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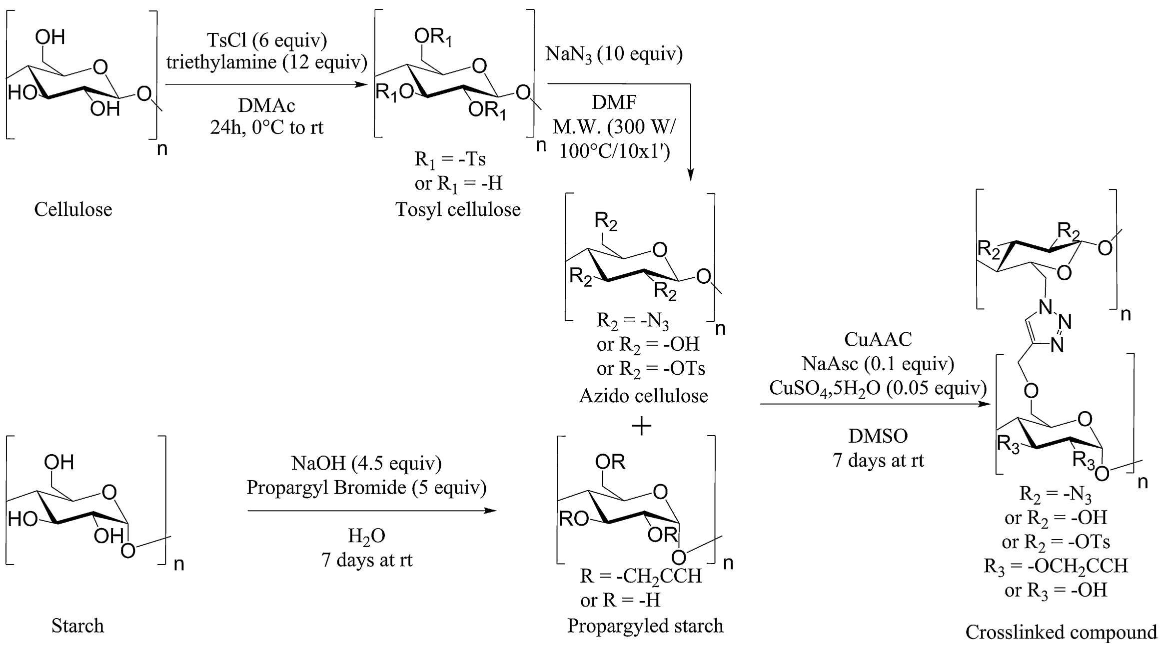

Scheme 1. Starch–cellulose reticulation.

In a tosyl unit there are 7 carbon atoms, 2 oxygen atoms, 1 sulfur atom and 7 hydrogen atoms. According to this point, in a tosyl unit there is seven times more carbon than sulfur so:

$$\%C_{\text{tosyl}} = \%S \times 7$$

When the percentage of carbon atoms in tosyls units is obtained, the percentage of carbon atoms of AGU is:

$$\%C_{\text{AGU}} = \%C_{\text{total}} - \%C_{\text{tosyl}}$$

In an AGU, there are 6 carbon atoms, 5 oxygen atoms and a number of hydrogen which is function of DS. So one AGU is represented by this percentage:

$$\%_{\text{One AGU}} = \frac{\%C_{\text{AGU}}}{6}$$

Finally the DS of tosylation is obtained with this:

$$\text{DS} = \frac{\%S}{\%_{\text{One AGU}}}$$

2.3. Instrumentation

Microwave irradiations were realized thanks to a Milestone Ethos 1600 Microsynth. Dialysis membranes (6000–8000 Da) were purchased from SpectrumLabs.

^{1}H NMR and ^{13}C NMR spectra were using a Bruker DPX-400 and DMSO-d^6 or $CDCl_3$ as solvant. Chemical shifts (δ) are expressed in ppm with Me_4Si as the internal standard (δ_0).

A Perkin Elmer 1000 FTIR spectrometer equipped with Spectrum software was used to perform FTIR analysis. The spectra were obtained by preparing dried KBr powder pellets containing 5% (w/w) of the investigated sample.

X-ray photoelectron spectroscopy (XPS) experiment was carried out using a Kratos Axis Ultra spectrometer that provided elemental composition information (a percentage in atom) to a depth of few nanometers. Three trials were completed for each sample, which were prepared with an homogeneous mashed compound.

