

Changes in Physicochemical, Morphological and Thermal Properties of Electron-Beam Irradiated Ethylene–Vinyl Alcohol Copolymer (EVOH) as a Function of Radiation Dose

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Abstract. In the present work, the changes in physicochemical, morphological and thermal properties of electron-beam irradiated ethylene–vinyl alcohol copolymer (EVOH) resin and EVOH resin reinforced with piassava (*Attalea funifera* Mart) fiber, as a function of radiation dose, were investigated. The materials were irradiated up to 90 kGy using a 1.5 MeV electron beam accelerator, at room temperature in presence of air. The changes in properties of the EVOH and of the reinforced EVOH, after irradiation, were investigated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and sol-gel analysis. The correlation between the properties of the EVOH and of the EVOH-piassava, both irradiated and non-irradiated samples, were discussed. The results showed that there were no significant differences ($p < 0.05$) in the enthalpy, crystallinity percentage variation and initial degradation temperature of the non-irradiated and irradiated EVOH. In relation to those properties for the non-irradiated and irradiated EVOH-piassava the results showed significant differences ($p < 0.05$) only at 90 kGy, except to EVOH-piassava initial degradation temperature. The results showed that EVOH-piassava presented a gain of crystallinity by 70-74 % and a gain of initial degradation temperature ca. 3% with relation the EVOH. The SEM micrographs samples materials indicated a better interfacial adhesion between piassava fiber and EVOH as a function of radiation doses applied. It also showed a large difference between the crystalline form of the EVOH and EVOH-piassava, which indicated changes in the order of macromolecules arrangement of EVOH due to piassava incorporation. These results are very important, since that could lead to the obtaining of materials with better barrier properties, lower water absorption and more stable thermal and mechanical properties in high relative humidity conditions compared with EVOH.

1. Introduction

A promising approach to the controllable modification of the properties of the polymer materials is based on treatment with ionizing radiation, particularly, electron-beam irradiation. The electron-beam irradiation can affect the polymeric materials leading to a production of free radicals. These free radicals can in turn lead to degradation and or cross-linking phenomena, with release of gases, discoloration, changes in mechanical, thermal and barrier properties [1]. In recent years electron-beam irradiation has been efficiently applied to promote cross-linking and scission of the polymeric chains to modify the properties of the different polymers for versatile applications. Ethylene-vinyl alcohol (EVOH) copolymers are a family of resins with excellent gas-barrier properties. The permeability of EVOH depends on the copolymerization ratio of ethylene and vinyl alcohol. EVOH copolymers with 25–45 mol% ethylene are considered to have the superior gas barrier properties compared to most of the polymeric materials. So EVOH is widely used in various fields such as food packaging and gasoline tanks due to their outstanding gas barrier properties to oxygen and organic compounds. They are used in the food packaging industry as gas-barrier materials for foods that are sensitive to certain levels of oxygen or carbon dioxide. For certain foods such as soups or juices in which any change in taste must be prevented, EVOH resins are ideal for flavor barrier, because EVOH has a low absorption rate of odor and flavor, and EVOH resins have almost no odor. Furthermore, the excellent resistance of EVOH to oils and organic solvents makes EVOH suitable for packaging edible oils, oily foods such as potato chips,

mineral oils, organic solvents and agricultural chemicals [2, 3]. EVOH presents a considerable chemical resistance, high transparency and easy processability on a wide range of conventional coextrusion processing equipment. However, EVOH are very sensitive to moisture and its gas barrier ability deteriorates in high relative humidity conditions. Besides the increase in the permeability values of EVOH due to water absorption at high relative humidity conditions, their thermal and mechanical properties are also affected [3-6].

Piassava (*Attalea funifera* Mart) is a Brazilian lignocellulosic fiber extracted from the leaves of a palm tree of natural occurrence in the Atlantic rain forest. This fiber has higher lignin content (around 48%) than any of the other common lignocellulosic fibers. This could be responsible for its inherent flexural rigidity and water proof resistance. The main use of these fibers is for industrial and domestic brooms, industrial brushes, ropes and baskets, carpets and roofs. It is estimated that around 30% of the fiber is disposed as residue by the transformation industries, before production [7-9]. This work studied the changes in physicochemical, morphological and thermal properties as a function of radiation dose of electron-beam irradiated EVOH resin and EVOH resin reinforced with piassava fiber, from the residues disposed by the transformation industries. The correlation between the properties of the EVOH resin and of the EVOH resin reinforced with piassava fiber residues, both irradiated and non-irradiated sample, were also discussed.

