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# Investigation of Physico-Chemical Properties of Agro-Industrial By-Products

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The objective of this work is to investigate the physico-chemical properties of agro-industrial by-products in order to determine some potential valorization applications in composites materials. Four different by-products have been studied: coconut nucifera shells, canarium schweinfurthii fruit cores, palm kernels shells and raffia vinifera fruit cores. The chemical composition of the materials was studied by Fourier transform infrared spectroscopy (FTIR). It made it possible to identify the presence of chemical compounds characteristic of biosourced materials such as cellulose, hemicellulose and lignin. The thermal properties were determined by thermogravimetric analysis (TGA), in order to determine the moisture content, the thermal degradation temperatures and the ash content of the biosourced materials. The results show a first phase with a loss of mass corresponding to the evaporation of water, with humidity contents varying between 7 and 10%. The second phase corresponds to the decomposition of cellulose and hemicellulose, starting between 185°C and 225°C. After the third phase of degradation, corresponding to the decomposition of lignin, the ash content is determined. The surface properties of the materials were also studied by wettability measurements. The contact angles of water (polar liquid) and diiodomethane (non-polar liquid) were measured. The surface energies could then be calculated, and vary between 54 and 65 mN/m. A correlation between the wettability and TGA results has been evidenced, the higher content of lignin inducing a lower surface energy, and potentially a better compatibility with polymer matrix. The targeted applications concern the use of these biosourced products as abrasive composite materials (associated with a polymer matrix), for example in the shoe industry (for the machining of soles), and also in mechanical stripping of surfaces.

## 1. Introduction

The valorization of waste or by-products from agriculture is of major importance from environmental and economic point of view. This work is focused on the investigation of physico-chemical properties of agro-industrial by-products. Four by-products: coconut nucifera shells, canarium schweinfurthii fruit cores, palm kernels shells and raffia vinifera fruit cores, all from Cameroon were chosen for their great availability, but also their interesting mechanical properties. Large quantities of palm nut shells are produced as waste every year due to the increasing demand for palm oil. The shell represents 7 to 8% of the weight of the palm (Mo et al. 2016)]. The palm nut shell is the hardest part of the palm nut.
The coconut is the fruit of the coconut tree (Cocos nucifera). The shells constitute the endocarp of the nut and are generally abandoned as agroindustrial waste. The core of canarium schweinfurthii is the hard component of the black fruit and is surrounded on the exterior by an edible pulp. Its length is close to 2.5 to 3 cm, with a diameter between 1 to 1.5 cm (Bostoen et al., 2013). Although the pulp is widely consumed and even used for the production of essential oil, the core of the fruit still remains very little valued.
Raffia vinefera bamboo is a plant which belongs to the palm family named arecaceae. The vinefera variety is very widespread in Cameroon. The stem is used for making handicraft products such as baskets and hats. The fruits are oval in shape and consist of a reddish-brown scaly shell and an oval core. The core of the raffia fruit

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is very little valued today unlike the fibers and stems of raffia. The chemical composition of the materials was studied by Fourier transform infrared spectroscopy (FTIR). The thermal properties were determined by thermogravimetric analysis (TGA), in order to quantify the moisture content, the thermal degradation steps and the ash content of the biosourced materials. The surface properties of the materials were also studied by wettability measurements. The contact angles of water (polar liquid) and diiodomethane (non-polar liquid) were measured. The results of these characterizations will be discussed in order to consider the use of these agro-industrial by-products in composites materials for industrial applications. These biosourced products could indeed be used as abrasive composite materials (associated with a polymer matrix), in the shoe industry (for the machining of soles), and also in mechanical stripping for surfaces cleaning and treatment.

## 2. Materials and techniques

### 2.1 Materials

Four by-products were studied. The shells of palm nuts (elaeis guineensis) variety tenera, the shells of coconut nucifera, the fruit cores of canarium schweinfurthii and the fruit cores of raffia vinifera come from Cameroon. Figure 1 shows a photography of the four biosourced materials.


