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Research Article

EXTRUDED POLY(ETHYLENE–CO–VINYL ALCOHOL) COMPOSITE FILMS REINFORCED WITH CELLULOSIC FIBERS ISOLATED FROM TWO LOCAL ABUNDONATES PLANTS

L. Benchikh[1*], A. Merzouki[1], Y. Grohens[2] and I. Pellin[2]

[1]Laboratoire de Physico-Chimie des Hauts Polymères, Département de Génie des Procédés, Faculté de Technologie, Université Ferhat Abbas Sétif 1, Algérie

[2] Institut de Recherche Dupuy de Lôme, UMR CNRS 6027, Université de Bretagne Sud, Lorient, France

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ABSTRACT

El Diss and El Retma fibers are in abundance in North Africa, collected from Setif (Algeria) and have been treated to isolate cellulose fibers with toluene-ethanol and HNO_3 to improve their dispersion into EVOH matrix. SEM micrographs and FTIR analyses of the treated fibers confirmed the elimination of non cellulosics materials and thier cristallinity was estimated by DRX. Thermal analyses by TGA indicate a slight improvement compared to the raw fibers. Composites were also prepared by incorporation of the cellulosic fibers in EVOH matrix. FTIR results and water absorption behavior indicate a reaction between the treated fiber and EVOH matrix by forming hydrogen bonds. Thermal properties of the composites reported by DSC results decreased compared to neat EVOH. The addition of cellulosic fibers led to an increase in the loss and storage modulus and melt viscosity of the composites.

Keywords: El Diss fibers, El Retma fibers, cellulose, biocomposites

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Author Correspondence, e-mail: lilia.benchikh@gmail.com

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1. INTRODUCTION

Environmental pollution from consumed plastics becomes serious because of their nonbiodegradability. Thus, there has been growing interest in the developing of biobased products to replace nonbiodegradable plastics and reduce the dependence on fossil fuel [1,2].

Biopolymers presented three main materials: The first is synthetic polymers with characteristics groups susceptible to hydrolysis attack by microbes, the second is composed of naturally occurring processible bacterial polymers as like as lignocellulosic fibers [1,3,4]. The third class is blends of polymers and additives that are readily consumed by microorganisms [5]. Cellulose based composites offers many advantages such as a high specific strength and stiffness, a low hardness which reduce wear on processing equipment, a relatively low density, a low cost and biodegradability. In fact, composites reinforced by cellulosic fibers may eventually be recycled or burned to recover heat, without the production of residues or toxic products [6,7].

Natural fibers also known as cellulosic or lignocellulosic fibers are principally composed by cellulose, lignin and hemicellulose, biosynthesized by plants, some amoebae, sea animals, bacteria and fungi. Their properties depends in chemical composition, internal fiber structure, microfibril angle, cell dimensions and structural defects, which differ from different parts of a plant as well as from their origin. The mechanical properties of natural fibers also depend on their crystalline organization [8,9].

Composites with lignocellulosics fillers found application in household, ornament and packaging uses, agricultural and biomedical applications, nonstructural or semistructural building products such as decking, fencing, siding, window frames, and roof tiles [7,10,11]. However, the inclusion of cellulose fibers as fillers for polyolefins has some drawbacks. The incompatibility, the poor interfacial adhesion of polar cellulose and nonpolar matrix and the poor fiber dispersion leads to poor mechanical properties [12].

Many efforts have been conducted to create interaction between the thermoplastic matrix and filler [6,13]. Numerous studies have used the functionalization of polyolefins by maleic anhydride (MA), also Isocyanates and silanes are used as coupling agents. Compatibilizers have been investigated which was found to act, not only as compatibilizer but also as impact modifier. Another way to improve adhesion in thermoplastic/cellulose composites is crosslinking [11,13,14]. Surface cellulosic fillers can be also modified by physical and chemical methods mainly based on the reactivity of the cellulose hydroxyls [11,15]. Such as alkali treatment, bleaching, acetylation and steaming [16-18].

Ethylene-vinyl alcohol (EVOH) is a hydrophilic semicrystalline copolymer with excellent gas-barrier properties to oxygen and organic compounds. It’s considered to have the superior gas barrier properties compared to the most of the polymeric materials depending on the copolymerization ratio of ethylene and vinyl alcohol. Thus, EVOH is widely used in food packaging industry, also because EVOH has a high transparency and easy processability on a wide range of conventional coextrusion processing [19,20].

Several blends of vinyl alcohol–ethylene copolymers (EVOHs), and polysaccharides, such as starch, corn fiber and sugar cane bagasse have been reported [21]. Morsyleide and al. [17] studied the incorporation of treated coconut fibers into formulations with starch and EVOH and prived to improve the thermal stability, increased the tensile strength of the composites and also improved values of Young’s modulus.

El Diss and El Retma fibers are a wild plants in abundance in the mountains of North Africa and in this case exactly collected from the Medjouness mountains of Ain El Kebira (Setif), Algeria. This present study was carried out to investigate the effects of the chemical treatements of two types of fibers after incorporation in ethylene venyl alcohol on their thermal, morphology, and tensile properties.

2. EXPERIMENTAL

2.1. Materials

The raw fibers used in this work are El Diss and El Retma, and were come from the region of Setif.

Fig.1. El Diss plant (a), El Retma plant (b)

Reagents that were used to extraction were Ethanol, Toluene which are from BIOCHEM chemical pharma and Nitric acid (HNO_3) is purchased from Sigma Aldrich.

EVOH/Cellulose formulations were based on EVOH (44 % ethylene) provided by Sigma Aldrich with the following physical characteristics: pellets density: 1.140, melting point: 165°C.

2.2. Fibers treatements

The aim to this chemical treatements was the elimination of hemicellulose and lignin for the extraction and isolation of cellulosics fibers.

El Diss and El Retma cellulosic fibers was prepared by using the method as following:

The raw fibers were washed, dried and then cuted, powdered in a coffee grinder and sieved (100 µm) to uniformize the particle sizes. The powder was then treated with 50:50 (v:v) toluene-ethanol mixture for 4h in a flask equipped with condenser. After several washs with distilled water, the precipitate was dried at 105°C for 24h. A treatment was then carried out 3 times with a mix of HNO_3 + ethanol solution in the propotion (1/4). The solution is carried out to ebulution in a water bath for 1 h under magnetic stirring and condenser. A successif washs was carried out with hot water until complete elimination of the solution. The obtained powder was dried at 105°C until a constant weight. The final product is a yellow powder.

2.3. Composites preparation

The cellulose fibers and EVOH were previously placed in an oven set at 50°C overnight to eliminate an eventual adsorbed water on the surface. Then, the two treated fibers (El Diss CF_D

and El Retma CF_R) were mixed respectively with EVOH into a co-rotating twin-screw configuration (MiniLab microcompounder by Thermo Scientific Haake, Germany), at 200°C, screw speeds at 100 rpm and a time of recirculation designed for 8 min. Two formulations were prepared with two differnt rate charge (5 and 10%). All samples were prepared with the same procedure, the EVOH/cellulose fibers mix was added in three aliquots (EVOH, cellulose fibers then EVOH) because of the high volume of cellulose, which could cause the blockage of the machine.