2. Experimental

2.1. Materials

The materials used in this study were EVOH resin containing 32 mol% ethylene (commercial grade by EVAL Company of America) and piassava residues disposed by some brooms and brushes manufacturers.

2.2. Preparation and Incorporation of Piassava fiber in EVOH resin

In order to remove the impurities, the piassava fiber residues were washed in distilled water for 24 h. The fiber was then dried at 70 °C in air oven. The dry fiber was reduced to fine powder, with particle sizes equal or lower than 200 µm by using ball mills. The EVOH resin reinforced with 10% of piassava fiber was obtained by mixing 10 parts of fiber with 90 parts of EVOH resin (in weight) using a double screw extruder machine.

2.3. Electron-beam Irradiation

EVOH resin and EVOH resin reinforced with piassava fiber (EVOH-piassava) were irradiated up to 90 kGy using a 1.5MeV electrostatic accelerator (Dynamitron II, Radiation Dynamics Inc., 1.5MeV energy, 25mA current and 37.5kW power), at room temperature, in air, dose rate 11.22 kGy/s. Irradiation doses were measured using cellulose triacetate film dosimeters “CTA-FTR-125” from Fuji Photo Film Co. Ltd.

2.4. Analyses

The analyses were carried out on materials eight day after irradiation. The difference between the results for irradiated and non-irradiated materials were then evaluated statistically by ANOVA using BioEstat software (version 5.0, 2007, Windows 95, Manaus, AM, Brazil). Significance was defined at $p < 0.05$.

2.4.1. Differential Scanning Calorimetry

The differential scanning calorimetry (DSC) analyses were carried out using a DSC 50 (Shimadzu, Japan). DSC analyses of the materials were performed on four weighed samples with 10.0 ± 1.0 mg of the irradiated and non-irradiated materials. Samples were heated from 25 to 300 °C, at a heating rate of 5 °C/min (in a nitrogen atmosphere).

2.4.2. Thermogravimetric Analysis

The thermogravimetric analyses (TGA) were carried out using a TGA 50 (Shimadzu, Japan). TGA analyses of the materials were performed on four weighed samples with 3.0 ± 1.0 mg of the irradiated and non-irradiated materials. Samples were heated from 25 to 500 °C, at a heating rate of 10 °C/min (in an oxygen atmosphere).

2.4.3. Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) analyses were carried out using a LX 30 (Philips). The samples were freeze-fractured under liquid nitrogen, and then the fractured surface was coated with a fine layer of gold and observed by scanning electron microscopy (SEM).

2.4.4. Sol-Gel Analysis

The sol-gel analyses of the materials were performed on four weighed samples with 300 ± 10 mg of the irradiated and non-irradiated materials. The gel content of the cross-linked samples was estimated by measuring its insoluble part in dried sample after immersion in solvent (acetic acid) for 12 hours at boiling point solvent (115°C) . The gel fraction was calculated as follows:

$$\text{Gel fraction (\%)} = \frac{W_d}{W_i} \cdot 100\%$$

Where:

W_i = initial weight of the dried sample

W_d = weight of the dried insoluble part of sample after extraction with acetic acid

3. Results and Discussion

3.1. Differential Scanning Calorimetry

The results of the DSC analysis showed that there were no significant differences ($p < 0.05$) for melting temperature (T_m) for both irradiated and non-irradiated EVOH and EVOH-piassava. The results of the DSC analysis for melting enthalpy (ΔH_m) of the EVOH and EVOH-piassava are given in Fig. 1. The results presented in Fig. 1 represent the average values calculated from the data obtained by DSC analysis. The standard deviation for DSC analysis was less than 10% for all tests. As it can be seen, there were significant increases ($p < 0.05$) between the EVOH-piassava ΔH_m and EVOH ΔH_m for all range of radiation dose studied. The values EVOH-piassava ΔH_m were by 336–380% higher than EVOH ΔH_m . The results of the DSC analysis for ΔH_m showed an increase by 345 % for non-irradiated samples of the EVOH-piassava and a 380% maximum increase for EVOH-piassava at 60 kGy compared with EVOH in the same conditions (Fig.1). In contrast, Fig.1 showed that evaluating each material individually , the ΔH_m of the EVOH and the ΔH_m of EVOH-piassava

basically were not affected by irradiation, since there were no significant differences ($p < 0.05$) of irradiated and non-irradiated samples, except for EVOH-piassava ΔH_m at 90 kGy.