*Figure 1: Biosourced materials: a) palm kernels shells, b) coconut nucifera shells, c) canarium schweinfurthii fruit cores and d) fruit cores of raffia vinifera*

The plant shells and cores have not undergone any particular chemical treatment in order to preserve their natural character. They were just cleaned in a distilled water bath to remove impurities. A drying at 105°C during 24 hours will then eliminate water (induced by the cleaning step) and moisture that may be contained in by-products. The following abbreviations have been used for the different samples: CNS for coconut nucifera shells, PKS for palm kernels shells, CSS for canarium schweinfurthii fruit cores and RVS for Raffia Vinifera fruit cores

### 2.2 Techniques

FTIR spectroscopy: The samples were ground into powder before being positioned on the diamond crystal of the spectrometer. The device used is a Bruker Vertex FTIR 70 spectrometer with Platinum ATR (Attenuated

Total Reflectance). These spectra are recorded at a resolution of 4 $cm^{-1}$ (50 scans) in a wave range of 400 to 4000 $cm^{-1}$. The objective of FTIR analysis is to determine the chemical composition of the materials.
Thermogravimetry: TGA is used to evaluate the mass losses as a function of the increase in temperature in order to determine the humidity content, thermal degradation temperatures and ash content. The device used is a TA Instruments Q500 apparatus. The samples (approximately 10 mg) are heated at a rate equal to 10°C/min from 20°C to 600°C under nitrogen
Wettability measurement: Measuring the contact angle will make it possible to determine the surface energy of the biosourced materials. The device used is Kruss DSA 100 contact angle apparatus. The material samples were cut, polished (to minimize the influence of the roughness), cleaned with acetone and finally dried before analysis. The sessile drop method is used, with the measurement of the contact angle of two liquids, one of which is polar (demineralized water) and the other is non-polar or dispersive (diiodomethane). The surface energy of the biosourced materials $\gamma_S$ is calculated by using the Owens–Wendt method (Owens et al., 1969).

## 3. Results and discussion

Fourier transform infrared spectroscopy (FTIR) made it possible to identify the presence of chemical compounds characteristic of the biosourced materials studied. The infrared range is between 400 $cm^{-1}$ and 4000 $cm^{-1}$ corresponding to the vibration energy range of the molecules. The samples are placed directly on the ATR crystal.
Figure 2 presents the IR spectra of coconut nucifera shells (CNS), canarium schweinfurthii fruit cores (CSS) and raffia vinifera fruit cores (RVS). For the palm kernels shells sample, the IR spectrum is not well defined due to a poor contact between the particles and the ATR crystal.

