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Chemical Modification of Xylan

Djamila Kerrouche, Nabila Rouba and Vincent Chaleix

Abstract

Our study is part of the general context of valuing by-products from the wood industry, which consists of the chemical modification of xylan by synthesis of branched copolymers such as xylan-g-PLLA. The used xylan is extracted from chestnut and 4-dimethylaminopyridine (DMAP) is the catalyst. In fact, the synthesis of xylan-graft-poly (L-lactide) copolymer starting from natural and renewable resource products xylan and L-lactide is performed under different conditions. The results of the grafting reaction are unfavorable due to longer time because of depolymerization reactions. Another result is the solubility and insolubility of the copolymers synthesized in water. This first result indicates that there is a change in the properties of xylan. Moreover, the solubility of the xylan-g-PLLA copolymers is different from one study to another. Grafting of PLLA onto xylan was confirmed by Fourier transform infrared (FT-IR) and ¹HNMR analyzes. The dynamic mechanical analysis showed that the xylan-g-PLLA plastic materials have interesting thermo-mechanical properties.

Keywords: extraction, graft copolymer, poly (L-lactide), valorization, xyans

1. Introduction

Xylan is a natural biodegradable polymer, a major component of hemicellulose which is one of the most abundant polysaccharides in nature after cellulose and starch. Hemicellulose can be extracted by alkaline solution from plants, including agricultural and forestry products [1, 2]. Xylan is a major component of the hemicellulose of straw, grasses and agricultural residues. It has a skeleton consisting of β (1 \rightarrow 4) xylopyranose units, and generally has individual arabinose units attached to some of the C3 positions of the xylan skeleton as the main substituent, and small amounts of 4-O-methylglucuronic acid residues essentially linked to C2 position [3]. The solubility of xylan is favored by the presence of charged substituents such as uronic acids, which increase the hydrophily of the polymer and the intermolecular electrostatic repulsions. Its original physico-chemical properties bring it closer to hydrocolloids. It is used in particular in the food, cosmetic and pharmaceutical sectors, as a thickener, emulsifier or gelling agent. In addition, its binding properties have been exploited as additives in the preparation of paper pulps. They provide better flexibility to fibers and improve the mechanical resistance of paper. In recent years, increasing attention has been paid to poly (lactic acid) due to increasing environmental concerns and the decrease in fossil resources [4–7]. In addition, this polymer comes from renewable plant resources and has excellent properties such as biodegradability, mechanical strength, transparency and biocompatibility. It has considerable market potential in the fields of packaging, agriculture and biomedical and it is considered as a substitute for polymers of

non-degradable basic products [8, 9]. In order to improve the specific, thermal and mechanical properties of xylan, modification is one of the ways that best responds to this limitation of properties and that can enhance it. For example, acetylation of xylan increases its hydrophobicity and thermal stability [10, 11]. Indeed, the grafting of poly (L-lactide) is one of the modifications which gives a product derived entirely from nature. The concept of grafting PLLA on polysaccharides is already studied. Recently, a study has shown that PLLA-g-hemicellulose is a good accounting for a mixture between wood hydrolysates and PLA [12]. The blocks or grafted copolymers such as cellulose-graft-PLA, xylans-grafts-PLA, PLA-grafted starch copolymers, having hydrophobic and hydrophilic segments, have been reported to form different types of microstructures and have been applied as biomaterials [13]. Several researchers have studied cellulose graft copolymers such as poly (lactide) grafted cellulose or poly (ϵ -caprolactone) grafted cellulose, as biodegradable plastics, and have indicated that chains of poly (lactide) or poly (ϵ -caprolactone) acted as internal plasticizers for the polysaccharide and it was found that the properties of the xylan-g-PLA copolymers strongly depend on the length of the PLA chains grafted on the xylan [14–17]. In fact, the grafting reaction depends on the method used according to the case of the modification of the xylan or of the PLLA [18] and also of several parameters such as: temperature, reaction time, type and quantity of catalysts, etc. Trimethylamine is the catalyst used for grafting PLLA on chitosan with a yield of less than 50%. Other catalysts are used for this type of reaction such as DMAP which can open the lactide cycle [12], carbene [19]. In a study [20], the catalyst used is triazobicyclodecene (TBD) at low temperatures and for short periods of time. This part is concerned with the structural analysis of xylans extracted from chestnut sawdust as well as their transformation into plastic films. After extraction and purification, the structure of these polysaccharides was characterized by IR and NMR. In a second part, the xylans were modified by the grafting of the PLLAs. Finally, a study of the physical and thermomechanical properties of the synthesized copolymers is carried out [21].