2.4. Characterization methods

2.4.1. Fiber's characterization methods

a. FT-IR spectroscopy

Chemical composition study of the fibers after treatment was conducted through FTIR spectroscopy. A FTIR VERTEX 70v was exploited to provide the spectrum of each sample. Spectra were taken at a resolution of 4 cm^{-1} and in the range of 4000–400 cm^{-1} in the absorbance mode.

b. X-ray diffraction analysis (XRD)

The degree of cristallinity and the treatement effect on the morphological cristallinity of the samples was estimated by XRD analysis on D8 Advance system (Bruker) apparatus using CuKα_radiation in the range 2q = 2–70° with a step of 0.01/S. Cristalinity index of the raw fibers were obtained using the following equation:

$$Ci= (I002- Iamorph/I002) \times\% \qquad (1)$$

Where I002 is the maximum intensity of the 002 peak which represents both crystalline and amorphous material and Iamorph is the lowest height which represents amorphous material only.

c. Thermogravimetric analysis (TGA)

The thermal behavior of the treated and untreated fibers were determined in a temperature range of 20–700 °C, at a heating rate of 10 °C/min, in a nitrogen environment (Purge rate details : Balance chamber flow rate = 30 cm^3/min, furnace flow rate = 150 cm^3/minute) using a Mettler Toledo TGA/DSC.

d. Scanning electronic microscopy (SEM)

The morphological characterization of the fibers samples were done with scanning electronic microscopy (SEM) using JSM-6460 appartus.

2.4.2. Characterization methods of EVOH/treated fibers composites

a. FT-IR spectroscopy

Molecular interactions between matrix and charges were established by FTIR. Analysis of the **EVOH/CF** composites films were performed using a VERTEX 70v spectrometer in the absorption mode in the range of 4000-400 cm^{-1} at a nominal resolution of 4 cm^{-1}.

b. Differential scanning calorimetry (DSC)

Thermals charasteristics were determined by DSC and were performed using a Mettler Toledo DSC 3 calorimeter under nitrogen flow and heating ramp of 10°C/min. The following heating program has been carried out : from 25°C to 200°C, 2 min at 200°C, from 200° to 0°C then 2 min at 0°C, finally from 0°C to 200°C. The crystallinity degree (% χ_C) for each blend was calculated according to eq. (2):

$$\% \chi_C = 100 \Delta H_m / (W \Delta H°_m) \qquad (2)$$

Where ΔH_m is the melting enthalpy of the blend sample (J/g), $\Delta H°_m$ is the melting enthalpy (169.2 J/g) of the EVOH sample assuming 100% crystallinity as in pure polyvinyl alcohol (PVOH), and W is the EVOH mass fraction in the composite [22].

c. Rheometer

An Anton Paar CTD 450 Physica MCR 301 rheometer, which works in parallel-plate oscillatory mode, was used to study the rheological behavior of materials at the temperature of 200 °C. Before characterizations, specimens were dried under vacuum and compression molded to the thickness of about 1 mm. Linear viscoelastic region was determined using dynamic strain sweep tests in the range of 0.01–10% strain at the constant frequency of 1 Hz. A strain of 5.0%, corresponding to the linear viscoelastic domain, was chosen to perform dynamic measurements over a frequency range of 0.01 to 20 Hz. For each material, three tests were made to verify the reproducibility of the results.

d. Water absorption measurements

Films were cut into samples of approximately 1*1 cm and were dried in a vacuum oven at 100°C for 24h. Weight of film samples were measured using an analytical balance with a resolution of 0.0001g (Metler Toledo). The samples were then immersed into a closed vessel containing water at room temperature for 72 h, and water uptake measurements were recorded at 24-h intervals.

$$\text{Water uptake } (\%) = (M_t - M_0)/M_0 \times 100 \qquad (3)$$

Where M_t is the mass of the sample at time t and M_0 is the mass of the sample before insertion into the water [23].

3. RESULTS AND DISCUSSION

3.1. Fibers characterization

a. Scanning electronic microscopy (SEM)

The modifications occured to the raw fibers after treatements were investigated by SEM and presented in figure 2. The SEM images (2a and 2b, 2c and 2d) showed the morphologies of untreated and treated fibers of El Diss and El Retma respectively.

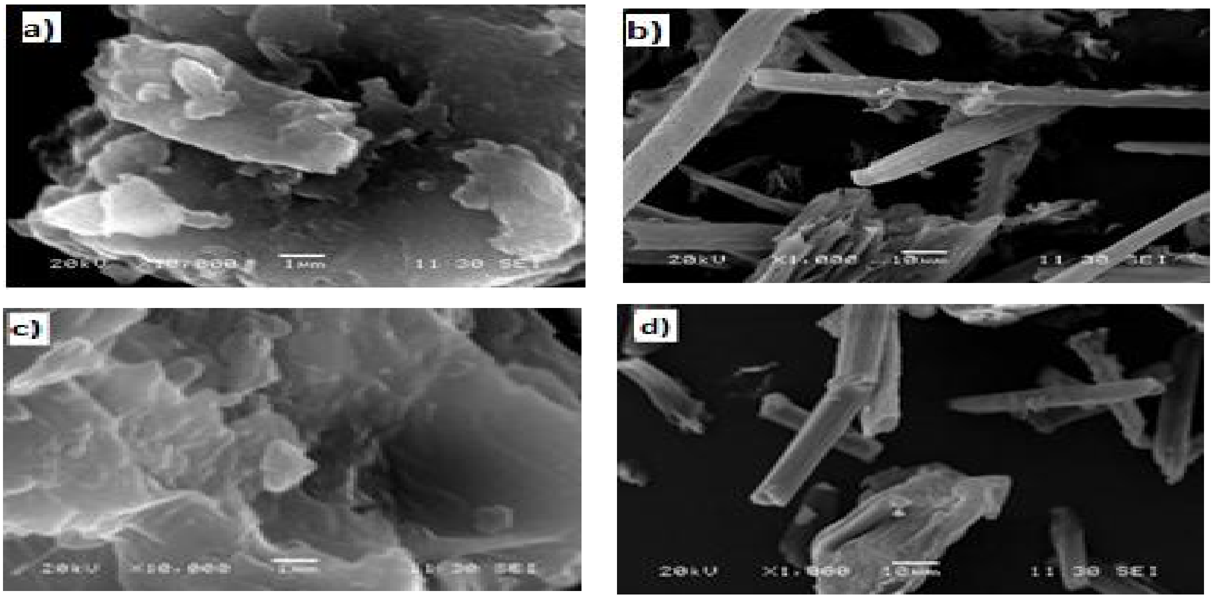

Fig.2. SEM images of El Diss raw fibers (a), El Diss treated fibers (b), El Retma raw fibers (c), El Retma treated fibers (d)

The SEM images for the two untreated fibers (El Diss, El Retma) exposed entities with different shapes and sizes with a diamater between 16 - 85 µm for El Diss fibers and 16 - 66 µm for El Retma ones. After treatements, the SEM images showed long fibers, well separated from each other and the diamater of the two fibers decreased and varied between 4 µm and 10 µm for El Diss fibers and between 5 µm and 9 µm for El Retma ones. Significant morphological changes can be also observed due to the loss of mass after removing extracellulosic compounds as lignin and hemicellulose to isolate cellulose. The cellulose samples showed a smoother surface compared to the initial fibers [24].

b. Fourier transform infrared spectroscopy (FTIR)

The chemical structure of the El Diss and El Retma fibers before and after treatments were studied by FTIR analysis and the results are reported in figure 3.