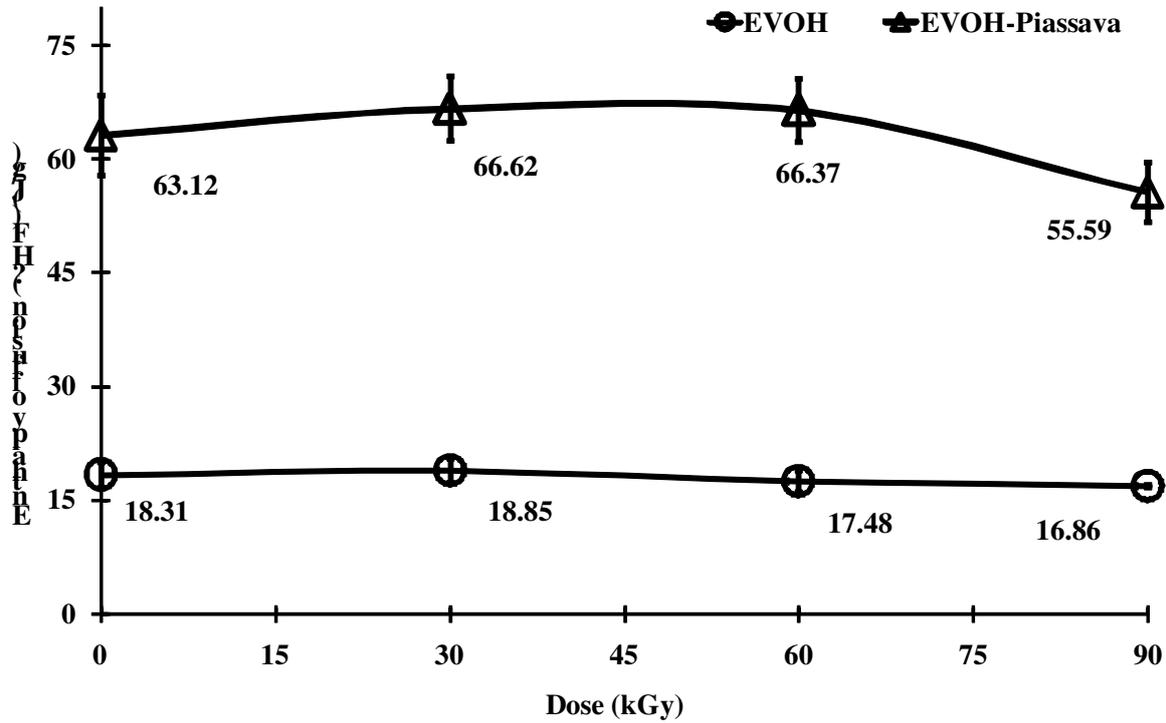


Figure 1. Effects of irradiation on melting enthalpy (ΔH_m) as a function of electron-beam radiation dose for the EVOH and EVOH-piassava.

The ΔH_m is directly related to crystallinity percentage variation ($\Delta\tau$) calculated by the following equations:

i) crystallinity percentage variation as a function of electron-beam radiation dose

$$\Delta\tau = \frac{\Delta H_m - \Delta H_m^*}{\Delta H_m} \cdot 100$$

where :

ΔH_m^* is the melting enthalpy of the irradiated sample

ΔH_m is the initial melting enthalpy of the non-irradiated sample.

ii) crystallinity percentage variation between EVOH-piassava and EVOH

$$\Delta\tau_p = \frac{\Delta H_m - \Delta H_m^\blacktriangle}{\Delta H_m} \cdot 100$$

where :

$\Delta H_m^\blacktriangle$ is the melting enthalpy of the irradiated or non-irradiated EVOH-piassava sample

ΔH_m is the melting enthalpy of the irradiated or non-irradiated EVOH sample

The results of the crystallinity percentage variation as a function of electron-beam dose ($\Delta\tau$) and crystallinity percentage variation between EVOH-piassava and EVOH ($\Delta\tau_p$) are presented in Table I. As it can be seen, the ($\Delta\tau$) showed the decrease around by 12% for EVOH-piassava at 90 kGy. On the other hand, Table I showed increase by 70-74% in EVOH-piassava crystallinity compared with EVOH crystallinity.