2. Industrial upgrading of xylans

Cellulose and starch are the main plant-based polysaccharides for industrial use. Hemicelluloses in general, xylans in particular, although they currently represent a modest volume of exploitation, are nevertheless receiving increasing attention [22]. Their original physico-chemical properties bring them closer to hydrocolloids. The latter denote polysaccharides of natural origin or their derivatives, which dissolve or disperse in water to form viscous solutions or suspensions. Hydrocolloids, which have a great affinity for water, affect the texture of the medium to which they are added and modify the consumer's perception of a product, hence their use in particular in the food, cosmetic and pharmaceutical sectors, as a thickener, emulsifier or gelling agent [23]. These polymers have in solution a low viscosity under stress and a high viscosity at rest at high concentration. These characteristics are those sought after for commercial naturally occurring thickeners such as xanthan gum and locust bean gum. In addition, their binding properties have been exploited as additives in the preparation of paper pulps. They provide better flexibility to the fibers and improve the mechanical strength of the paper [24]. Finally, their nutritional properties are not negligible. Xylans are in fact used as dietary fibers. They are not degraded by human digestive enzymes and thus accelerate intestinal transit. In addition, their ingestion would significantly decrease the accumulation of lipids in the liver and the blood cholesterol level [25]. Xylans can therefore be used in the native state, on the basis of their physicochemical properties, but the main ways

of upgrading these polysaccharides are based either on their hydrolysis to form precursors used in the chemical industry, or on their functionalization which allows to consider new applications.

2.1 A new way of chemical upgrading of plastic xylans of plant origin

The petrochemical plants of the world consume 270 million tonnes of oil and gas every year in the production of plastics [26]. Fossil fuels provide the energy and raw material needed to transform crude oil into materials such as polystyrene, polyethylene or polypropylene. The progressive scarcity of these organic materials will inevitably be accompanied by a significant increase in their cost. Biotechnologies and organic chemistry can nevertheless provide solutions and literature offers numerous references on this subject [27, 28]. Biotechnologies currently seem to favor three approaches to replace plastics with products derived from plants: the direct production of plastics by micro-organisms, by cultivated plants or the transformation of sugars. It was in 1977 that the American companies Cargill and Dow Chemical joined their efforts to produce, after fermentation sugars of plant origin into lactic acid and polymerization of the latter, a plastic called polylactic acid [26] or PLA. A few years later, Imperial Chemical Industries marketed another plastic obtained after fermentation of sugars of plant origin [29], Biopol, which is a copolymer of the family of poly-3-hydroxyalkanoates (PHA). This bioplastic is however significantly more expensive than its synthetic counterparts derived from fossil fuels. Its only advantage is its biodegradability. Faced with high production costs, scientists have directed their research towards the direct synthesis of plastics by plants. The objective here is to modify the genetic heritage of cultivated plants in order to make them synthesize plastic directly. However, these works face a series of problems linked to: the physiology of the plant: the chloroplasts of the leaves which are the seat of photosynthesis seem to be a privileged place for the production of plastics by the plant. Too much synthesis at this level lowers the yields of photosynthesis and therefore the amount of produced plastic; to the methods of extraction and purification of plastics from the plant: These methods require the use of huge amounts of solvent; to public opinion: the dissemination of genetically modified organisms (GMOs) in our environment is currently causing sometimes violent controversies. The recent statement of the precautionary principle and the tightening of the regulations linked to this type of manipulation undoubtedly constitute a serious obstacle to the development of such technologies since they impose strictly controlled cultivation conditions incompatible with large-scale production. Organic synthesis provides different responses. One strategy is to chemically modify plant polymers. Remember that the first synthetic polymers were obtained by chemical modification of cellulose, such as nitrocellulose or cellulose acetate, used among others as thermoplastics. The esterification of the hydroxyl groups of the cellulosic fibers by aliphatic chains profoundly modifies their properties, and in particular the thermoplasticity and the hydrophobic character, but also the biodegradability, the solubility, the inflammability, etc. The properties of the material obtained then depend on the length of the grafted chain, as well as on the degree of substitution of the esterified polymer or DS; ie, the number of esterified hydroxyl functions per anhydroglucose unit in the case of cellulose. Cellulosic esters with a short carbon chain (less than six carbon atoms) currently represent an important industrial market, used and marketed in fields as varied as textile fibers, films, film substrates and membranes, coatings and varnishes, thermoplastic materials or composite materials. Cellulose esters, such as cellulose acetate (CA) or mixed esters such as cellulose acetate propionate (CAP) and acetate butyrate (CAB), all made from highly purified microcrystalline cellulose, compete with plastics derived from