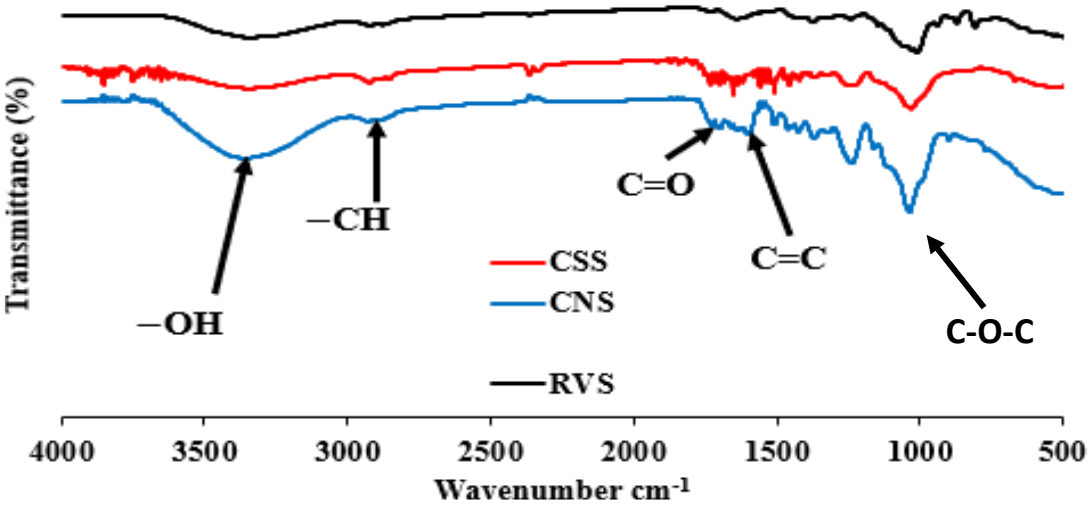


*Figure 2: IR spectra of coconut nucifera shells (CNS), canarium schweinfurthii fruit cores (CSS) and raffia vinifera fruit cores (RVS)*

All the IR spectra show the presence of OH bonds assigned to hydroxyl groups from 3330 to 3365 $cm^{-1}$. These broad-band hydroxyl bonds are almost present in the cellulose and hemicellulose, and also in lignin (Liyanage et al., 2015). The -CH bonds of the aliphatic groups appeared between 2921 and 2929 $cm^{-1}$. These bonds are mostly present in cellulose and hemicellulose (Colom et al., 2003). The C=O bonds between 1706 and 1739 $cm^{-1}$ are associated with the carbonyl groups present in lignin and hemicellulose (Evans,1991). The C=C bonds of the aromatic rings of lignin appeared in the region of 1510 -1600 $cm^{-1}$. The C-O-C bonds of the cellulose and hemicellulose cycles are visible between 1010 and 1037 $cm^{-1}$ (Feni et al., 2022). The characteristic chemical groups of lignin, cellulose and hemicellulose were therefore observed for all the samples, whose exhibit quite similar IR spectra.
Thermogravimetric analysis (TGA) has been performed on the biosourced materials in order to investigate the thermal degradation and to quantify the moisture and ash contents. The thermogravimetric curve (TG) and the corresponding derivative (DTG) are presented on Figure 3.