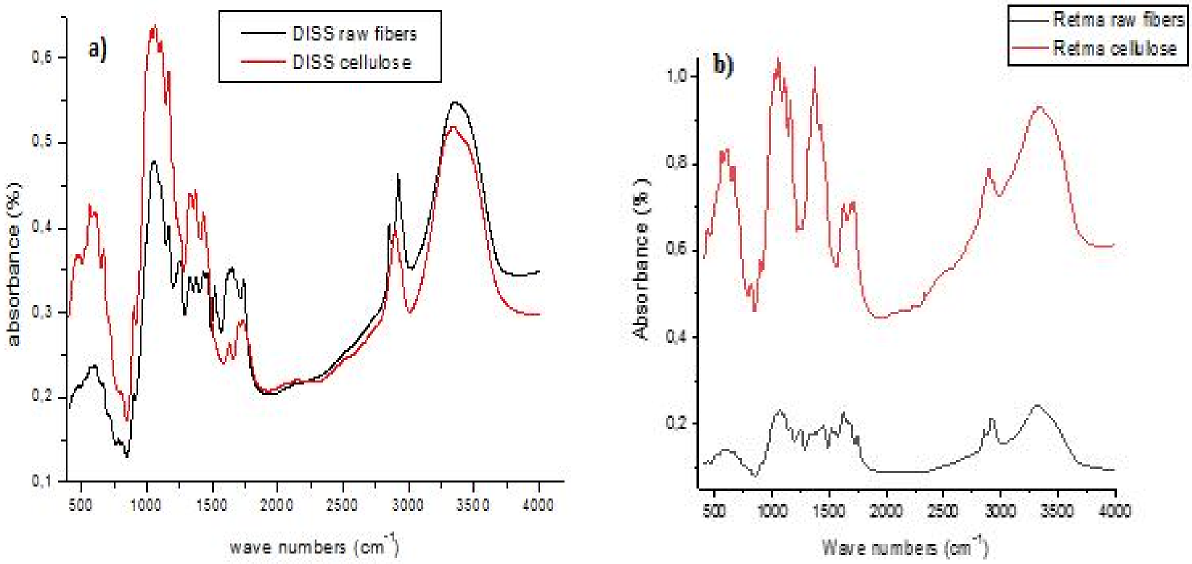

Fig.3. FTIR spectra of El Diss (a) and El Retma (b) raw fibers and their celluloses

The FTIR spectra corresponding to the two fibers present two mains band at 3300 and 684 cm^{-1} which was attribuated to stretching vibrations and the out-of-phase bending vibrations respectively of O-H in cellulose and lignin, the second band is at 2875 cm^{-1} which presents the stretching vibrations of the aliphatic C-H of lignin. The absorbance pic at 1730 and 1427 cm^{-1} were attributed to stretching vibrations and bending of the hydrogen-carbonyl band in hemicellulose and CH_2, respectively. Lignin structure presents also a band at 1500-1600 cm^{-1} corresponding to C=C bonds in aromatic rings. The hydrophilic character of the cellulosic fibers highlights a band of adsorbed water around 1630cm^{-1} [25-27]. The pics around 1110 and 1060 cm^{-1} corresponds to skeletal vibrations of C−O stretching and the pic at 1161 cm $^{-1}$

is due to asymmetric stretching of C-O-C of glucose ring in cellulose structure [28].

After fibers treatments, the elimination of extracellulosic substances was confirmed by the absence of the lignin bands at 2875 cm^{-1} and 1500 cm^{-1} in the spectra of the treated fibers [29]. Also, the characteristic bands of hemicellulose and pectin disappear from El Diss and El Retma celluloses spectra.

c. X-ray diffraction analysis (XRD)

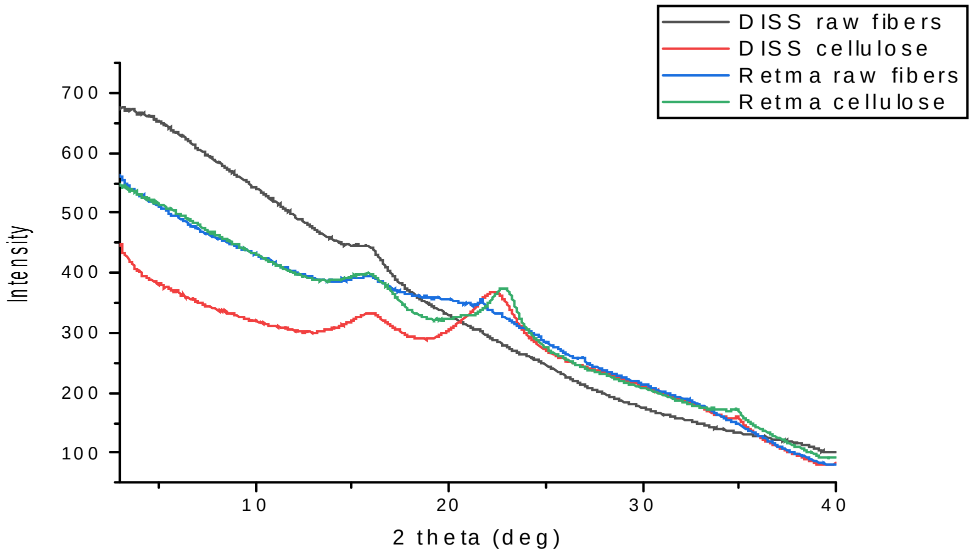

Fig.4. X-ray diffraction patterns of El Diss, El Retma raw fibers and their cellulose

Figure 4 displays the cristallinity of the treated and untreated El Diss and El Retma fibers by X-ray diffraction analysis.

The raw and cellulose fibers of El Diss and El Retma have a typical XRD patterns of a semi-crystalline material constitued of an amorphous and christalline parts [30]. Native cellulose presents a diffraction signals at 2θ values of 15°, 16°, 22,5° and 34°, attributed to the diffraction planes 101, 101, 002 and 040, respectively [29,31,32].

The raw fibers display only one peak at 2θ of 15.7° assigned to the (101) typical reflection plane of cellulose I, unlike the treated fibers which exposed a second peak at about 22.4° for El Diss cellulose and at 22.9° for El Retma one, attributed to the (002) reflection plane of cellulose I [33], because of the large peak attributed to the important part of amourphous substance in raw fibers which prevents the appearance of the second peak. Also, the peaks exhibited at 15.7° are more intense in the cellulose patterns than in the raw fibers ones indicating an increase in the cristallinity after treatements. The determination of the crystallinity using equation 1 gives values of 21.19 % for El Diss cellulose fibers, while for El Retma cellulose fibers it approximates 13.94 %.

d. Thermogravimetric analysis (TGA)

The TGA thermograms of the raw fibers of El Diss, El Retma and their cellulose are obtained and showed in figure 5. The analysis were carried out to highlight the influence of the treatments on the thermal degradation characteristics of the fibers.

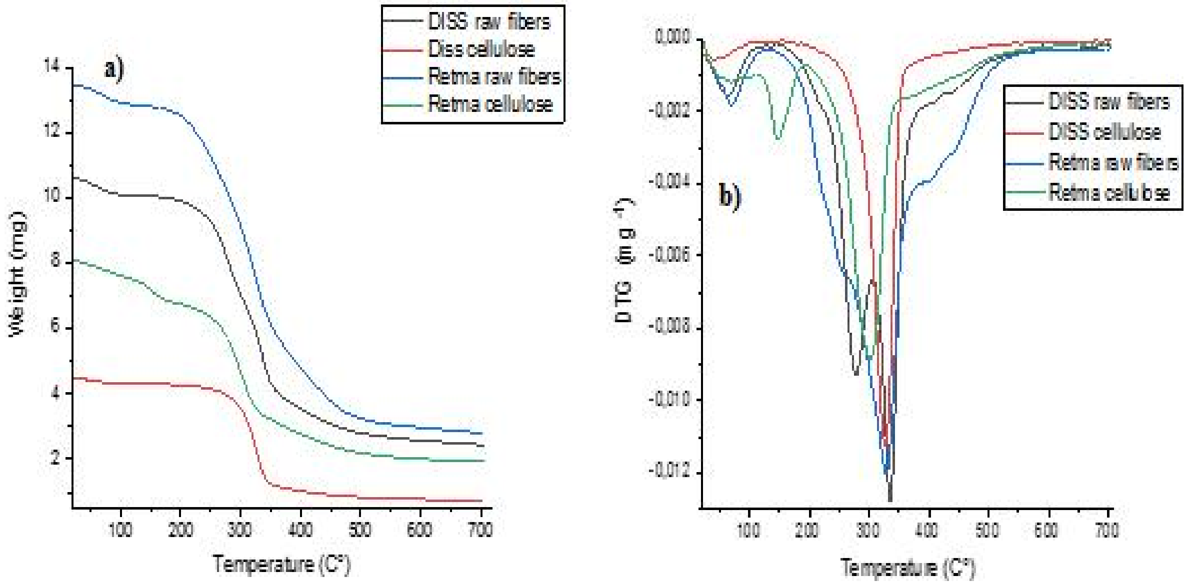

Fig.5. TG (a) and DTG (b) curves of El Diss and El Retma raw fibers and their cellulose