the petrochemical industry such as polyethylene, polypropylene, polyethylene terephthalate, polycarbonates, nylons, etc., for which the basic products, ethylene, propylene, xylene or even ethylene glycol are still very economically attractive. In addition, obtaining cellulose esters requires the prior solubilization of the cellulose, which generates the implementation of a heavy and costly methodology, unlike the synthetic polymers derived from polycondensations. Their properties remain original, however, and they continue to satisfy certain markets. The thermomechanical qualities of cellulose esters remain their main handicap. Indeed, due to the fragility of the polysaccharide chains at high temperatures, the glass transition temperature (T_g) and the material decomposition temperature are often very close. The glass transition temperature corresponds to the transition from a glassy state, in which the polymer is hard and brittle, to a rubbery state for which the polymer is soft and flexible. From this temperature, the material is more flexible and easier to work. This is the reason why a plasticizer is often added in order to lower the glass transition temperature and therefore widen the field of application of thermoplastics. Several plasticizers are commonly used, including on an industrial scale. This is the case for triethylcitrate for cellulose acetate and dioctyladipate for CAP. However, the use of plasticizer can sometimes be inconvenient for certain applications. These small molecules tend to evaporate over time, which can change the performance of the material in the short or medium term. Another solution for lowering the T_g of a polymer is to graft long chain substituents, so as to increase the free volume and therefore reduce the interactions between the polymer chains. The presence of bulky and flexible side substituents such as fatty chains, by removing the polysaccharide chains, lowers their T_g and therefore influences the field of use of these thermoplastics. Studies have shown on a series of cellulose esters ranging from acetate to palmitate (C16), that T_g decreases significantly with the increase in the length of the grafted fatty chains [30]. Thus, without adding plasticizer, it is possible to obtain hydrophobic plastics that are more flexible, more deformable, less brittle, which suggests new areas of application, such as packaging or plasticulture and, in particular, agriculture mulch films [31, 32]. All of these works, initiated from a model substrate, cellulose, makes it possible to envisage new ways of upgrading for polysaccharides, and in particular for wood xylans. The objective of this study is the synthesis of new plastic materials by grafting poly (lactic acid) on xylan (4-O-methylglucuronoxylanes) extracted from chestnut sawdust.

2.2 Xylan extraction from wood

The main problem facing the experimenter is that of the chemical richness of the plant cell wall, which is reflected in the great structural diversity of the macromolecules, essentially polysaccharides, which are represented there. The protocols to be used must therefore be sufficiently selective to allow the extraction of a category of macromolecules; they must also be concerned with protecting the integrity of molecular structures by limiting the degradation of the latter. A detailed study of literature in the field of hemicellulose extraction reveals the existence of a large number of protocols. This observation can only be explained by the wide variety of hemicellulosic structures identified within the plant cell wall. The development of a specific extraction protocol for xylans with a view to their commercial exploitation is the subject of numerous studies. The question to be answered by the experimenter is what type of xylans to extract, from which plant material, for what properties, for what applications and using which protocols. The presence of a polyphenolic frame formed by lignin, as well as the existence of chemical bonds between the different hemicelluloses which constitute the wall, and between the hemicelluloses and lignin limits the extraction of xylans. It is

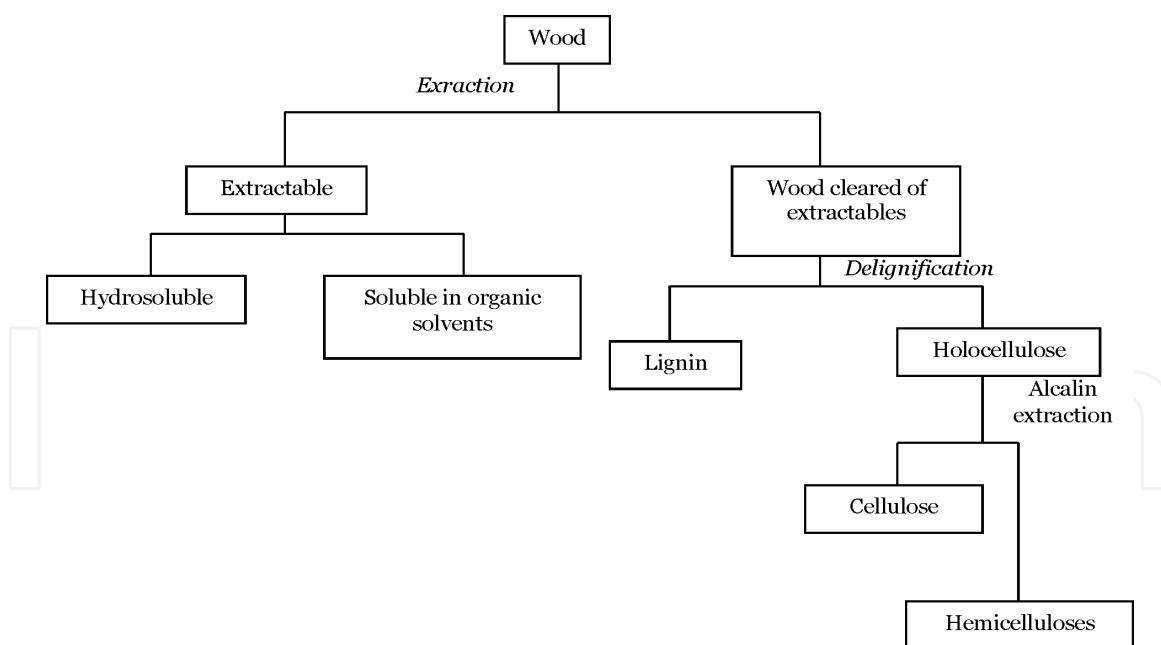


Figure 1.
 Separation of wood constituents.

then impossible to extract a type of polysaccharide without breaking these bonds and therefore without modifying the polymer with respect to its state in situ. It is therefore necessary to apply sufficiently strong extraction conditions to allow the rupture of these bonds, without degrading the extracted molecules. In the case of extraction from wood, the xylans are conventionally collected, after delignification in the presence of sodium chlorite, by an alkaline extraction. Beforehand, it is necessary to eliminate the extractables, so that they do not interfere in the analyses later. A schematic representation of the separation of the constituents of wood is illustrated in **Figure 1**.

