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International Journal of Current Research
Vol. 5, Issue, 01, pp.136-140, January, 2013

INTERNATIONAL JOURNAL
OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

Green Gluing of Tropical Wood Part I: Surface Analysis of Frake (*Terminalia superba*) and Ayous (*Triplochyton scleroxylon*) Woods by X-Ray Photoelectron Spectroscopy (XPS) and FOURIER Transform InfraRed Spectroscopy (FTIR)

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ARTICLE INFO

Article History:
Received 15th October, 2012
Received in revised form
20th November, 2012
Accepted 22th December, 2012
Published online 16th January, 2013

Key words:
Green gluing, Tropical woods, Sanding, XPS, FTIR, Atomic ratio, Hydrocarbon impurities, Extractives.

ABSTRACT

X-Ray Photoelectron Spectroscopy and Fourier Transform Infra Red Spectroscopy (FTIR) were used, to characterize tropical ayous (*triplochyton scleroxylon*) and fraké (*terminalia superba*) sanded wood surface prior to gluing. As expected, O_{1s} and C_{1s} were the predominant species in the spectra of the two woods. C_{1s} peak have been decomposed into several components. Earlier study reveled tree classes of carbon for frake. Unlike these result the two woods characterized in this work exhibit carbon atoms in classes C1 (carbon atoms bonded by a C-C or a C-H bond), C2 (carbon atoms bonded by C-O bond), C3 (carbon atoms bonded by C=O or by a O-C-O bond), C4 (carbon atoms bonded by O-C=O bond), C0 (carbon attributed to inhomogeous charges, and à non attributed carbon at 285,6 eV. The four principal classes were confirmed by FTIR. The oxygen-to-carbon (O/C) ratio of wood was determined. The deviation of the O/C ratios from theoretical values was interpreted as indicative of surface rich in lignin, surface hydrocarbon impurities or extractives and wood density.

INTRODUCTION

Process of woods' bonding is usually achieved through the application of an adhesive on wood surface. Among the different mechanisms involved in the bonding of woods, two synergistic effects seem essential to achieve a good bonding strength: the penetration and anchoring of the adhesive in the void spaces of the wood surface and the occurrence of a strong interaction or chemical reaction between the adhesive and the major constituents of wood. This latter condition is governed by the surface properties that depend not only on the bulk composition, but also in the surface building process. In this study, X-ray Photoelectron Spectroscopy (XPS) also referred to as Electron Spectroscopy for chemical analysis (ESCA) and Fourier Transform InfraRed Spectroscopy (FTIR) which have proved to be two suitable investigation methods to characterize the composition of a material surface have been used. These methods are powerful analytical and non-destructive techniques which have already been used for the analysis of the surfaces of natural or synthetic polymers (Dorris and Gray, 1978; Briggs, 1998), natural and textile fibers (Briggs Seah 1990; Gao, *et al*. 2005; Ostmeyer *et al*.,1988; Ostmeyer and Litterell,1989; Noah and Prud'homme 1994; Sinn, 2001), and in the characterization of wood surfaces (Istone, 1995; Vicherman, 1999) and wood reactions (Gray, 1978).They were used to investigate the surface of ayous and frake prior to gluing, in an attempt to identify the chemical functional groups that are responsible of the interaction of both tropical wood species with an adhesive and hence to elucidate the mechanism of bonding of these woods

MATERIALS AND METHODS

Samples preparation

Unseasoned wood blocks of ayous and frake were purchased in Yaoundé area. Their specific weights were determined at 12% moisture content and are respectively 0.36 g/cm^3 for ayous and 0,45g/cm^3 for frake. Their void fractions calculated at 12% moisture content according to the Siau formula (Siau, 1984) are respectively 75% and 66%. To reduce variability the sample material for the analysis was cut from the same or single wood flitches. Specimen surfaces for XPS and FTIR analysis were prepared by cutting defect free and smooth surface using fine sand paper and kept in polyethylene bags until the measurement were carried out. Samples are of 10*10*2mm^3. Cutting was performed such that all material originated from the core rather than the surface of the original sample. It was not possible to separate the specimens into earlywood and latewood portions, since ayous and frake usually display a diffuse porous structure, without any regular annual growth ring. It has been reported that mechanical treatment could influence the surface of wood (Sinn, 2001). For this study the treatment of the samples was conducted according to the same procedure as that use in bonding without altering the nature of the sample during preparation such that chemical groups involved in the reaction between the constituents of wood and the adhesives could be detected. The samples were not extracted or modified otherwise by

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chemical or thermal treatment nor dried in an oven since we are interested by green gluing.