The thermal degradation of the raw fibers of both El Diss and El Retma plants exposed three main weight loss regions indicating the presence of different composants which decomposed at different temperatures (hemicellulose, lignin and cellulose). The first loss is mainly due to moisture evaporation of the adsorbed water, the second region temperature occurring between 220 and 350°C is mainly attributed to the thermal depolymerization of hemicelluloses and the cleavage of the glycoside bonds of cellulose. The peak that appears above 350°C is attributed to lignin decomposition, it has low degradation rate and decompose at lower temperature than cellulose and it has more heat resistant than hemicelluloses [34,35].

The thermogramms of the treated fibers display two stages decomposition process; the first one corresponds to moisture evaporation and the second to the cellulose decomposition. The peaks corresponding to the paracellulosic composants disappeared confirming their elimination by the diffirent fiber treatements in the case of El Diss fibers but stills exist in the El Retma thermogramms suggesting that these composants have not been totally removed and the paramaters treatements are not efficients for El Retma fibers. It is observed that the cellulose of the two plants degraded at a slight higher temperatures compared to the raw fibers.

3.2. Composites characterization

a. Fourier transform infrared spectroscopy (FTIR)

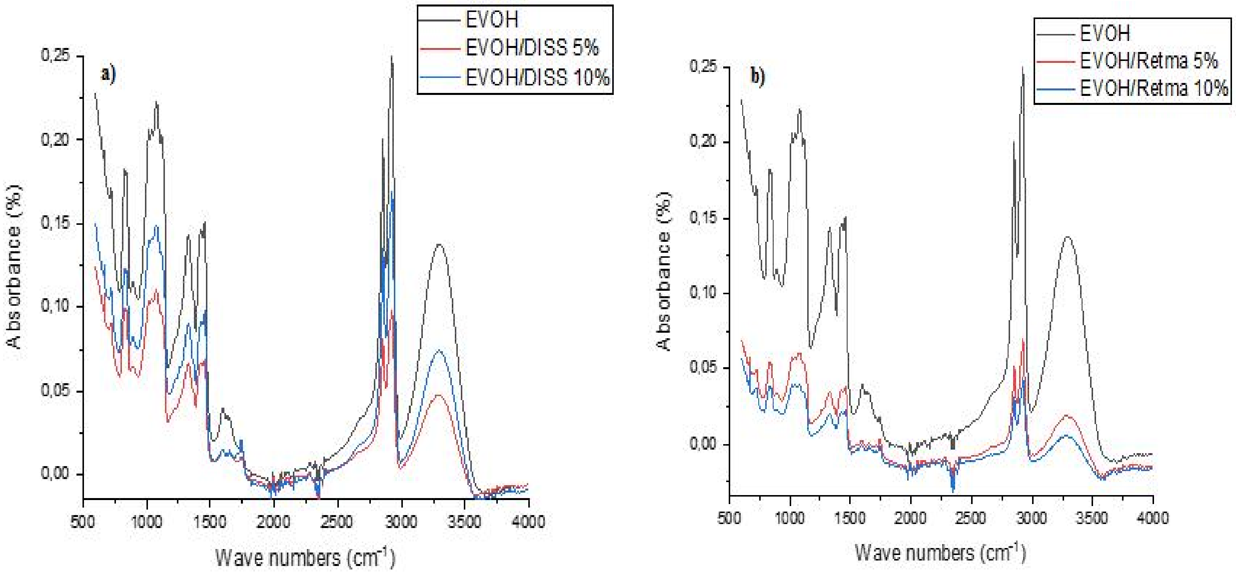

Fig.6. FTIR of EVOH/CF$_D$ (a) and EVOH/CF$_R$ (b) composites at 5 and 10%

The FTIR spectra obtained for the two types of composites presented a similar characteristic band. Two characteristics bands of common functional groups to both cellulose and EVOH structure appears at 3600–3000, 3000–2800 and 2900 cm^{-1} assigned to the OH, CH and CH$_2$ stretching vibration respectively [21]. The presence of cellulose in the EVOH matrix induces a decrease in the intensity of the OH band suggesting to the fact that the EVOH as well as the cellulose are polar and these hydroxyl groups present in the two structures tend to form inter and intra molecular hydrogen bonds [36,37], in the other hand, the intensity of OH increased when 10% of El Diss cellulose was incorporated suggesting an important number of OH groups and are more important with El Diss fibers unlike El Retma fibers confirming the FTIR results of the fibers that the treatment undergone did not lead to complete elimination of lignin and hemicellulose and led to minimal OH exposure.

b. Differential scanning calorimetry DSC

Thermal properties of EVOH/CF composites films were carried out by DSC. Figure 7 shows the DSC thermograms of neat EVOH, EVOH/CF$_D$ and EVOH/CF$_R$ composites at 5 and 10% and table I showed the melting point, melting enthalpy, and the glass transition temperature of neat EVOH, and EVOH/CF composites films.

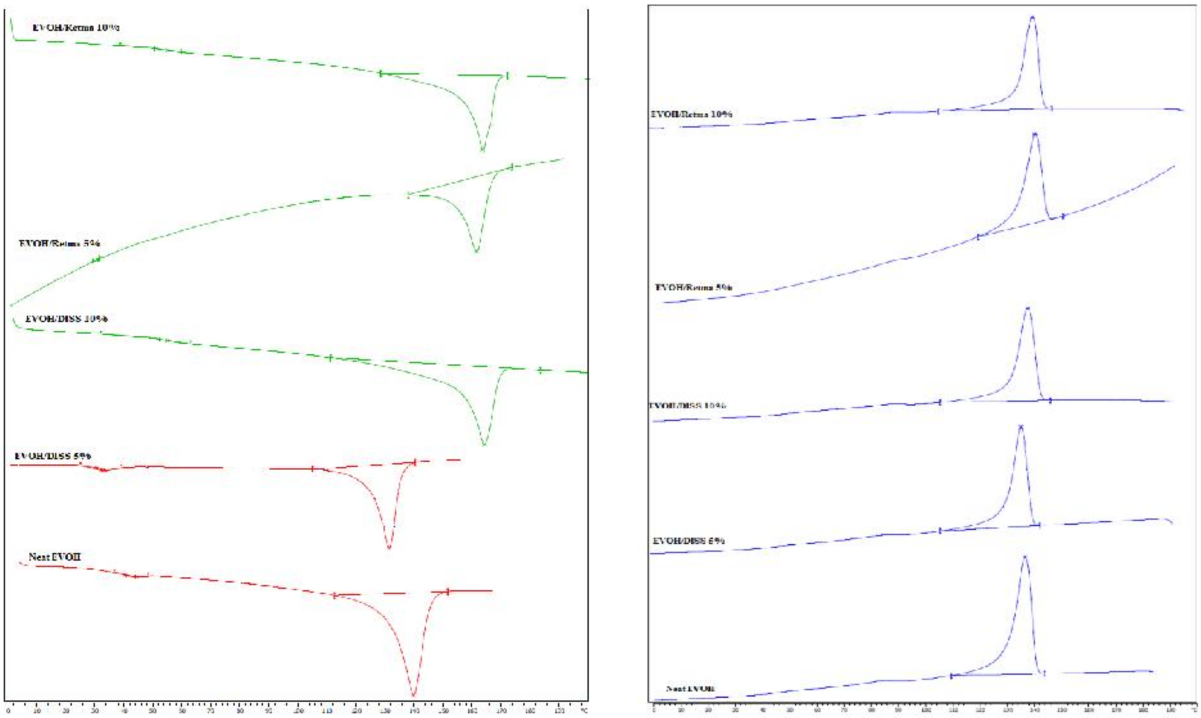

Fig.7. DSC thermograms of treated and untreated EVOH/CF at 5% and 10% composites films