3. Preparation of the copolymers

The DMAc/LiCl solution is prepared for 1 hour at a temperature of 80° C with mechanical stirring. In a flask equipped with a condenser, we mixed a quantity of the solution of DMAc/LiCl, L-lactide (2, 4 or 8 equiv./ OH) and DMAP catalyst (0.1, 0.5 or 1 equiv./OH) then heated it to 80° C with magnetic stirring at different reaction times (8, 16, 24 h). At the end of the reaction, a quantity of ethanol is added in order to precipitate the xylan-g-PLLA. The product obtained is purified with the solvent dimethyl sulfoxide (DMSO) and precipitated in ethanol. The obtained copolymer is dried at room temperature and is characterized by different methods.

3.1 Xylan extraction

Chestnut wood glucuronoxylans were extracted by this procedure (**Figure 2**). They were obtained from chlorite-delignified sawdust by aqueous KOH extraction. The MGX has been extracted with a yield of 19%. The obtained fraction is characteristic of a classical MGX with more than 99% of xylose and 4-*O*-methylglucuronic acid (typical markers of glucuronoxylans). 4-*O*-methylglucuronic acid contents were 16.6% (molar ratio), which is in agreement with the data obtained by the colorimetric assays (17.4, mass ratio) and the

Xyl/4-*O*-MeGlcA ratio was found: 6.1. However, concerning the size of the extracted molecules, a DP of about 200 was found which is a typical result for this kind of products. This MGX is represented in **Figure 3**.

3.2 RMN

The result of ¹H NMR spectra of xylan (*D*₂O) is presented in **Table 1** and **Figure 4**.

3.3 Infrared analysis

The IR spectra of xylans (**Figure 5**), and more particularly of 4-*O*-methylglucuronoxylans, have been studied in detail by Marchessault and Liang (1962) (see [33]) and more recently by Kacurakovaetcoll. (2000) (see [34]). The absorption bands appearing in the figure and listed in the table are characteristic of xylans of type (1 → 4), with a maximum absorption band at 1044 cm⁻¹, corresponding to the vibrations of elongation of the ring bonds and C-OH bonds. The weak, but very clear band at 896 cm⁻¹ is characteristic of glycosidic bonds [35].

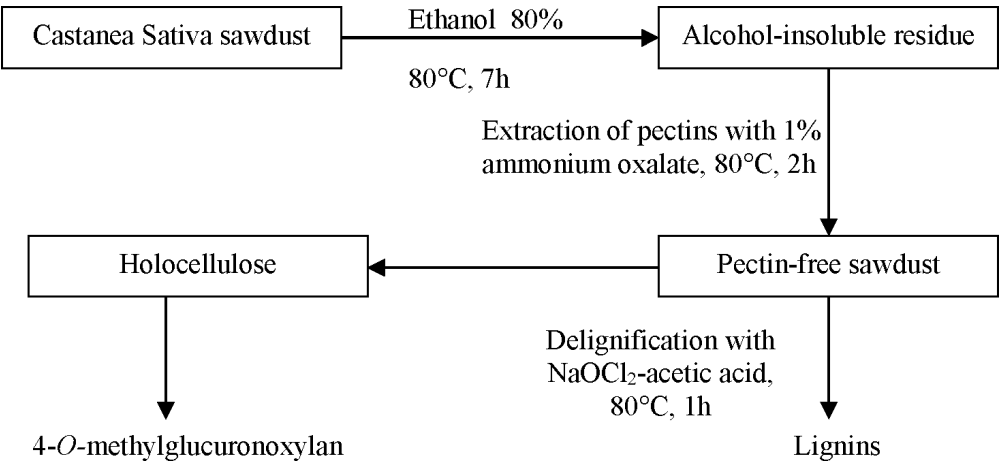


Figure 2. Scheme of fractionalization of 4-*O*-methylglucuronoxylans (MGX) from chestnut wood.