Samples analysis

XPS analysis was perform using an ESCALAB VG 220i-XL spectrometer fitted on a microlab system from Vacuum Generators and equipped with a condition source of non monochromatized Mg Kα anode X-rays source with an excitation energy of 1253,6 eV. K Kinetic energy measurements were made using a hemispherical electrostatic analyzer (r =150 µm) and a detector pass energy of 150 eV. Thin samples having a thickness of (2mm) or less were mounted onto an indium sample older and introduced in the working chamber maintained at a pressure of 10^{-7} Pa. Under these conditions, the order of the magnitude of the X-rays penetration is estimated within 1-10 nanometers. Electrons from the inner part of the sample are recaptured by the charging effect of the surface. Infrared spectroscopy (IR) is a nondestructive analytical technique to determine ideal, identify or confirm the presence of functional groups. In this case, this technique has been used to confirm the observations made using the XPS analysis highlighting the presence of functional groups on the surface characteristics of materials and possibly the chemical reactions on the substrate-polymer interface. The FTIR measurement were performed using an infrared spectrometer Fourier transform Magna IR 550 coupled to an MCT detector cooled with liquid nitrogen. The accessory "ATR" is placed in the sample compartment. A microscope allows focusing on the desired wood analysis area.

RESULTS AND DISCUSSION

Figure 1(A) and (B) shows the XPS survey of ayous wood and fraké respectively. Wood is à natural biopolymer. As expected, the spectrum is dominated by carbon and oxygen peaks, which are the elements that make up the constituents of wood. The high-resolution spectrum of the carbon peak shows the presence of different chemical states, or classes, of carbon on the wood surface peak shows the presence of different chemical states, or classes, of carbon on the wood surface. Other elements such as nitrogen appear as traces in the two species with a characteristic presence of calcium and silica in ayous only.