Table 1. The melting, cristallisation point and melting, cristallisation enthalpy of composites EVOH/CF

	Tg	Tc	ΔHc	Tm	ΔHm
EVOH	71.90	142.33	41.64	167.83	-39.01
EVOH/CF$_D$ 5%	65.35	140.50	20.03	166.17	-18.90
EVOH/CF$_D$ 10%	67.27	140.33	49.83	165.50	-49.30
EVOH/CF $_R$ 5%	72.23	141.83	20.86	170.83	-20.50
EVOH/CF$_R$ 10%	50.67	141.50	45.95	163.00	-43.98

Compared to neat EVOH, the Tg of EVOH / CF$_D$ at 5%, 10% and EVOH / CF$_R$ at 10% composites decreased from 71.9 to 65.35, 67.27 and 50.67 respectively, they also have lower (Tc) and (Tm) temperatures. The decrease in Tm and especially the Tg observed could be explain by the plasticization effect of cellulose on the EVOH as it was observed in the case of EVOH / SBO [22]. Whereas EVOH / CF$_R$ at 5% shows a slight higher (Tg) and (Tm) temperatures (72.23, 170.83 ° C respectively). The cristallisation enthalpy also reached to a lower temperatures (from 40 to around 20) for both composites with 5% of CF but increased slightly for 10% of fillers from 39.01 to 49.3 and 43.98 for CF$_D$ and CF$_R$ respectively. According to Dikobe and Luyt [23], Ethylene Vinyl Acetate Copolymer–Wood Fiber Composites has a decrease in ΔHm as more WF was present in the samples.

c. Rheogical caracterization

The elasticity modulus G', the elasticity complex modulus G", and the complex viscosity of the EVOH composites with the different charge levels were represented in Figure 8.

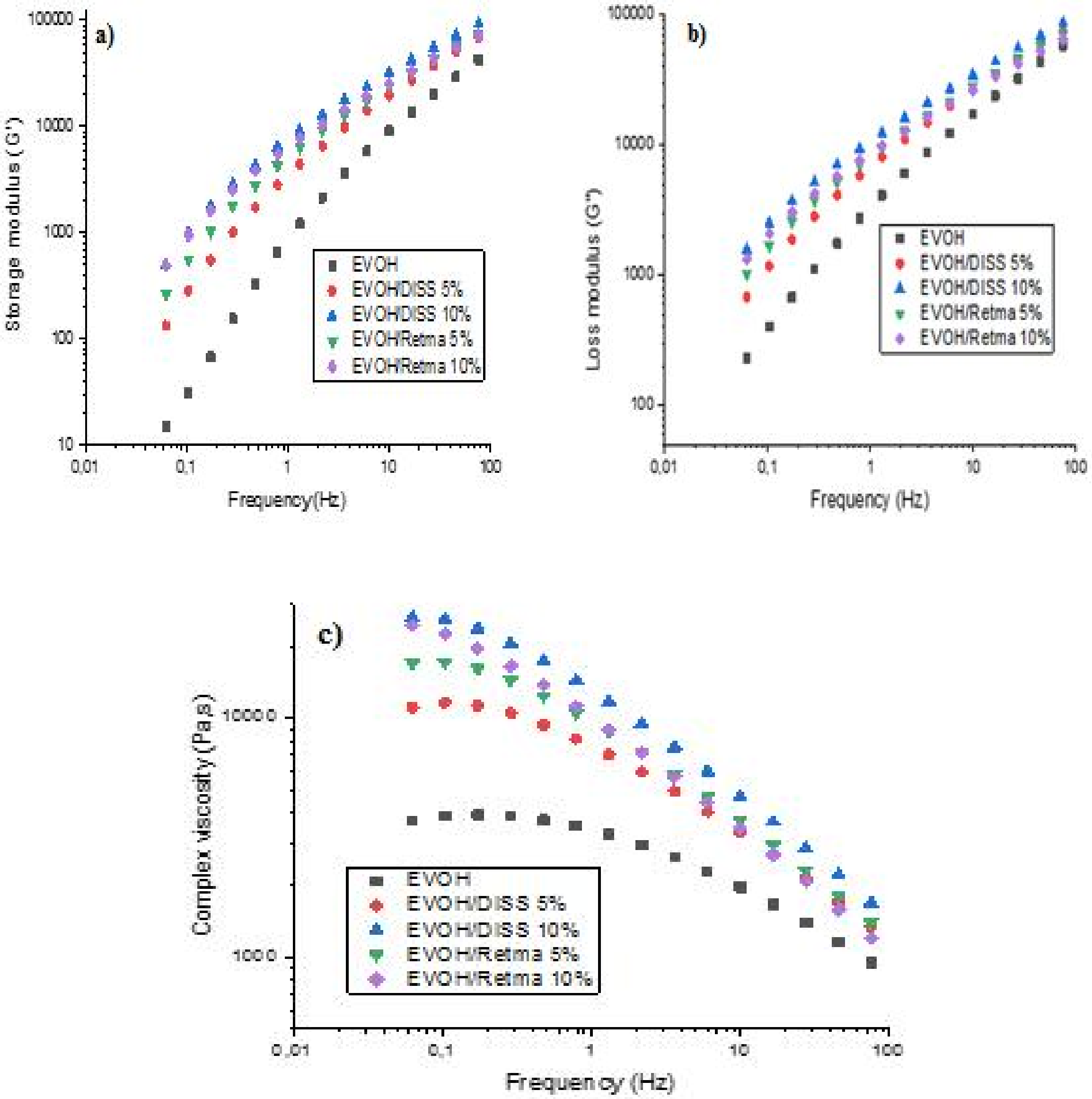

Fig.8. Spectra of G' (a), G" (b) modulus, complex viscosity (c)