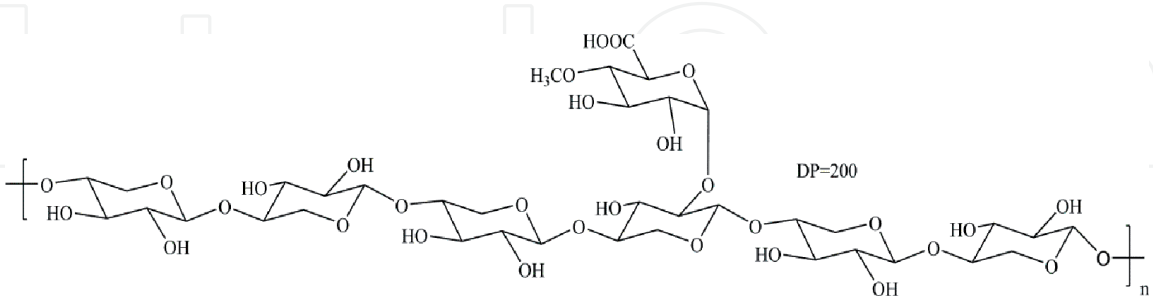


Figure 3. Structure of 4-*O*-methylglucuronoxylan extracted from *Castanea sativa*.

Glycoside residues	Chemical shifts in ppm (J en Hz)					
		1	2	3	4	5
(1 → 4)- D-Xylp	¹ H	4,48 (7,5)	3,29 (8,2)	3,55 (9,0)	3,79	4,10 (4,5; 11,5); 3,38 (11,0)

Table 1. Chemical shifts of glycosidic residues of xylan (*D*₂O).

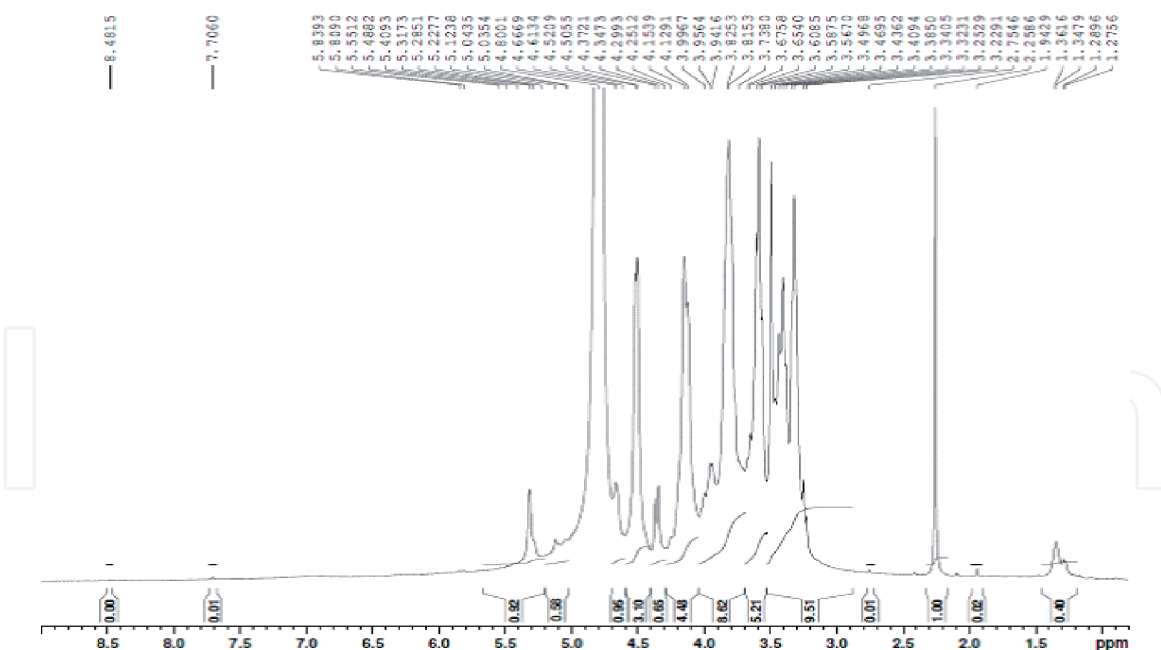


Figure 4.
¹H NMR spectra of xylan (D₂O).

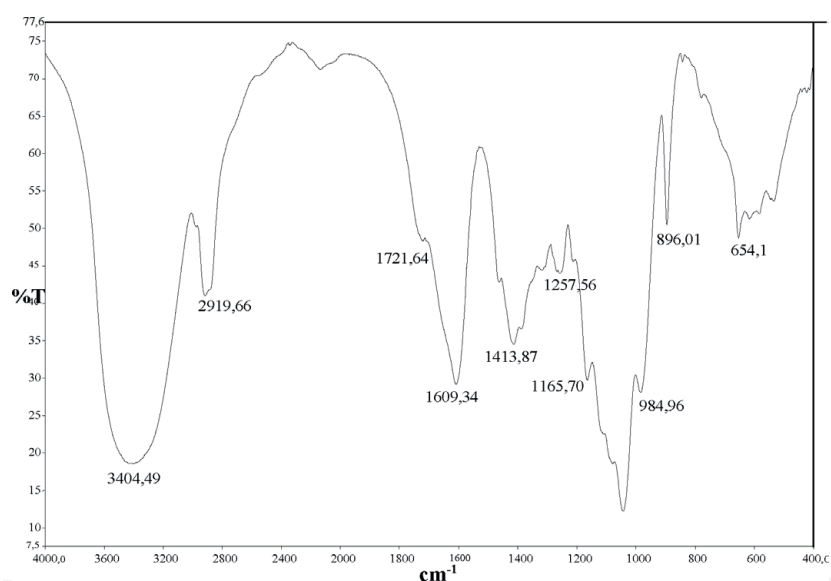


Figure 5.
FT-IR spectra of xylan.