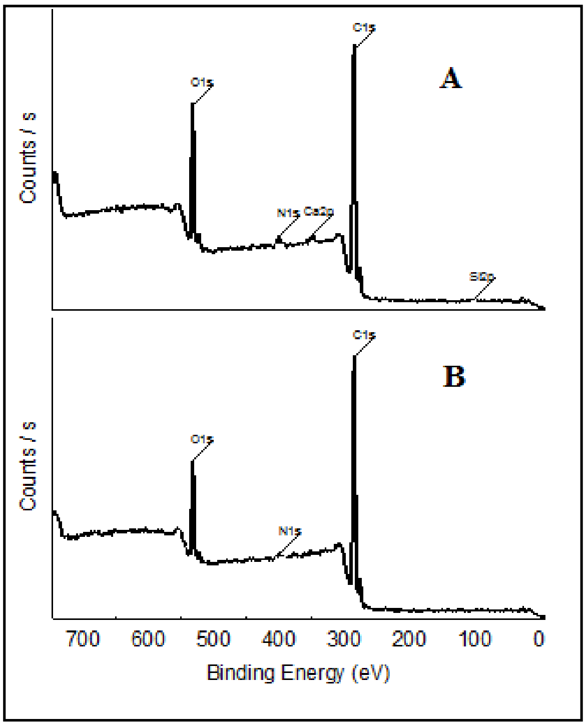

Figure 1 : Survey of ESCA spectra for(A) untreated Ayous and (B) untreated Fraké

The binding energies of different chemical elements present in the two species are summarized in Table 1. Since woods are perfect quality the presence of nitrogen in both ayous and frake less or never reported from temperate zone woods could probably attributed to amino acid eventually present in this species. Permanent presence after Ar^+ bombardment indicates of its presence in the structure of wood and not a contamination. On the other hand, trees are living being which collect most of the necessary nutrients such as inorganic ions in the soil. Nitrogen element absorbed by the plant is vital to its growth. This element is usually combined with oxygen in the form of nitrate ions (NO_3^-) taken from the grown. The presence of limestone and silica is the composition of the soil of the tree growth place. Major peak assignments were performed in closed relation with the four classes of carbons found in the high resolution XPS spectra. Peaks of interest in relation with C-H and C-C bonds, C-O, C=O and O-C=O bonds carbons classes have been assigned. Dorris and Gray (Dorris, G.M. and Gray, D.G. 1978) reported four different types of carbon atoms in wood. C1 denotes a carbon atom bonded only to a carbon or a hydrogen atom (C-H/C-C), C2 denotes a carbon atom singly bonded to a oxygen atom (C-O) other than a carbonyl atom, C3 denotes a carbon atom single bonded to two oxygen atoms or to a single carbonyl atom (O-C-O/C=O) and C4 denotes a carbon atom single bonded to a oxygen atom and to a carbonyl oxygen atom (O-C=O). Observation of O_{1s} peaks indicates a relatively greater height for ayous compared to fraké. This difference reflects the presence of higher proportion of oxygen. The abundance of oxygen may be due to the presence of calcium mineral (Ca), silicon and nitrogen N probably in their oxidative form (CaO, SiO_2 and NO_3^-)

Table 1: Binding energy of different chemicals elements on ESCA (XPS) survey spectra

Wood species	Binding energy (±2eV)				
	C_{1s}	O_{1s}	N_{1s}	Ca_{2p}	Si_{2p}
Ayous	284,6	531,88	399,37	347,16	101,95
fraké	284,5	532,03	399,17	-	-

O/C Ratio

A determination of O/C ratio provides useful information on the surface composition of the samples. From the determination of peak area and the calculation of the O/C ratio as shown in Table 2, the sanded woods has a rather low O/C ratios of 0,26 and 0,19 for ayous and fraké respectively as compared to 0,83 for cellulose (Mjorberg, 1981). According to the literature a low O/C ratio suggests a surface rich in extractives and lignin materials that exhibit low O/C ratios with theoretical value of 0.10 and 0,33-0,36 (Mjorberg, 1981; Tshabalala *et al.*, 2003; Ben *et al.*, 1993) respectively. Calculation of the Cl/C2 ratio provided additional evidence in support of the O/C interpretation of the wood surface chemistry. The Cl and C2 components represent different chemical bonding states of carbon. The Cl component is related to carbon-carbon or carbon-hydrogen bonds in extractives and lignin. The bond involving C2 can result from all three classes of wood components, but predominantly from the carbohydrates as -CHOH and from lignin as β-ether and -C-OH bonds. The calculated theoretical C1/C2 ratio for pure cellulose is 0, for lignin close to 1, and for extractives up to 10. This evidence can be used to roughly describe wood surface composition-the higher the Cl/C2 ratio, the higher the relative concentration of extractives and possibly lignin on a wood surface (Boras, L., Gatenholm, P.1999). The result showed a higly C1/C2 ratio (3, 84) for the relatively dense wood frake and a low C1/C2 ratio (2.11) for ayous indicating more lignin on frake sanded wood than ayous wood surface.

Peak Assignments

In order to get more information, O_{1s} and C_{1s} peaks have been expanded and deconvoluted into their component peaks. The results are shown in Figures 2 and 3 for O_{1s} and C_{1s} expansion and deconvolution respectively. The O_{1s} peak is symmetrical in all cases

Table 2: C_{1s} peak analysis of sanded ayous and frake

Sample	O/C	Fractional Area				Bonding Energy Corrected(eV)				FWHM(eV)				Chemical Shifts (eV)			
		C_1	C_2	C_3	C_4	C_1	C_2	C_3	C_4	C_1	C_2	C_3	C_4	C_1	C_2	C_3	C_4
Fraké untreated	0,19	0,73	0,19	0,06	0,02	284,7	286,7	287,9	288,9	1,36	1,36	1,46	1,45	0,1	2,1	3,3	4,3
Ayous untreated	0,26	0,59	0,28	0,09	0,04	284,6	286,5	287,7	288,7	1,31	1,5	1,46	1,45	0,0	1,9	3,1	4,1
Maple wood(ref)	0,15	0,50	0,43	0,07	-	285,2	287,0	288,8	-	-	-	-	-	0,2	2,0	3,8	-
Fraké literature (Noah, J. N., Prud'homme R. E., 1994)	0,27	0,66	0,30	0,04	-	285,1	286,9	288,5	-	1,9	2,0	2,2	-	0,1	1,9	3,5	-