Table I. Crystallinity percentage variation as a function of electron-beam radiation dose

DOSE (kGy)	$\Delta\tau$ EVOH ^(a)			$\Delta\tau$ EVOH-piassava ^(b)			$\Delta\tau_p$ EVOH- piassava/ EVOH ^(c)
	ΔH_m (J/g)	statistic differences ($p < 0.05$)	$\Delta\tau$ (%)	ΔH_m (J/g)	statistic differences ($p < 0.05$)	$\Delta\tau_p$ (%)	$\Delta\tau_p$ (%)
0	18.31		-	63.12		-	71.00
30	18.85	ns ^(d)	-	66.62	ns ^(d)	-	69.72
60	17.48	ns ^(d)	-	66.37	ns ^(d)	-	73.66
90	16.86	ns ^(d)	-	55.59	s ^(e)	11.93	70.18

^(a) crystallinity percentage variation EVOH as a function of electron-beam radiation dose; ^(b) crystallinity percentage variation EVOH-piassava as a function of electron-beam radiation dose; ^(c) crystallinity percentage variation between EVOH-piassava and EVOH; ^(d) non-significant; ^(e) significant.

These results are very important because the increase in EVOH-piassava crystallinity can show a gain in barrier properties and consequently, a reduction of their water absorption rate at high relative humidity conditions. An increase in crystallinity reduces the mobility of the amorphous chains leading to more efficient molecular orientation and to significant fall in permeation rates, since a rise in molecular organization makes the diffusivity of the liquid or gas more difficult. Considering that there is a direct influence between the EVOH water absorption rate, in their permeability, thermal and mechanical properties [3], these results can contribute to a better thermal and mechanical response of the EVOH-piassava at high relative humidity conditions compared to EVOH.

3. 2. Thermogravimetric Analysis

The results of the thermogravimetric analyses (TGA) are presented in Table II. It showed the effects of the electron-beam radiation doses in the initial degradation temperature and weight loss of the EVOH and EVOH-piassava. The results presented in Table II represent the average values calculated from the data obtained by TGA analysis. The standard deviation for TGA analysis was less than 10% for all tests. As it can be seen, there were no significant differences ($p < 0.05$) in the initial degradation temperature and weight loss of the irradiated and non-irradiated samples of the EVOH and EVOH-piassava. In contrast, Table II showed that the initial degradation temperature of the EVOH-piassava significantly increased ($p < 0.05$) compared with the EVOH for all range of radiation dose studied, which shows a slight gain of ca 3% of the EVOH-piassava thermal stability compared to EVOH. With relation to the weight loss after the samples heating up to 500 °C, Table II showed that there were significant increases ($p < 0.05$) at EVOH-piassava weight loss (7-13%) compared with EVOH weight loss for all range of radiation dose studied.

Table II. Initial degradation temperature and weight loss of the EVOH and EVOH-piassava as a function of electron-beam radiation dose

Dose (kGy)	EVOH			EVOH-piassava			EVOH-piassava/ EVOH
	$T_i^{(a)}$ (°C)	$T_f^{(b)}$ (°C)	Weight Loss (%)	$T_i^{(a)}$ (°C)	$T_f^{(b)}$ (°C)	Weight Loss(%)	T_i Dif ^(c) (%)
0	370.60	412.13	76.79	378.67	430.75	85.91	2.18 s ^(e)
30	367.29 ns ^(d)	416.08 ns ^(d)	75.52 ns ^(d)	379.41 ns ^(d)	429.16 ns ^(d)	85.07 ns ^(d)	3.30 s ^(e)
60	368.40 ns ^(d)	425.71 ns ^(d)	77.87 ns ^(d)	379.70 ns ^(d)	438.03 s ^(e)	84.62 ns ^(d)	3.07 s ^(e)
90	368.23 ns ^(d)	425.58 ns ^(d)	77.65 ns ^(d)	378.61 ns ^(d)	434.26 s ^(e)	83.08 ns ^(d)	2.82 s ^(e)

^(a) initial degradation temperature; ^(b) final degradation temperature; ^(c) difference of initial degradation temperature between EVOH and EVOH-piassava; ^(d) statistically non-significant ($p < 0.05$); ^(e) statistically significant ($p < 0.05$).