4. The results

The synthesis of the biodegradable xylan-g-PLLA copolymers is carried out at atmospheric pressure by opening the L-lactide ring and the DMAc/LiCl/xylan solution (0.2 g/l) in the presence of DMAP as catalyst. The degree of substitution and the degree of polymerization express the efficiency of the grafting reaction. They are calculated from ¹H NMR spectra. The medium DS is defined as the medium number of grafted PLLA chains per repeat unit which is calculated by comparing the integration of the 3 protons of the terminal CH₃ with the equatorial proton H₅ of xylose. The medium DP, meanwhile, is calculated by comparing the integration of internal CH₃s with terminal CH₃s. The yield is defined as the ratio between the weight of plastic film and the initial weight of polysaccharide.

It should be noted that the DS and the DP show that the latter both increase with the amount of L-lactide and the DMAP and decrease beyond the 16 h time.

In addition, it has been proven that DMAP is used as a hyper nucleophilia catalyst which is 104 times more active than pyridine [10], this is more favorable when the reaction time is longer, favoring depolymerization reactions. The maximum conditions for having a larger DS and DP are: 16 h, 8 eq/OH, 1 eq/OH.

4.1 Characterization of copolymers

One of the properties verified after the grafting reaction is the solubility of the copolymers and some have been found to be soluble in water and others not; which confirms the modification of the properties of xylan. A copolymer is dissolved in water in a petri dish after evaporation of the solvent at 40° C in an oven, a casting plastic film was obtained (**Figure 6**).

The IR analysis of xylan, PLLA and xylan-g-PLLA is presented in the **Figure 7**. All the xylan absorption bands of type (1 → 4) are presented in the **Table 2**. An absorption band of the groups of hydroxyl is observed at 3544 cm⁻¹, another absorption band at 897 cm⁻¹ of glycosidic C-H (β). [36] Other bands at 1096 cm⁻¹ and 1044 cm⁻¹ of the C-O, C-C and C-OH groups of the ring. A strong absorption band at 1784 cm⁻¹ is observed on the chemically modified xylan characteristic of ester functions (C = O) [36, 37]. Other bands that characterize CH and CH₃ are seen at 2984 and 2934 cm⁻¹. All of these absorption bands confirm the modification of the xylan structure.

The ¹H NMR spectrum (**Figure 8**) shows intense signals corresponding to the protons of the xylose units of the unsubstituted main chain, as well as less intense signals attributed to the uronic acid units and to the xylose units which carry them in position 2. The intensity of these signals depends on the degree of substitution by uronic acid. The doublets attributed to the anomeric protons of the xylose units, substituted (4.5 ppm) or not (4.6 ppm), are associated with a coupling constant of about 7 Hz, characteristic of an osidic bond. The coupling constant of the doublet corresponding to the anomeric protons of uronic acid, at 5.3 ppm, is in the order of 2 Hz, which characterizes an osidic bond. It is also possible to observe on the different ¹H spectra of xylans, a fine singlet around 3.4 ppm, which is to be associated with the existence of methyl groups carried, given the integration, by the uronic acid. This last remark confirms the presence of 4-O-methylglucuronic acid. This is fixed in position 2 of the xylose, which



Figure 6.
Photograph of a xylan-g-PLLA film. Note: Xylan-g-PLLA, xylan-graft-poly(L-lactide).

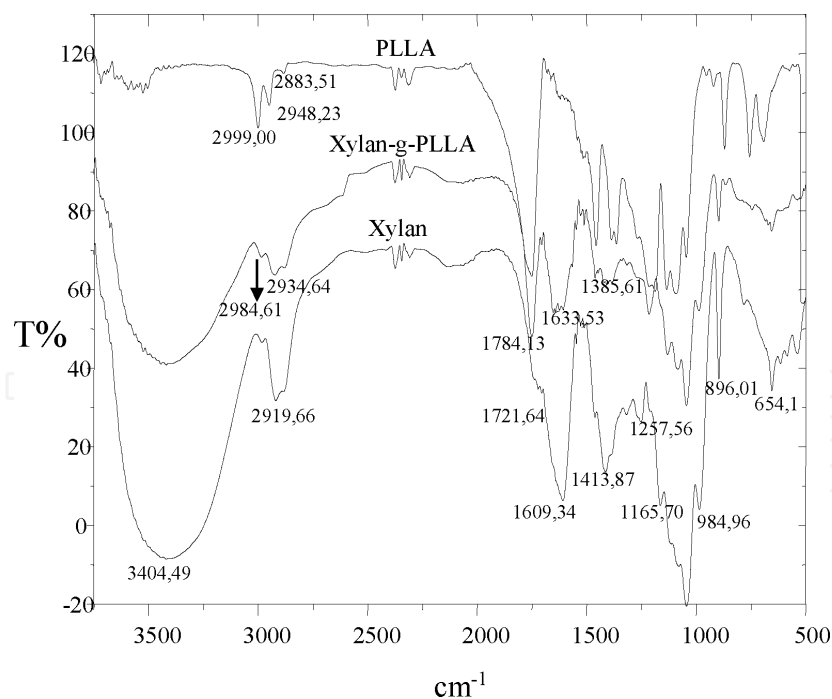


Figure 7.
Fourier transform infrared spectra of xylan, PLLA, xylan-graft- poly (L-lactide) copolymer.