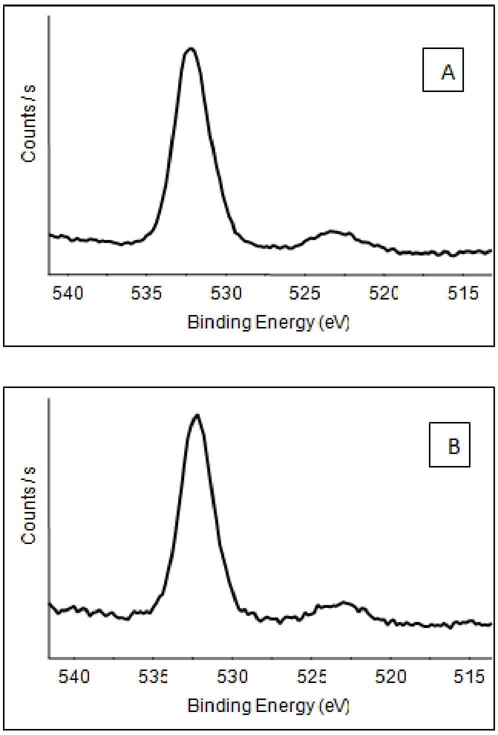

Figure 2: Expansion of O_{1s} peak obtained from ESCA spectra of (A) sanded ayous and (B) sanded fraké

and is describe as a single peak. The C_{1s} shows evidence of shoulders, indicating that it is made up of several components, which is justified since wood contains different constituents, polysaccharides, lignin and extractives, each of which has carbon atoms in different chemical environments. On the basis of their chemical shifts, the carbon atoms in woody materials have already been classified into four categories as illustrated in table III (Noah and Prud'homme, 1994). The contribution of these different carbon atoms to the C_{1s} peak has been calculated and is report in Table I. It is noted that chemical shifts, binding energy at half height (WHH) of the different carbon classes are in very good agreement with values reported for woody materials (Noah and Prud'homme, 1994). In Fig. 3 a deconvoluted high resolution spectrum of the C_{1s} peak of sanded ayous and fraké as the different parts contributing to the peak are shown. Contamination of the samples by carbon is one of the most important problems when using XPS for the investigation of polymers. This is even more problematic for wood than for other materials. First, just the C_{1s} peak is of greatest importance when interpreting XPS data from wood. Second, some handling of the specimens has to be done prior to the measurements (dehydration, encapsulating in a foil, etc.). Therefore the C_0 and carbon at 285,6 ev class was introduced. Such a C_0 sub peak was also found by Sinn *et al.* (2001) and Torr *et al.* (1996). It was interpreted as recondensed polyaromatics respectively as adsorbed hydrocarbon contamination. This C_0 class have been measured by Sinn *et al.* (2001) on woods specimen and assigned to electrical conducting material or inhomogeneous sample charging. The non assigned carbon at 285,6 eV could result of others contaminants. Moreover, the standard deviation for the sub peak position when considering all samples was lowest for C_0 and nearly fixed at (284.5±0.1) eV.