SEM analyses were performed using a Jeol JSM-5500 scanning electron microscope. These analyses provided us with a visual appearance of the compounds at high resolution (micrometer scale).

3. Experimental

3.1. Preparation of propargyl starch

Propargylated starch was prepared using a modified procedure describe by P.F. Tankam et al. Starch (8 g, 49.6 mmol) was solubilized in water (700 mL) under magnetic stirring for 10 min at room temperature. Sodium hydroxide (8.96 g, 260 mmol, 4.5 equiv/AGU) was added under magnetic stirrer, until it dissolves, and then propargyl bromide (28 mL, 260 mmol, 5 equiv/AGU) was added to the solution. One week later, the solution left at room temperature and under stirring was dialyzed (6000–8000 Da). And after that was dried under vacuum (8.435 g, yield: 69%, DSProp: 2.2).

3.2. Dissolution of cellulose (Dawsey & McCormick, 1990; Morgenstern & Kammer, 1996)

Cellulose (30 g) was suspended in MeOH (100 mL) for 30 min while stirring at room temperature. Suspension is filtered; afterwards cellulose was suspended in DMAc (100 mL), under the same conditions. Then suspension was filtered again. In parallel, LiCl (105 g) was dissolved in DMAc (1.5 L) at 70 °C. After, LiCl dissolution, pre-treated cellulose was added for complete solubilization in DMAc/LiCl solution at 70 °C over 4 h.

3.3. Preparation of tosyl cellulose

Tosylation of cellulose was achieved by combining solubilized cellulose (200 mL, 25 mmol) and triethylamine (41.2 mL, 298 mmol, 12 equiv) under continuous stirring at 0 °C. TsCl (28.36 g, 149 mmol, 6 equiv) in DMAc (100 mL) was added dropwise within 30 min. The homogeneous reaction mixture was stirred for 24 h while temperature gradually rose up to room temperature. After 24 h, the reaction mixture was poured into ice water (1 L). The precipitate was filtered off and washed with hot distilled water (500 mL) and hot EtOH (500 mL). The product was dried at 50 °C over night under vacuum (9.199 g, yield: 84%, DSTos: 1.8).