Absorptions (cm ⁻¹)	Relative Intensity	Type of vibration
3404	w	$\nu(\text{O-H})$
2919	m	$\nu(\text{C-H})$
1721	m	$\nu(\text{C=O})$ uronic acid
1609	e	$\nu(\text{C=O})$ acid salt, anti-symmetric vibration
1465	f	$\delta(\text{CH}_2)$ symmetric
1413	f	$\nu(\text{C=O})$ acid salt, symmetric vibration
1257	f	$\delta(\text{CH}_2)$
1165–1149	m	$\nu(\text{C-O-C}), \nu(\text{C-C})$
1131–1121	e	$\nu(\text{C-O-C}), \nu(\text{C-C})$
1096	s	$\nu(\text{C-O}),$ cycle, $\nu(\text{C-C})$
1044	s	$\nu(\text{C-O}), \nu(\text{C-C})$
984	m	$\nu(\text{C-O}), \delta(\text{OH}),$ cycle vibrations
896	m	$\delta(\text{CH})$ glycosidic (β), cycle vibrations

w: wide, m: medium, f: weak, s: strong, e: shoulder; ν : valence vibrations; δ : deformation vibrations.

Table 2.
Absorption bands characteristic of glucuronoxylans.

results in a greater deshielding of the H2 compared to the unsubstituted xylose units. We can distinguish on the ¹H NMR spectrum of the modified xylan, signals between 1 and 2.5 ppm of the protons of the aliphatic chains shows a signal at 5.20 ppm which corresponds to the CH group, another signal at 1.47 ppm of the proton of the internal methyl group CH₃ and at 1.27 ppm for the proton of CH₃ at the end of the chains of PLLA (Guang-Xin, 2006). These intense signals corresponding to the protons of the xylose units of the main chain and to the protons of the PLLA groups confirm the chemical modification of xylan.

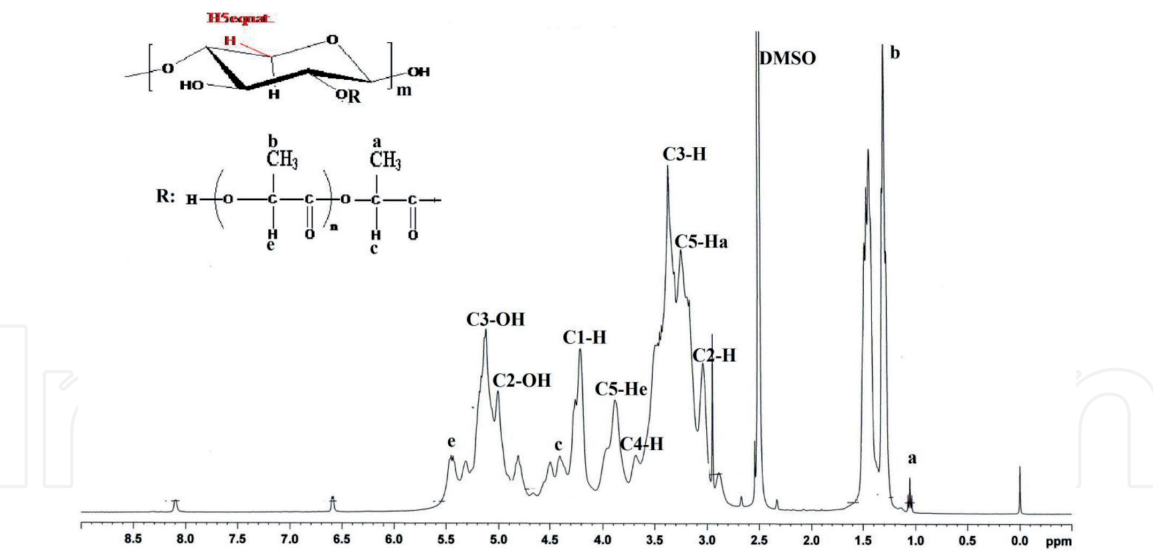


Figure 8.
¹H RMN spectra of xylan-graft-poly (L-lactide) copolymer (DMSO).