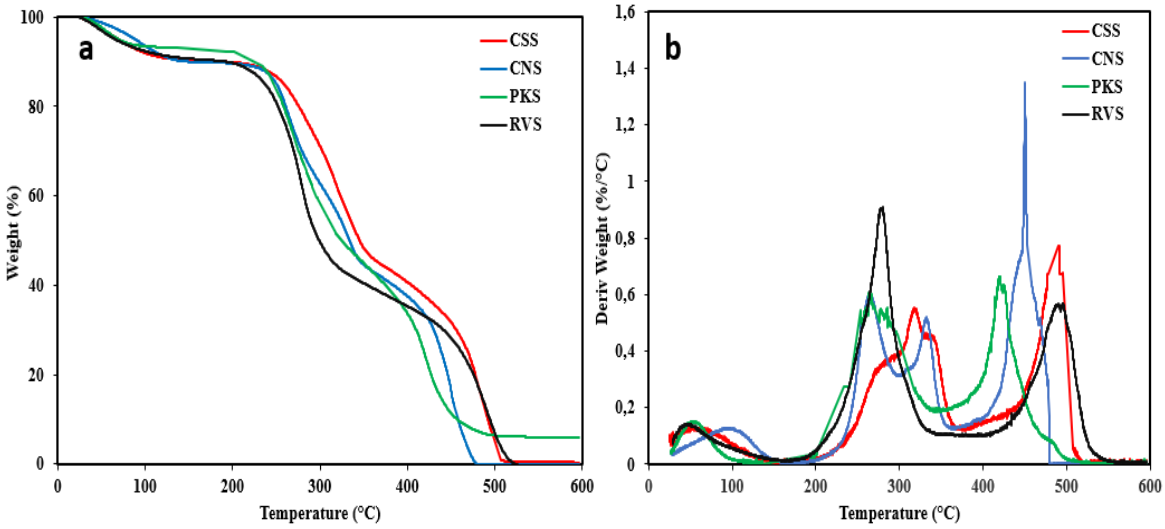


*Figure 3.: TG (a) and DTG (b) curves of the biosourced materials*

Figure 3.a shows different steps of weight loss. The first step corresponds to the evaporation of water (moisture content). The second phase of weight loss is induced by the decomposition of cellulose and hemicellulose (Diez et al., 2020) and the third phase corresponds to the decomposition of lignin (Gongxiang et al., 2022). The ash content corresponds to the residual weight measured around 600°C.
Table 1 presents the weight loss values and the degradation temperatures obtained for the four samples.

*Table 1 : Moisture and ash contents and weight loss and degradation temperature values of the biosourced materials*

| | | First degradation step | | | Second degradation step | | |
|---|---|---|---|---|---|---|---|
| Sample | Moisture content | Weight loss | T1°(ºC) | T2° (ºC) | Weight loss | T°(ºC) | Ash content |
| CNS | 10 % | 47 % | 330 | 367 | 41 % | 450 | 0,6 % |
| PKS | 7 % | 42 % | 270 | 360 | 37 % | 420 | 5 % |
| CSS | 10 % | 53 % | 322 | 415 | 34 % | 482 | 0,4 % |
| RVS | 9 % | 55 % | 277 | 396 | 36 % | 491 | 0 % |

The moisture content of CNS, PKS, CCS and RVS samples are close and respectively equal to 10%, 7%, 10% and 9%. These humidity levels are similar to the value found in the literature for plant hulls (Ehiem et al., 2019). Water absorption is due to the presence of numerous hydroxyl groups of cellulose and hemicellulose, which are both hydrophilic polymers.
All the samples of CNS, PKS, CCS and RVS are then thermally stable until respectively 203°C, 205°C, 225°C and 185°C, temperature at which the degradation starts. The weight loss measured during the first step of degradation are between 42 and 55%. This first step corresponds to the of thermal decomposition of cellulose and hemicellulose, for which 2 temperatures, T1 and T2 can be determined on the derivative DTG curves. T1 and T2 temperatures could be assigned to the decomposition of hemicellulose and cellulose, respectively (Diez et al., 2020). The higher weight loss is measured for RVS, indicating that raffia vinifera fruit cores contain a higher proportion of cellulose and hemicellulose. The degradation temperature T1 and T2 of RVS are also lower. The last step of thermal degradation corresponds to the decomposition of lignin (Windeisen et al., 2009), with weight loss values between 34 and 41 %. The higher value is measured for CNS, indicating a greater lignin content for coconut nucifera shells. After this last phase of degradation, the ash content can be determined. The measured values are very low, the higher value (5%) is measured for PKS. The lowest ash content is measured for RVS (the accuracy of the TGA device being equal to 0.01%). The TGA results indicate consequently that

raffia vinifera fruit cores (RVS) have the higher content of cellulose and hemicellulose, and that coconut nucifera shells (CNS) have the higher content of lignin.
Wettability measurements have been performed in order to determine the surface energies of the biomaterials Surface energy can indeed be calculated from contact angles values of water (polar liquid) and diiodomethane (non-polar liquid). Table 2 presents the contact angles and surface energy values of the materials.

*Table 2 : Contact angle of the diiodomethane $\theta_d$ and water $\theta_p$ and surface energy $\gamma_s$ values, with the dispersive component $\gamma^d$ and the polar component $\gamma^p$ of the biosourced materials*

| | $\theta_d$(°) | $\theta_p$(°) | $\gamma^d$ (mN/m) | $\gamma^p$(mN/m) | $\gamma_S$ (mN/m) |
|---|---|---|---|---|---|
| CNS | 37 ±2 | 59 ±5 | 41 ±1 | 13 ±2 | 54 ±3 |
| PKS | 34 ±4 | 41 ±2 | 42 ±2 | 23 ±2 | 65 ±3 |
| CSS | 34 ±3 | 46 ±2 | 42 ±1 | 20 ±1 | 62 ±2 |
| RVS | 54 ±4 | 35 ±2 | 32 ±2 | 31 ±2 | 63 ±4 |