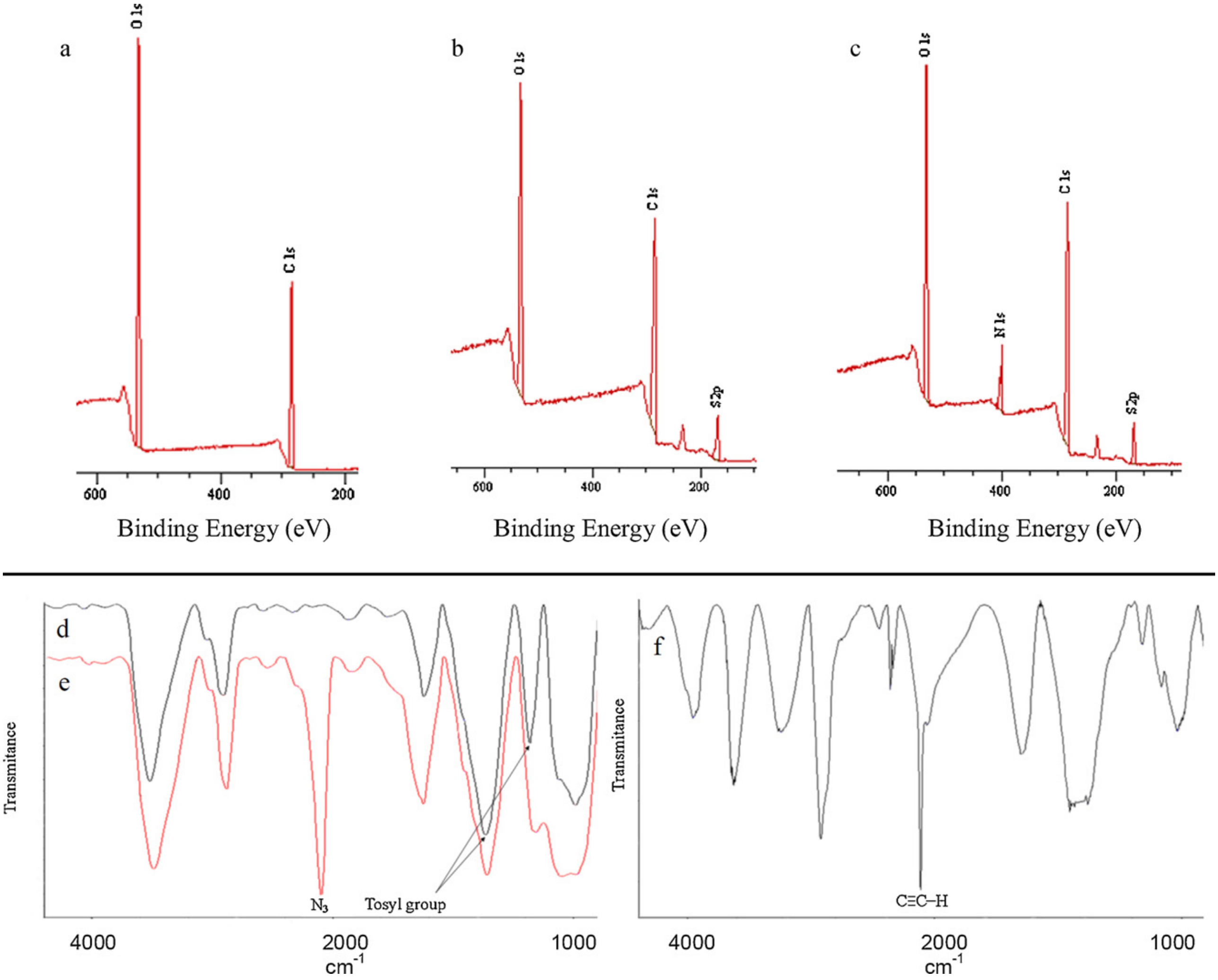

Fig. 1. Product analysis: XPS spectrum of (a) cellulose, (b) tosyl cellulose, (c) azido cellulose; comparative FTIR spectra of: (d) tosyl cellulose, (e) azido cellulose, and (f) propargyl starch.

3.4. *Preparation of azido cellulose*

Azido cellulose was prepared using a modified procedure described by Liebert, Hänsch, and Heinze (2006). Tosyl cellulose (4 g, 9.4 mmol) and NaN_3 (5.53 g, 85 mmol, 10 equiv) were added in DMF (150 mL). Reaction was activated using microwave irradiation (300 W, 100 °C, 10× 1 min). After cooling down to room temperature, the reaction mixture was poured in distilled water (500 mL). The precipitate was filtered off and washed with hot distilled water (100 mL) and warm EtOH (150 mL). The product was dried at 50 °C over night under vacuum (3.02 g, yield: 80%, DSAzido: 0.4).

3.5. *Preparation of crosslinked product*

Azido cellulose (800 mg, 4 mmol) and propargylated starch (1.2 g, 4.9 mmol) were added to 60 mL of DMSO. Sodium ascorbate (80 mg, 0.4 mmol, 0.1 equiv) was dissolved in 5 mL of water and was added to reaction medium. Copper sulfate pentahydrate (50 mg, 0.2 mmol, 0.05 equiv), dissolved in 5 mL of water, was also added to the solution. The mixture was then left to react under continuous stirring, during one week at room temperature. After that, the reaction product was filtered and washed with distilled water (80 mL) and EtOH (60 mL), and then was dried at 50 °C over night under vacuum (1.663 g, mass yield: 83%).

4. Results and discussion

Using a cellulose solution in DMAc/LiCl is the common way to prepare tosyl cellulose. This compound was prepared applying p-toluenesulfonyl chloride as reagent and triethylamine as a base at low temperature, to prevent side reactions resulting in chlorodeoxycellulose (Heinze, Rahn, Jaspers, & Berghmans, 1996). A solution of cellulose and triethylamine was cooled to 0 °C, then p-toluenesulfonyl chloride was added and the mixture was stirred while temperature gradually rose to room temperature. The precipitated tosyl cellulose was then recovered by filtration and was washed with ethanol. Modified cellulose was analyzed by infrared and NMR spectroscopies. The ^{1}H NMR spectra showed peaks between 7.4 and 7.8 ppm, corresponding to aromatic groups, a peak at 2.4 ppm corresponding to methyl group and peaks of anhydroglucose unit between 3.4 and 5.3 ppm. ^{1}H NMR data allowed the determination of the substitution degree (the number of tosylated hydroxyl groups per anhydroglucose moiety), which is equal to 1.8. X-ray photoelectron spectroscopy (XPS) confirmed this DS (Table 1) (Dorris & Gray, 1978a, 1978b; Montplaisir, Daneault, & Chabot, 2008). The spectra of tosyl cellulose revealed the presence of carbon, oxygen and sulfur signals at 284 eV (C 1s), 532 eV (O 1s) and 168 eV (S 1s), respectively (Fig. 1b).