The parameters values obtained for the EVOH composites were close to the value of the neat EVOH. The G' and G" modulus of EVOH/CF_D increased slightly and proportionally with fibers ratio, this results can be explain that EVOH is a hydrophile polymer which potentially make it compatible with the cellulose and it can also attribuated to the surface fibers treatement where many hydroxyl groups are more exposed on the surface of the fibers which leads to the creation of bonds between the fibers and the matrix as showed in the FTIR results [38,20]. According to the study reported earlier about EVOH reinforced with water-soluble lignin-like biopolymers (SLP) which found have similar or higher mechanical strength as the pristine synthetic polymer [39]. The composites HDPE/hard wood, HDPE/Flax, HDPE/ rice hulls, PP/ bleached hemp fiber, PP/Kenaf and PP/ white jute presented also an increasing in the Young's modulus with the fiber ratio. In the other hand, some researches found a contrary behaviour with increasing fiber ratio. This could be attribued to many factors like the incompatibility between the two phases, improper preparation process, fiber degradation or it can be also attribuated to a poor dispersion [40]. The main objective of the rheological study is to better understand how the viscosity of these composites evolves. EVOH behavior is characteristic of pseudo-plastic materials, characterized by a Newtonian plateau at low frequencies and a decrease in viscosity as the frequency increases. Fibers effect on the composites viscosity increases is more obvious at lower frequency. This viscous behavior is determined by the nature of the interactions between the fibers, which can be easily explained in terms of the flow hindrance produced by the fibers [41]. For lower shear rates, the fibers are distributed with more disorder, which causes more fiber–fiber contact, further leading to increased viscosity. Adding the fiber to the polymer disrupts normal flow and hinders the mobility of the polymer segments, which increases the viscosity of the polymer [42].

d. Water absorption

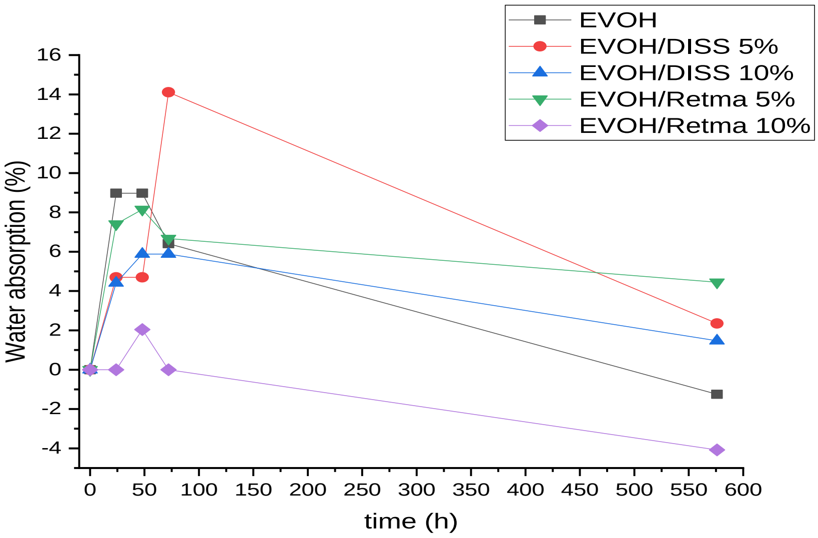

Fig.9. Water absorption of EVOH/CF composites films at 5 and 10%

The hydrophobic nature of EVOH leads to absorption of significant amounts of moisture in high relative humidity conditions [43], the polar hydroxyl group in EVOH structure cause its moisture sensitivity because they are not totally self associated, but partly isolated in the matrix which interacts with water molecules by hydrogen bonding [44,45]. The absorption of water in EVOH's composites occurs in the EVOH matrix through polar sites present in the polymer which increaseing with ethylene content, the fibers where the –OH of the glucose is a potential site for water-absorption and the polymer –fibers interface [45-47]. The EVOH matrix has a mass gain of 8.97% which is compatible with the results reported earlier by others studies (Lagaron et al. [48] (2001) 9.0%, Aucejo et al. [49] (1999) 13%, Zhang et al. [50] (1999) 8.4% for EVOH films with 32 mol% ethylene). The water permeability decrease with increasing the degree of crystallinity, wich increase with vinyl alcohol content and restricted chain mobility by intermolecular hydrogen-bonding interactions, but in the other hand, an increasing in vinyl alcohol unit means increasing hydroxyl groups that will interacts with water molecule [45]. It is observed that the water absorption of the different composites is lower than that of the neat matrix. The water uptake of composite films filled with 5% decreased compared to the neat EVOH up to 4% and 1% for EVOH/CF_R and EVOH/CF_D respectively, which indicates that the water resistance capacity of EVOH is greatly enhanced by incorporation of the cellulosic fibers. Its also observed that composites with 10% cellulose are far less absorbent of water. An earlier study with MCS/PVA film, where the amount of starch in the film did not noticeably affect the water absorption capacity of the samples, this phenomen can be explained that, the water in the nanopores may form hydrogen bonds with the polymer, blocking the nanopores and reducing water uptake [51]. In this case, the decreasing in water absorption observed with composites films is related to the fact that the polar groups contained in the structure of the fibers and matrix reacted together, this results are compatible with the FTIR results which indicates a decrease in OH number. Also, the water absorption decreased less in the case of CF_R, thus confirming that the treatment of El Retma fibers could not expose more OH groups leading to a fewer interactions with the matrix and leaving more OH groups in the EVOH structure to interact with water. In the other hand, it's found that both the initial rate of water absorption and the maximum water uptake increases for all hemp fiber reinforced unsaturated polyester composites samples as the fiber volume fraction increases. The author attributed the water absorption to the hemp fiber [52]. Similar experiments using a softwood kraft fiber as reinforcement in a xylan film was found that with 5% pulp fibers, specific water vapor transmission rate increases which increases in adding 10% pulp fibers to xylan [53].The mass of the samples decreases as the immersion time increase, due to the partial solubilization of the PVA. The loss of mass is much more significant for the virgin matrix and decreases after the addition of the cellulosic fibers which is due to the interactions of OH groups contained on the cellulose surface which react with the OH in the PVA structure preventing it from solubilization.

4. CONCLUSION

In this present study, El Diss and El Retma fibers are two new abondonate sources which were treated to eliminate extracellulosic composants (lignin and hemicellulose) and then incorporated to EVOH copolymer to obtain EVOH/CF composites. SEM images showed a significant morphological changes and FTIR results confirms the elimination of lignin and hemicellulose from the raw fibers. Thermal characterization indicate that the treated fibers degraded at slightly higher temperatures than the raw fibers, also suggesting that El Retma celluloses are not completely isolated.

After incorporation of the treated fibers into EVOH matrix, the FTIR results reported a formation of inter and intra molecular hydrogen bonds between EVOH matrix and cellulosic fibers. The G' and G'' modulus has been improved after treated fibers addition in EVOH matrix which is compatible with literature reports and water absorptions results which decreased in the composites films because of the total involvement of the OH groups of the EVOH structure on the creation of inter and intramolecular bonds with cellulosic fibers preventing the formation of bonds with H_2O.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

[1] Liu W, Wang Y J, Sun Z. Effects of Polyethylene-Grafted Maleic Anhydride (PE-gMA) on Thermal Properties, Morphology, and Tensile Properties of Low-Density Polyethylene (LDPE) and Corn Starch Blends. J. APPL. POLYM. SCI. 2003, 88, (13), 2904 –2911. https://doi.org/10.1002/app.11965

[2] Siqueira G, Bras J, Dufresne A. Cellulose Whiskers versus Microfibrils : Influence of the Nature of the Nanoparticle and its Surface Functionalization on the Thermal and Mechanical Properties of Nanocomposites. Biomacromolecules. 2009, 10, (2). https://doi.org/10.1021/bm801193d

[3] Kamel S. Nanotechnology and its Applications in Lignocellulosic Composites, a Mini Review. EXPRESS POLYM LETT. 2007, 1, (9), 546–575. https://doi.org/10.3144/expresspolymlett.2007.78

[4] Prachayawarakorn J, Sangnitidej P, Boonpasith P. Properties of Thermoplastic Rice Starch Composites Reinforced by Cotton Fiber or Low-Density Polyethylene. *Carbohydr. Polym*. 2010, 81, (2), 425–433. https://doi.org/10.1016/j.carbpol.2010.02.041