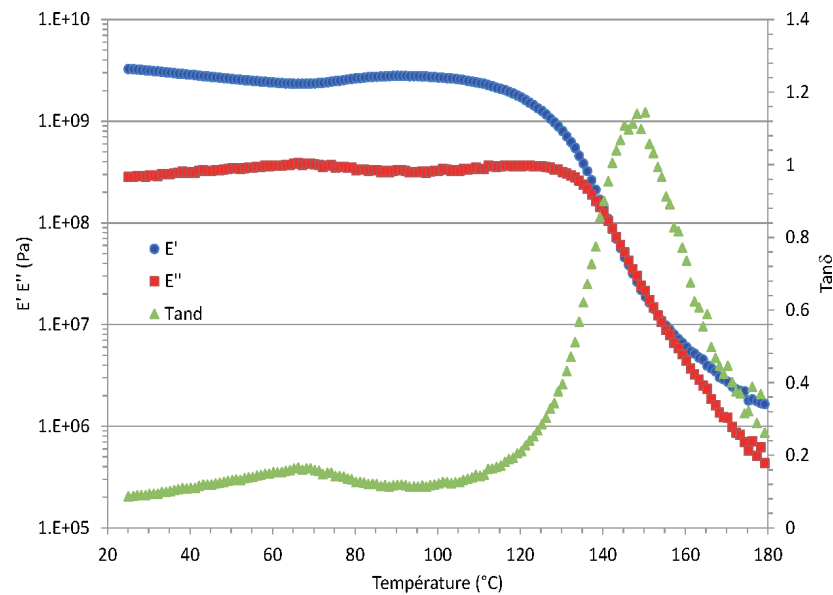


Figure 9.
Evaluation of the tangent of the loss angle and the loss modulus E'' of xylan-g-PLLA as a function of temperature.

For medium DP of fixed PLLA, it did not vary a lot (about 2 or 3). It confirms that the chains are very short but long enough to enhance the filmogenic character of materials [21].

4.2 Mechanical properties

The mechanical properties of PLA have been studied by various researchers [38, 39]. PLA has mechanical properties similar to those of polystyrene [40]. Dynamic mechanical analysis (**Figure 9**) showed that the glass transition temperature of the xylan-g-PLLA film is 147°C. For the new PLLA-g-xylan material, the results of mechanical tests (**Figure 10**) show that the film has a nominal strain $\epsilon_{\text{rupture}} = 8 \pm 2.5\%$, its Young's modulus $E = 1.2 \pm 0.1 \text{ GPa}$ (1200Mpa) and a nominal stress of about 60 MPa. These mechanical properties are close to those of polypropylene [41].

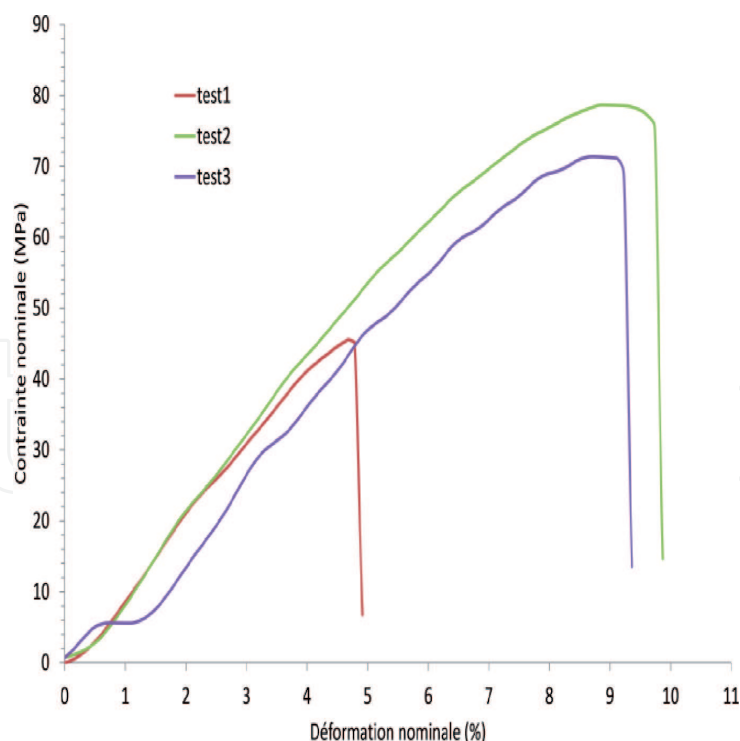


Figure 10.
Elongation at break according to the nominal strain (5%).

5. Conclusion

The modification of xylan by grafting the PLLA on the xylan extracted from the sawdust of chestnut was carried out in this work. The synthesis of branched xylan-g-PLA co-polymers is carried out from L-lactide and xylan using DMA as solvent for the xylan and 4-dimethylaminopyridine (DMAP) as catalyst at a temperature of 80° C. These copolymers are characterized and infrared analysis has shown the appearance of the characteristic band of the esters at 1784 cm⁻¹ and of other bands of the group CH₃ on the xylan-g-PLLA spectrum. Following the ¹H NMR analysis, the appearance of the PLLA aliphatic protons was observed on the spectrum of the grafted xylan. The xylan copolymers are insoluble in water. The higher the DS, the more difficult the solubility is in water. Dynamic mechanical analysis has shown that Tg of the xylan-g-PLLA film is 147°C.

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