Azidation of tosyl cellulose using sodium azide in DMF (10 equiv/UAG) led to the 6-azido-6-deoxycellulose after 6 min of

Table 1
Chemical data.

Sample	C (%)	O (%)	S (%)	N (%)	DS XPS	DS RMN
Tosyl cellulose	64.80	27.27	6.17	0.51	DS = 1.8	DS = 1.8
Azido cellulose	63.06	27.05	5.85	4.03	DS_{Ts} = 1.5, DSN3 = 0.4	DSTs = 1.5, DSN3 = 0.4
Propargyl starch	69.87	27.36	–	0.53	DS = 2.2	–
Starch-grafted cellulose	64.96	29.43	1.92	1.57	–	–

microwave activation (100 °C, 300 W) in 80% yield (Liebert et al., 2006). The IR spectrum showed a peak corresponding to the azide group, at 2118 cm^{-1} (Fig. 1e) and XPS spectra revealed the presence of carbon, oxygen, sulfur and nitrogen signals at around 284 eV (C 1s), 532 eV (O 1s), 168 eV (S 1s) and 399 eV (N 1s), respectively (Fig. 1c). DS were determined by NMR and confirmed by XPS (Table 1).

Propargyl starch was prepared with sodium hydroxide and propargyl bromide (5 equiv/AGU) in aqueous media contrary to Tankam, Müller, Mischnick, and Hopf (2007) who propargylated starch in DMSO. The sample was isolated by dialysis. Propargyl starch was obtained in 69% yield. The resulting propargyl starch was poorly soluble in all organic solvents tested such as DMSO, chloroform, methanol, DMF or water. The FTIR spectrum demonstrated that considerable degree of acetylene functional groups were retained (Fig. 1f). The characteristic absorption of the (C≡C) bond at 2118 cm^{-1} was clearly visible. XPS was used to obtain the chemical composition of propargyl starch (DS 2.2) (Table 1).