[5] Chandra R, Rustgi R. Biodegradation of Maleated Linear Low-Density Polyethylene and Starch Blends. POLYM DEGRAD STABIL. 1997, 56, 185-202. https://doi.org/10.1016/S0141-3910(96)00212-1

[6] Marcovich N E, Villar M A. Thermal and Mechanical Characterization of Linear Low Density Polyethylene/Wood Flour Composites. J. APPL. POLYM. SCI. 2003, 90, (10), 2775–2784. https://doi.org/10.1002/app.12934

[7] Xiong Ch, Rongrong Q, Yanling W. Wood-Thermoplastic Composites from Wood Flour and High-Density Polyethylene. J. APPL. POLYM. SCI. 2009, 114, (2), 1160–1168. https://doi.org/10.1002/app.30707

[8] Siqueira G, Bras J, Dufresne A. Cellulosic Bionanocomposites : A Review of Preparation, Properties and Applications. Polymers. 2010, 2, (4), 728-765. https://doi.org/10.3390/polym2040728

[9] Ambjornsson H A, Schenzel K, Germgard U. Carboxylmethyl Cellulose Produced at Different Mercerization Conditions and Characterized by NIR FT Raman Spectroscopy in

Combination with Multivariate Analytical Methods. Bioressources. 2013, 8, (2), 1918-1932. https://doi.org/10.15376/biores.8.2.1918-1932

[10] Ozdemir T, Mengeloglu F. Some Properties of Composite Panels Made from Wood Flour and Recycled Polyethylene. Int J Mol Sci. 2008, 9, (12), 2559–2569. https://doi.org/10.3390/ijms9122559

[11] Lai S M, Yeh F C, Wang Y, Chan H C, Shen H F. Comparative Study of Maleated Polyolefins as Compatibilizers for Polyethylene/Wood Flour Composites. J. APPL. POLYM. SCI. 2003, 87, (3), 487–496. https://doi.org/10.1002/app.11419

[12] Myers G E, Chahyadi I S, Gonzalez C, Coberly C A, Ermer D S. Wood Flour and Polypropylene or High Density Polyethylene Composites : Influence of Maleated Polypropylene Concentration and Extrusion Temperature on Properties. Intern. J. Polymeric Mater. 1991, 15, (3-4), 171-186. https://doi.org/10.1080/00914039108041082

[13] Bengtsson M, Gatenholm P, Oksman K. The Effect of Crosslinking on the Properties of Polyethylene/wood Flour Composites. Compos Sci Technol. 2005, 65, (10), 1468–1479. 10.1016/j.compscitech.2004.12.050

[14] Bengtsson M, Oksman K. The Use of Silane Technology in Crosslinking Polyethylene/Wood Flour Composites. Compos Part A Appl Sci Manuf. 2006, 37, (5), 752–765. https://doi.org/10.1016/j.compositesa.2005.06.014

[15] Wang Y, Yeh F C, Lai S M, Chan H C, Shen H F. Effectiveness of Functionalized Polyolefins as Compatibilizers for PolyethyIene/Wood FIour Composites. POLYM ENG SCI. 2003, 43, (4), 933-945. https://doi.org/10.1002/pen.10077

[16] Pereira P H F, Morsyleide de Freitas R, Cioffi M O H, Benini K C C C, Milanese A C, Voorwald H C J, Mulinari D R. Vegetal Fibers in Polymeric Composites : a Review. Polímeros. 2015, 25, (1), 9-22. http://dx.doi.org/10.1590/0104-1428.1722

[17] Morsyleide F R, Bor-sen Ch B, Medeiros E S, Wood D F, Williams T G, Mattoso L H C, Orts W J, Imam S H. Effect of Fiber Treatments on Tensile and Thermal Properties of Starch/Ethylene Vinyl Alcohol Copolymers/Coir Biocomposites. Bioresour. Technol. 2009, 100, (21), 5196–5202. http://dx.doi.org/10.1016/j.biortech.2009.03.085

[18] Raabe J, de Souza Fonseca A, Bufalino L. Biocomposite of Cassava Starch Reinforced

with Cellulose Pulp Fibers Modified with Deposition of Silica (SiO2) Nanoparticles. J Nanomater. 2015, 9 pages. http://dx.doi.org/10.1155/2015/493439

[19] Moura E A B, Nogueira B R, Ortiz A V. Changes in Physicochemical, Morphological and Thermal Properties of Electron-Beam Irradiated Ethylene–Vinyl Alcohol Copolymer (EVOH) as a Function of Radiation Dose. SM/EB-16.

[20] Nogueira B R, Lima N B, Chinellato A C, Parveen A, Rangari V K, Moura E A B. Thermal and Morphological Behavior of EVOH/Piassava Fiber Composites Treated by Electron-beam Irradiation.

[21] Franzoso F, Tabasso S, Antonioli D. Films Made from Poly (vinyl alcohol-co-ethylene) and Soluble Biopolymers Isolated from Municipal Biowaste. J. APPL. POLYM. SCI. 2015, 132, (4), 41359-11. http://dx.doi.org/10.1002/app.41359

[22] Franzoso F, Vaca-Garcia C, Rouilly A, Evon Ph, Montoneri E, Persico P, Nistico R, Mendichi R, Francavilla M. Extruded Versus Solvent Cast Blends of Poly(vinyl alcohol-co-ethylene) and Biopolymers Isolated from Municipal Biowaste. J. APPL. POLYM. SCI. 2011, 139, (9), 1-17. http://dx.10.1002/app.43009

[23] Dikobe D G, Luyt A S. Effect of Filler Content and Size on the Properties of Ethylene Vinyl Acetate Copolymer–Wood Fiber Composites. J. APPL. POLYM. SCI. 2007, 103, (6), 3645–3654. https://doi.org/10.1002/app.25513

[24] Khiari R, Marrakchi Z, Belgacem M N, Mauret E, Mhenni F. New Lignocellulosic Fibres-Reinforced Composite Materials : A Stepforward in the Valorisation of the Posidonia Oceanica Balls. Compos Sci Technol. 2011, 71, (16), 1867–1872. https://doi.org/10.1016/j.compscitech.2011.08.022

[25] Pineda-Pimentel M G, Flores-Ramirez N, Farías Sanchez J C, Domratcheva-Lvova L, Vasquez-Garcia SR, García-Gonzalez L. Theoretical Analysis and FTIR of Cellulose Nanowhiskers/Poly(ButylAcrylate). Superficies y Vacío. 2016, 29, (3). http://www.redalyc.org/articulo.oa?id=94251122005

[26] Zhang X, Wu X, Lu C, Lu C, Zhou Z. Dialysis-Free and in Situ Doping Synthesis of Polypyrrole@Cellulose Nanowhiskers Nanohybrid for Preparation of Conductive Nanocomposites with Enhanced Properties. ACS Sustainable Chem. Eng. 2015, 3, (4),

675–682. https://doi.org/10.1021/sc500853m

[27] Li R, Fei J, Cai Y, Li Y, Feng J, Yao J. Cellulose Whiskers Extracted from Mulberry: A Novel Biomass Production. *Carbohydr. Polym*. 2009, 76, (1), 94–99. https://doi.org/10.1016/j.carbpol.2008.09.034

[28] Kargarzadeh H, Ahmad I, Abdullah I. Effects of Hydrolysis Conditions on the Morphology, Crystallinity, and Thermal Stability of Cellulose Nanocrystals Extracted from kenaf bast Fibers. Cellulose. 2012, 19, (3), 855–866. https://doi.org/10.1007/s10570-012-9684-6

[29] de Menezes A J, Siqueira G, Curvelo A, Dufresne A. Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites. Polymer. 2009, 50, (19), 5052–4563. https://doi.org/10.1016/j.polymer.2009.07.038