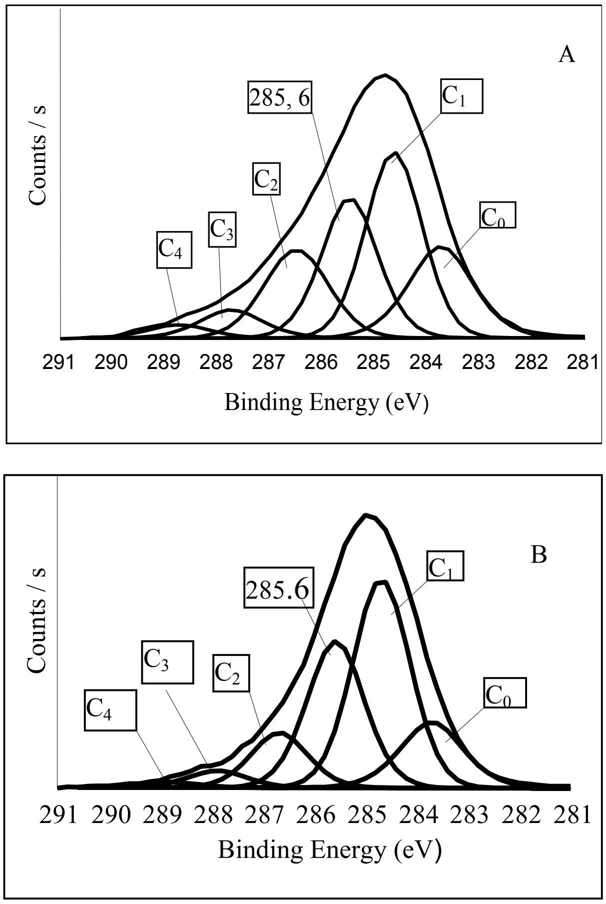

Figure 3: Expansion and deconvolution of C_{1s} peaks obtained from ESCA spectra of (A) sanded ayous an (B) sanded fraké

Therefore, the contribution of the C_0 and carbon at 285,5 eV classes were interpreted as contaminations and were excluded from the further analysis. The four carbons classes exhibited by XPS are confirmed by the ATR-IR analysis as shown in Figure 4. FTIR of ayous and frake are displayed in Figure 4. Major peaks of interest have been assigned according to wood bulk composition which is mainly constituted of polysaccharides (cellulose, hemicelluloses) and lignin. Strong broad OH stretching band is detected at 3500-3100 cm^{-1}, corresponding to the vibration of the large number of hydroxyl groups present in lignin, in polysaccharides and those of carboxylic acids (Pandey and Theagarajan, 1997; Pandey, 1999; Pandey and Pitman, 2003). The band at about 3020-2790 $cm^{-1}$are attributed to CH asymmetric stretching modes (Pandey and Theagarajan,1997; Pandey, 1999; Pandey and Pitman, 2003). Stretching bands around 1740-1710 cm^{-1} are attributed to non conjugate carbonyl C=O bonds due to ketones, carboxylic acids and esters and the end glucose group of the polysaccharides repeating unit(molecule), which has one semi-acetal hydroxyl group that transforms into aldehyde; which contribute to the carbonyl peak. Conjugate carbonyl C=O groups are detected at 1700-1650 cm^{-1}; they are attributed to aryl ketones of the lignin moiety. Aromatic peaks due to aromatic rings of lignin encountered in the region 1520-1420 cm^{-1} CH asymmetric stretching band of lignin and polysaccharides are located at 1400-1380 cm^{-1} whereas symmetric CH stretching peak of polysaccharides is at 1380-1320