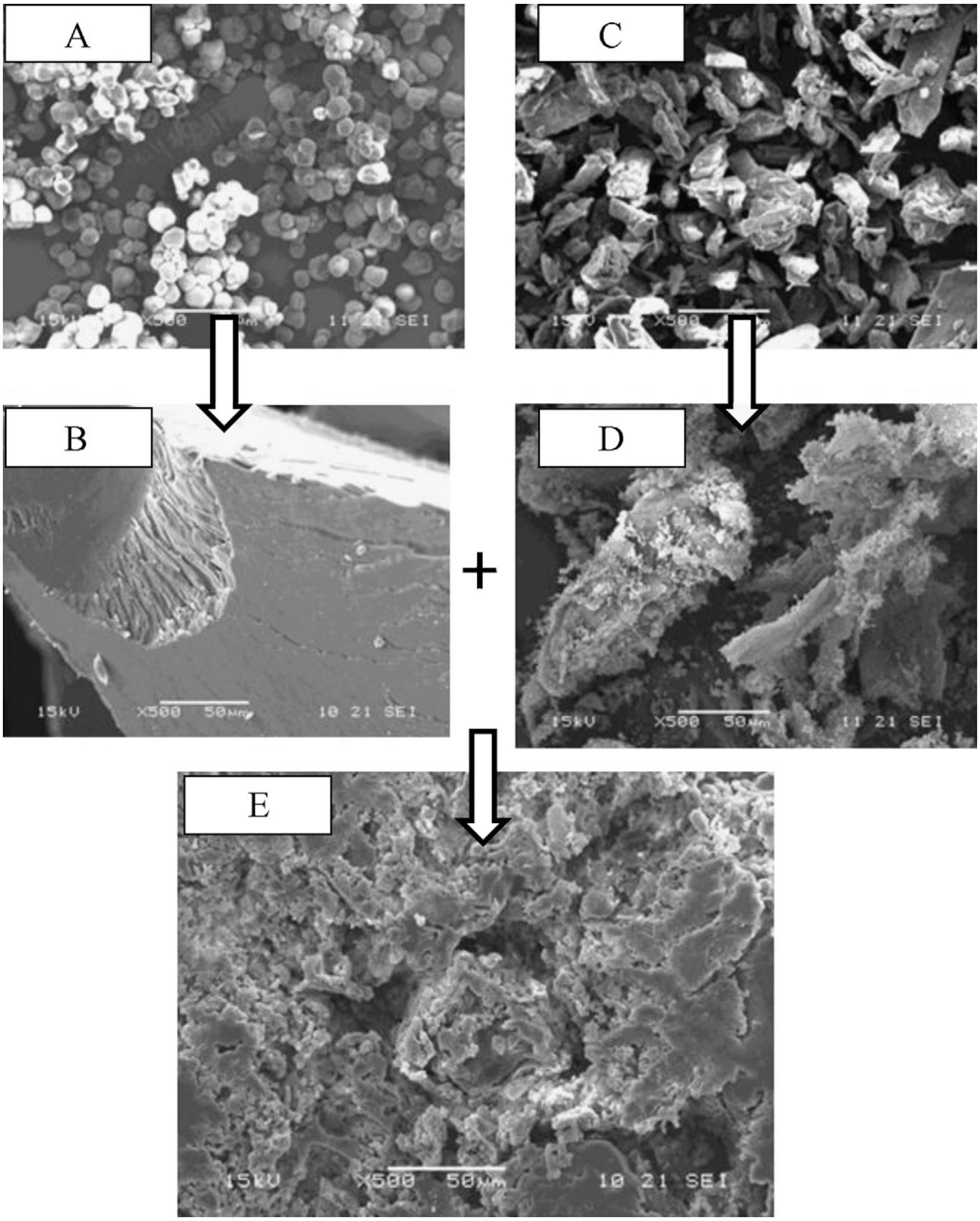

Fig. 2. SEM pictures (500×) of: (A) unmodified starch; (B) propargyl starch; (C) unmodified cellulose; (D) azido cellulose; (E) starch-grafted cellulose.

Azido cellulose and propargyl starch were then coupled using copper(I)-catalyzed reaction. Alkyne and azide precursors were suspended in DMSO, along with the catalyst and sodium ascorbate previously dissolved in water. After one week at room temperature, the reaction product was recovered by precipitation and filtration. SEM analysis was carried out to highlight structural modification as shown in Fig. 2. Fig. 2a represents native starch in granular form, while Fig. 2b shows dried modified starch polymer suspension. The previous granular form disappeared, and starch polymers have been deployed to lead to a dispersed form distribution. Fig. 2c and d shows unmodified and chemically modified cellulose, respectively. The microcrystalline cellulose was dissolved and chemically modified. The polymer suspension was dried, and a small amount of fine particles, probably cellulose can be seen. As shown in Fig. 2b and d, a change of substrates shape is observed after chemical modification. But for the last figure (Fig. 2e) evidence of the continuity in the material is observed, seems a consequence of the structure reticulation. Furthermore, XPS analysis revealed a decrease in the percentage of sulfur in click compound, compared to azido cellulose, confirming therefore this modification (Table 1).

5. Conclusion

The crosslinking of starch on cellulose was performed for the first time in a direct way using CuAAC, to produce a new material. This new strategy was achieved in four steps without heating except for the azidation where microwave irradiation was used. NMR and XPS confirmed all polysaccharides DS, ensuring the reliability of our method. SEM analysis supported the polymer grafting evidence.

The remaining terminal alkynyl groups are interesting candidates due to their CH acidity. They can be functionalized and modified by additional reactions. The tosyl groups also allow easy functionalization by simple nucleophilic substitution. These new materials, derived from polysaccharides, could be used for grafting molecules of interest.

This work is presently continuing toward two ways. A physical study of the crosslinked product is carried out in parallel with the adaptation of these reactions on Kraft and thermomechanical pulp, separately. It is important to specify that Kraft pulp is essentially composed of cellulose and hemicellulose while thermomechanical pulp is defibrilated wood fiber composed of cellulose, hemicellulose and lignin. These major differences between pulp and cellulose powder (our model) explains the complexity involved in adapting these reactions to thermomechanical pulp.

Finally an optimization of all reactions cited above is underway in order to reduce reactions times and improve purifications.

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