[30] Silvério H A, Neto W P F, Dantas N O, Pasquini D. Extraction and Characterization of Cellulose Nanocrystals from Corncob for Application as Reinforcing Agent in Nanocomposites. Ind Crops Prod. 2013, 44, 427–436. https://doi.org/10.1016/j.indcrop.2012.10.014

[31] Zhou Z, Yang Y, Han Y, Guo Qu, Zhang X, Lu C. In Situ Doping Enables the Multifunctionalization of Templately Synthesized Polyaniline@Cellulose Nanocomposites. *Carbohydr. Polym*. 2017, 177, 241-248. https://doi.org/10.1016/j.carbpol.2017.08.136

[32] Lu P, Hsieh Y. Preparation and Properties of Cellulose Nanocrystals: Rods, Spheres, and Network. *Carbohydr. Polym*. 2010, 82, (2), 329–336. https://doi.org/10.1016/j.carbpol.2010.04.073

[33] Abraham E, Kam D, Nevo Y, Slattegard R, Rivkin A, Lapidot, Sh, Shoseyov O. Highly Modified Cellulose Nanocrystals and Formation of Epoxy-CNC Nanocomposites. ACS Appl. Mater. Interfaces. 2016, 8, (41), 28086–28095. https://doi.org/10.1021/acsami.6b09852

[34] Hammiche D, Boukerrou A, Djidjelli H, Grohens Y, Bendahou A, Seantier B. Characterization of Cellulose Nanowhiskers Extracted from Alfa Fiber and the Effect of Their Dispersion Methods on Nanocomposite Properties. J ADHES SCI TECHNOL. 2016, 30, (17), 1899–1912. https://doi.org/10.1080/01694243.2016.1170586

[35] Chirayil C J, Mathew L, Thomas S. Review of Recent Research in Nano Cellulose

Preparation from Different Lignocellulosic Fibers. Rev.Adv. Mater. Sci. 2014, 37, 20-28.

[36] Fortunati E, Luzi F, Puglia D, Terenzi A, Vercellino M, Visai L, Santulli C, Torrea L, Kennyand J M. Ternary PVA Nanocomposites Containing Cellulose Nanocrystals from Different Sources and Silver Particles : Part II. *Carbohydr. Polym*. 2013, 97, (2), 837–848. https://doi.org/10.1016/j.carbpol.2013.05.015

[37] Tang X, Alavi S. Recent Advances in Starch, Polyvinyl Alcohol Based Polymer Blends, Nanocomposites and Their Biodegradability. *Carbohydr. Polym*. 2011 ; 85, (1), 7–16. 10.1016/j.carbpol.2011.01.030

[38] Martinez-Sanz M, Olsson R T, López-Rubio A, Lagaron J M. Development of Bacterial Cellulose Nanowhiskers Reinforced EVOH Composites by Electrospinning. J. APPL. POLYM. SCI. 2012, 124, (2), 1398–1408. https://doi.org/10.1002/app.35052

[39] Nistico R, Evon Ph, Labonne L, Vaca-Medina G, Montoneri E, Francavilla M, Vaca-Garcia C, Magnacca G, Franzoso F, Negre M. Extruded Poly(ethylene–co–vinyl alcohol) Composite Films Containing Biopolymers Isolated from Municipal Biowaste. CHEMISTRYSELECT. 2016, 1, (10), 2354-2365. https://doi.org/10.1002/slct.201600335

[40] Ku H, Wang H, Pattarachaiyakoop N, Trada M. A Review on the Tensile Properties of Natural Fiber Reinforced Polymer Composites. COMPOS PART B-ENG. 2011, 42, (4), 856–873. https://doi.org/10.1016/j.compositesb.2011.01.010

[41] Pezmanchado M A, Biagiotti J, Kenny J M. Comparative Study of the Effects of Different Fibers on the Processing and Properties of Ternary Composites Based on PP-EPDM Blends. Polym. Compos. 2002, 23, (5), 779-789. https://doi.org/10.1002/pc.10476

[42] Borsoi C, Scienza L C, Zattera A J. Characterization of Composites Based on Recycled Expanded Polystyrene Reinforced with Curaua Fibers. J. APPL. POLYM. SCI. 2012, 128, (1), 653–659. https://doi.org/10.1002/app.38236

[43] Cabedo L, Giménez E, Lagaron J M, Gavara R, Saura J J. Development of EVOH-Kaolinite Nanocomposites. Polymer. 2004, 45, (15), 5233-5238. https://doi.org/10.1016/j.polymer.2004.05.018

[44] López-de-Dicastillo C, Alonso J M, Catalá R, Gavara R, Hernández-Muñoz P. Improving the Antioxidant Protection of Packaged Food by Incorporating Natural Flavonoids

into Ethylene−Vinyl Alcohol Copolymer (EVOH) Films. J Agric Food Chem. 2010, 58, (20), 10958-64. https://doi.org/10.1021/jf1022324

[45] Mokwena K KH, Tang J. Ethylene Vinyl Alcohol: A Review of Barrier Properties for Packaging Shelf Stable Foods. Crit. Rev. Food Sci. Nutr. 2012, 52, (7), 640-50. https://doi.org/10.1080/10408398.2010.504903

[46] Pothan L A, Thomas S. Effect of Hybridization and Chemical Modification on the Water-Absorption Behavior of Banana Fiber–Reinforced Polyester Composites. J. APPL. POLYM. SCI. 2004, 91, (6), 3856-3865. https://doi.org/10.1002/app.13586

[47] Garcia de Rodriguez N L, Thielemans W, Dufresne A. Sisal Cellulose Whiskers Reinforced Polyvinyl Acetate Nanocomposites. Cellulose. 2006, 13, (3), 261-270. https://doi.org/10.1007/s10570-005-9039-7

[48] Lagaron J M, Powell A K, Bonner G. Permeation of Water, Methanol, Fuel and Alcohol Containing Fuels in High Barrier Ethylene Vinyl Alcohol Copolymer. Polym. Test. 2001, 20, (5), 569-577. https://doi:10.1016/s0142-9418(00)00077-5

[49] Aucejo S, Marco C, Gavara R. Water Effect on Morphology of EVOH Copolymers. J. Appl. Polym. Sci. 1999, 74, (5), 1201-1206. https://doi:10.1002/(sici)1097-4628(19991031)74:5<1201::aid-app17>3.0.co;2-8

[50] Zhang Z, Britt I J, Tung M A. Water Absorption in EVOH Films and its Influence on Glass Transition Temperature. J. Polym. Sci. B. 1999, 37, (7), 691-699. https://doi:10.1002/(sici)1099-0488(19990401)37:7<691::aid-polb20>3.0.co;2-v

[51] Guohua Z, Ya L, Cuilan F, Min Z, Caiqiong Z, Zongdao Ch. Water Resistance, Mechanical Properties and Biodegradability of Methylated-cornstarch/poly(vinyl alcohol) Blend Film. POLYM DEGRAD STABIL. 2006, 91, (4), 703-711. https://doi.org/10.1016/j.polymdegradstab.2005.06.008

[52] Dhakal H N, Zhang Z Y, Richardson M O W. Effect of Water Absorption on the Mechanical Properties of Hemp Fibre Reinforced Unsaturated Polyester Composites. Compos Sci Technol. 2007, 67, (7-8), 1674–1683. https://doi.org/10.1016/j.compscitech.2006.06.019

[53] Saxena A. Nanocomposites Based on Nanocellulose Whiskers. [Dissertation]. Atlanta : School of Chemistry and Biochemistry Georgia Institute of Technology, 2013.

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