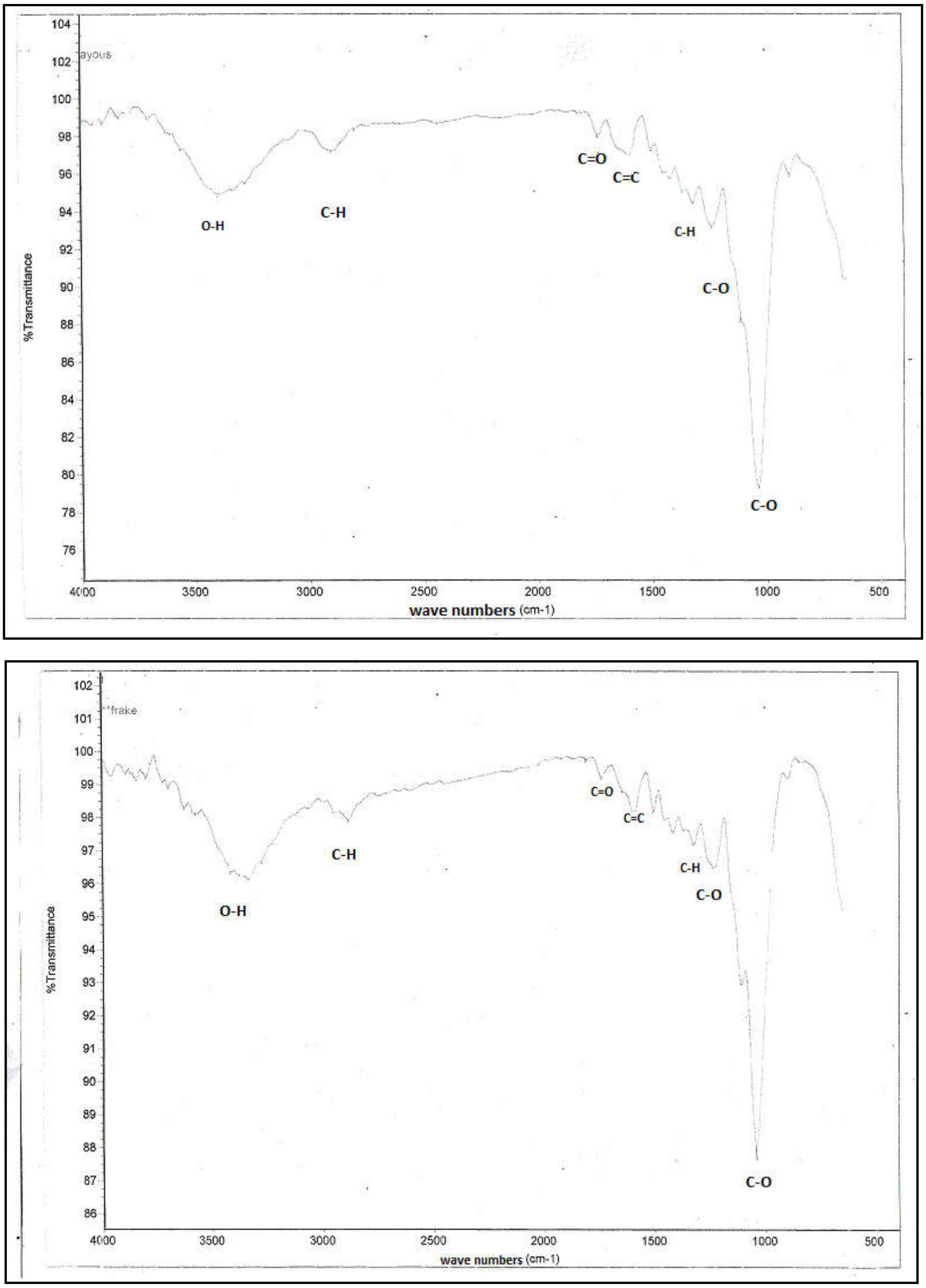

Figure 4 :FTIR spectra of sanded ayous (A) and sanded fraké (B)

cm^{-1}. C-O stretching band of metoxy group of lignin are detected at 1300-1250 cm^{-1}. A very strong C-O stretching peaks centered at 1120 cm^{-1} is detected at 1200-900 cm^{-1}; it includes ether bonds C-O-C and alcoholic bonds C-O-H vibration of both lignin and polysaccharides overlapping C-C of aromatic rings bond stretching. XPS and ATR-IR analysis of sanded wood prior to gluing converge to confirm that in wood some of the functional groups of importance are carboxyl (-COOH), hydroxyl (-OH), and carbonyl (C=O). The carboxyl group is composed of a carbonyl and hydroxyl group. Morrison (1987) states that the hydroxyl group within the carboxyl functional group is what actually undergo nearly every reaction that occurs to it. Since wood is intend to be glued with isocyanate glue (1C-PU) it is of great importance to understand how this glue could perform with green wood which is supposed to contain free water that could highly influence its performance. The study of glue line is therefore for a great importance, why part II for the article on mechanical properties.

Conclusion

In this paper, XPS and ATR-IR was used to characterize the surfaces of sanded tropical (ayous and fraké) wood prior to gluing. The atomic ratio of oxygen to carbon (O/C) ratio determine from the survey spectra was found to be lower for sanded wood sample. The amount of decrease was influenced by the wood density and the probable presence of amino acid. A detailed analysis of the C_{1s} peak showed that contributions mainly attributed to the cellulose decreased due to sanding process. In contrast, contribution attributed mainly to lignin or carbon contaminations were increased. This is explained by the fact that the more ductile wood components are enriched on the surface during the sanding process. More over it was shown that tropical wood are difficult to be characterized by XPS due to constant charging when there is no flood gun during the analysis process. However XPS analysis reeled that, oxygen and carbon are the most abundant wood chemical elements. FTIR and XPS analysis succeed to identify O-H, C-O, C=O even O-C=O as the principal chemical functional groups in both ayous and fraké sanded wood surface. Further XPS analysis with flood gun should provide better information (results) of tropical wood chemical composition. It would be necessary to characterize the glue line for better understanding of tropical green wood interaction with one component polyurethane (1C-PU) adhesive.

Acknowledgements

The financial support from the French Government through the Aires Sud program for this research work is highly acknowledged.

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