3.3. Scanning Electron Microscopy (SEM)

SEM micrographs for EVOH and EVOH-piassava at the electron-beam radiation dose range studied in this work are showed in Fig.2. The Fig. 2(a)-2(d) are the SEM micrographs of the EVOH. The SEM micrographs of the EVOH-piassava are presented in Fig. 2(e)-2(h). The non-irradiated and irradiated EVOH micrographs, Fig. 2(a)-2(d), revealed rough, dense and compact cryofractured surface morphologies. However, EVOH at 30 kGy Fig. 2(b) exhibited a slightly smoother surface and with a more brittle aspect than the others, which can indicate that a more important degradation by irradiation took place. Comparing Fig. 2(a)-2(d) with Fig. 2(e)-2(h), it can be seen that there was a large difference between the crystalline form of the EVOH and EVOH-piassava. It means that the order of macromolecules arrangement of EVOH was changed by piassava incorporation. From the micrographs showed in Fig. 2(e)-2(h) it undoubted appears that there were two phases, one due to presence of the irregular form particles from the piassava as a dispersed phase distributed on a continuous phase, which is the EVOH phase. The non-irradiated EVOH-piassava micrographs, Fig. 2(e) showed a large number of cavities containing piassava particles in the EVOH phase that can indicate a poor interfacial adhesion between piassava fiber and EVOH. In contrast, the irradiated EVOH-piassava micrographs showed that there were a clear two-phase, however, between the phases, no distinct interspaces existed, and this indicated that electron-beam irradiation caused a certain interfacial adhesion between EVOH and piassava. Comparing the Fig. 2(e)-2(h), it can be seen that the surface morphologies of the EVOH-piassava samples become smooth and with better interfacial adhesion between EVOH and piassava as a consequence of the electron-beam irradiation. However, the EVOH-piassava at 60 kGy, Fig. 2(g), appears to present a smoother surface and better interfacial adhesion between phases than irradiated EVOH-piassava with other radiation doses. These results are very important because they can lead to the obtaining of materials with better water barrier properties than the original EVOH resin.

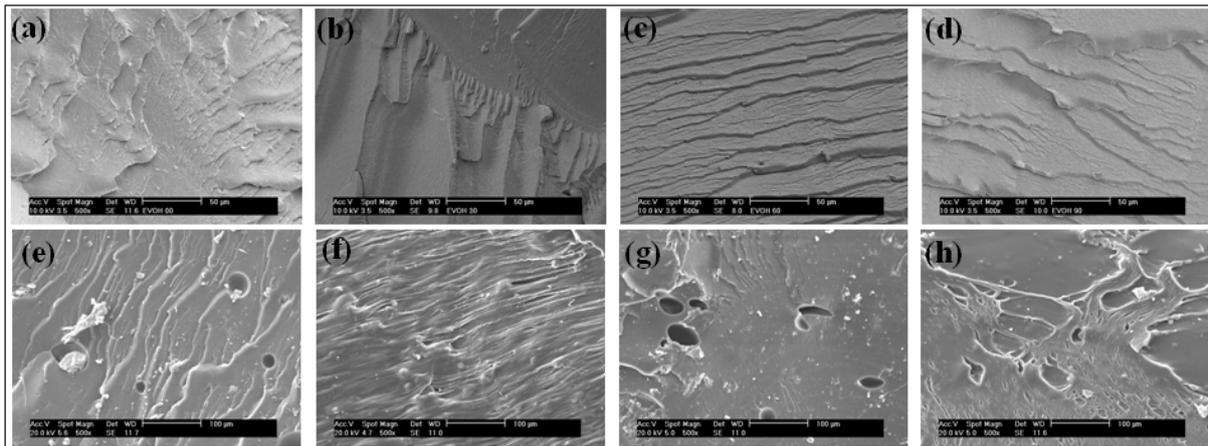


Figure 2. Scanning Electron Microscopy (SEM) micrographs for EVOH and EVOH-piassava at range electron-beam radiation dose studied. Fig. 2(a) non-irradiated EVOH; Fig. 2(b) EVOH at 30 kGy; Fig. 2(c) EVOH at 60 kGy; Fig. 2(d) EVOH at 90 kGy; Fig. 2(e) non-irradiated EVOH-piassava; Fig. 2(f) EVOH-piassava at 30 kGy; Fig. 2(g) EVOH-piassava at 60 kGy; Fig. 2(h) EVOH-piassava at 90 kGy.