Water contact angles are between 35° (for RVS) and 59° (for CNS). A lower water contact angle indicates a better liquid spreading and consequently a more polar surface, and inversely (De Meijer et al., 2000). The diiodomethane contact angles are between 34 and 54°, with similar values measured for CNS, PKS and CSS. The higher diodomethane contact angle is measured for RVS, indicating a lower wetting of the material by the non-polar liquid. Furthermore, surface energies vary between 54 mN/m and 65 mN/m. These values are consistent with the surface energy determined for different wood species (Mantanis et al., 1997).
The lower water contact angle is measured for raffia vinifera fruit cores (RVS), which consequently exhibits the higher polar component (31 mN/m), showing a greater hydrophilic character. Coconut nucifera shells (CNS) exhibits the higher water contact angle value and consequently the lower polar component (13 mN/m), showing a less hydrophilic character. Coconut nucifera shells has also the lower surface energy. Significant differences in surface properties have been consequently evidenced through wettability measurements.
Surface energy results are consistent with the thermogravimetric results. Indeed, the 3 major components of the biosourced materials are cellulose, hemicellulose and lignin. FTIR analysis has confirmed the presence of these polymers. The different thermal degradation steps observed on TGA curves allow us to quantify the ratio of polysaccharides (first step of degradation) and lignin (second step of degradation). TGA results have evidenced a higher content of cellulose and hemicellulose in raffia vinifera fruit cores (RVS), and a higher amount of lignin.in coconut nucifera shells (CNS). Cellulose and hemicellulose are polar and hydrophilic polymers (Pasquini et al., 2066). A higher amount of these polysaccharides inside the materials could then induced a more pronounced hydrophilic character, associated to a lower water contact angle (Rbihi et al., 2020). Inversely, a higher amount of lignin, which exhibits a hydrophobic character will consequently decreases the hydrophilic character (Géradin et al., 2007), inducing a higher water contact angle. The higher water contact angle and then the lowest polar component are measured for coconut nucifera shells (CNS). This result can therefore be explained by its higher lignin amount measured by TGA. Inversely, the lower water contact angle, and the higher polar component, are determined for raffia vinifera fruit cores (RVS), in correlation with the higher polysaccharides amount measured by TGA.
These results could be useful for the optimization of interface properties between a polymer matrix and the biosourced particles used as reinforcement in composites materials (Defo et al., 2023). Polymer matrix are indeed generally less hydrophilic compared to polysaccharides. The lower surface energy of coconut nucifera shells is then able to favour the compatibility between the CNS particles and the matrix. This better wetting and impregnation of the particles by the matrix wiould allow to avoid the presence of voids inside the composite.

## 4.Conclusions

The objective of this work was to investigate physico-chemical properties of four biomaterials through the determination of chemical composition by FTIR, the study of thermal degradation by TGA and the characterization of surface properties by wettability measurements.
FTIR analysis has confirmed the presence of cellulose, hemicellulose and lignin in the biosourced materials, and TGA, through the different thermal degradation steps, has evidenced a higher content of polysaccharides (cellulose and hemicellulose) in raffia vinifera fruit cores (RVS), and a higher amount of lignin in coconut nucifera shells (CNS). TGA results can therefore explain the wettability behaviours. Indeed, the lower surface energy, and especially the lowest polar component determined for coconut nucifera shells (CNS) can be the

consequence of its higher lignin amount measured by TGA, and the higher polar component, calculated for raffia vinifera fruit cores (RVS), can be induced by the higher polysaccharides amount measured by TGA. Coupling TGA and wettability analysis appears to be a fruitful approach to investigate the surface properties in correlation with the bulk compositions of the biosourced material, in order to predict their use as reinforcement particles in composite formulations.

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