3.4. Sol-Gel Analysis

EVOH and EVOH-piassava at the electron-beam radiation dose range studied in this work did not present any gel content in samples after extraction with solvent. These results showed that electron-beam radiation for the doses applied in this work were not enough for cross-linking neither the EVOH nor the EVOH-piassava materials.

4. Conclusions

The objective of the present study was to evaluate the influence of electron-beam radiation dose on physicochemical, morphological and thermal properties of EVOH resin and EVOH resin reinforced with piassava fiber. The EVOH-piassava presented a gain of crystallinity by 70-74 % and a gain of initial degradation temperature ca. 3% with relation the EVOH resin. The non-irradiated and irradiated EVOH micrographs revealed rough, dense and compact cryofractured surface morphologies, but EVOH at 30 kGy exhibited a slightly smoother surface and with a more brittle aspect than the others, which can indicate that a more important degradation by irradiation took place. The results showed there was a large difference between the crystalline form of the EVOH and EVOH-piassava. It means that the order of macromolecules arrangement of EVOH was changed by piassava incorporation. The non-irradiated and irradiated EVOH-piassava micrographs presented two phases, one due to presence of the irregular form particles from the piassava as a dispersed phase distributed on a continuous EVOH phase. The SEM micrographs indicated a better interfacial adhesion between piassava fiber and EVOH as a function of electron-beam radiation doses applied. These results are very important, since that could lead to the obtaining of materials with better barrier properties, lower water absorption, more stable thermal and mechanical properties in high relative humidity conditions when compared with EVOH resin.

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References

- [1] BUCHALLA, R., SCHUTTLER, C., BOGL, K.W., “Effect of ionizing radiation on plastic food packaging materials: a review, Part 1. Chemical and physical changes”, *J. Food Prot.* **56** (1993) 991–997.
- [2] CABEDO, L.; LAGARO, J.M.; CAVAA, D.; SAURAB, J.J.; GIMENEZ, E. “The effect of ethylene content on the interaction between ethylene-vinyl alcohol copolymers and water - II: Influence of water sorption on the mechanical properties of EVOH copolymers”, *Polymer Testing* **25** (2006) 860–867.
- [3] KUCUKPINAR, E.; DORUKER, P., “Effect of absorbed water on oxygen transport in EVOH matrices. A molecular dynamics study”, *Polymer* **45** (2004) 3555–3564.
- [4] KIM, K.B., SUNG, W.M., PARK, H.J., LEE, Y.H., HAN, S.H., “Hydrophobic properties of ethylene–vinyl alcohol copolymer treated with plasma source ion implantation”, *J. Appl. Polym. Sci.* **92** (4) (2004) 2069–2075.
- [5] ARMSTRONG, R.B., “New EVAL® EVOH Resins for Flexible Packaging”, In: <<http://www.tappi.org/content/enewsletters/eplace/2004/27-1Armstrong.pdf>>
- [6] MOKWENA, K. K.; TANG, J.; DUNNE, C. P.; YANG, T.C.S.; CHOW, E. “Oxygen transmission of multilayer EVOH films after microwave sterilization”, *Journal of Food Engineering* **92** (2009) 291–296.
- [7] SATYANARAYANA, K.G.; GUIMARÃES, J.L.; WYPYCH, F., “Studies on lignocellulosic fibers of Brazil. Part I: Source, production, morphology, properties and applications”, *Composites: Part A* **38** (2007) 1694–1709.
- [8] SCHUCHARDT U.; BIANCHI M.L.; GONÇALVES, A.R.; CURVELO, A.A.S.; BISCOLLA, F.C.; PERES, L.O., “Piassava fibers (*Attalea funifera*). I. Chemical analysis, extraction and reactivity of its lignin”, *Cellulose Chem. Technol.* **29** (1995)705–712.
- [9] D’ALMEIDA, J.R.M.; AQUINO, R.C.M.P.; MONTEIRO, S.N., “Tensile mechanical properties, morphological aspects and chemical characterization of piassava (*Attalea funifera*) fibers”, *Composites: Part A* **37** (2006) 1473–1479.