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Thi Phuong Thao Tran, Jean-Charles Benezet, Anne Bergeret. Rice and Einkorn wheat husks reinforced poly(lactic acid) (PLA) biocomposites: Effects of alkaline and silane surface treatments of husks. *Industrial Crops and Products*, 2014, 58, pp.111-124. 10.1016/j.indcrop.2014.04.012 . hal-02914351

HAL Id: hal-02914351

<https://hal.science/hal-02914351>

Submitted on 25 May 2021

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Rice and Einkorn wheat husks reinforced poly(lactic acid) (PLA) biocomposites: Effects of alkaline and silane surface treatments of husks

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A B S T R A C T

This paper investigated specific surface treatments, aimed to improve the adhesion between PLA and rice and Einkorn wheat husks. In the first part, husks were treated by alkaline solutions at three concentrations (2, 5 and 10%) at room temperature for different times between 6 and 48 h. Results revealed that the alkaline treatment dissolved a fraction of waxes, lignin and hemicellulose, so that the polarity of their surface was increased and therefore alkaline treated husks were more sensitive to moisture. Moreover the alkaline treatments have more influence on wheat than on rice husks, as shown by chemical composition determination, FTIR measurements and ESEM observations. In the second part, husks were treated by two kinds of organosilanes (γ -aminopropyltriethoxysilane (APS) and γ -glycidoxypolytrimethoxysilane (GPS)). These silane treatments were applied either alone or on previously alkaline treated husks (NaOH 5% for 24 h). The results showed that silane treatments reduced the moisture sensitivity and raise the energy surface of the husks. In the last part, treated husks were incorporated into polylactic acid (PLA) to produce biocomposites. Biocomposites reinforced by husks treated by alkaline solution and silane have higher bending moduli and stresses than those reinforced by untreated husks and husks treated by silane alone. It can be supposed that the PLA/husks adhesion was enhanced. No difference was observed according to the silane nature.

Keyword:

Rice husk

Einkorn wheat husk

PLA

Silane treatment surface

Alkaline treatment

1. Introduction

The rice and wheat grains are coated by husks to protect them during the growing season. Husks are hard materials and they are composed of holocellulose (cellulose and hemicellulose), lignin, silica and wax that impede microbial attack (Bledzki et al., 2010; Khalil, 2008). In most of the cases these husks are incinerated by cereal producers without any energetic valorization despite the abundant volume deposited throughout the world. Because of the large fraction of cellulose present in these husks, they may be considered as potential candidates for the reinforcement of biodegradable composites.

One of the purposes of using husks as fillers is cost reduction as the cost of bio-sourced and biodegradable polymers are still high.

However like other natural fibres, using husks has drawbacks such as a high hydrophily due to the presence of hydroxyl groups on the husk surface. Furthermore the presence of non-cellulosic components (e.g. lignin and wax) may prevent husks having a good interfacial adhesion with the host polymer. Therefore, chemical treatments for husks are commonly investigated.

An huge amount of researches had been investigated on the modification of natural fibres and their subsequent characterization in composites. Many chemical treatments have been screened to enhance fibre/matrix interface such as alkali treatment (Gomes et al., 2007; Islam et al., 2010), acetylation (Bledzki et al., 2008), silane treatment (Lung et al. and Matinlinna, 2012), maleation (Park et al., 2004).

Alkali treatment is believed to remove non-cellulosic components away from fibre surface and activates hydroxyl group. However, the surface properties of treated fibres depend on various factors such as the concentration of the alkaline solution, the fibre immersion time and temperature. Oh et al. (2005a,b) reported the effect of the concentration of the alkaline solution and of the temperature on the physicochemical changes and the crystalline structure of pulp sheet. They found that the crystallinity ratio was

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thermo-mechanical properties composites were significantly higher than those of the PLA matrix itself. [Huda et al. \(2008\)](#) treated kenaf fibres by APS and incorporated with PLA to fabric laminated composites. The flexural modulus of composite is increased from 5.6 GPa for untreated fibres to 9.5 GPa for silane treated fibres (a 69% increase). This result suggests that APS may be a good coupling agent for husk and PLA also.

2. Materials and methods

The poly (lactic acid) PLA 7000D was supplied by Nature-Works LLC with the following characteristics: Mn = 179 200 Da, polydispersity index I = 1.75 (SEC, THF, T = 25 °C), Tg = 58 °C and Tm = 152 °C (DSC, 10 °C/min, nitrogen atmosphere).

2.2. Processing conditions

2.3. Procedures for husk surface modifications

To study the effect of sodium hydroxide concentration on husks, R and W were dried at 100 °C in vacuum for 24 h until reaching a constant weight (m1) then immersed in sodium hydroxide (NaOH) solutions at 2, 5 and 10%, for 24 h at room temperature. To study the effect of treatment duration on the husk, R and W were immersed in sodium hydroxide solution (5%) for 6 h, 12 h, 18 h, 24 h and 48 h at room temperature. The husks were washed in running tap water to eliminate NaOH, and then the husks were washed with acetic acid (1%). Finally, the husks were washed again by tap water. After washing, the husks were dried through a two-steps process: (i) highly wet husks were first kept in air for 3 days to reduce significantly the water content, and (ii) then husks were dried at 100 °C in an

It can be observed that γ -aminopropyltriethoxysilane (named APS) and γ -glycidoxypropyltrimethoxysilane (named GPS) were widely applied for natural fibre reinforced PLA (Chun et al., 2012; Huda et al., 2008; Yu et al., 2010). Mechanisms were proposed for the reaction taking place at the fibres surface as shown in Fig. 1. The first step consisted in the reaction between alkoxy groups from silane agents and hydroxyl groups on the glucose units of the cellulose molecules in the husks cell-wall leading to a polysiloxane network at the husk surface. Some reactions with lignin hydroxyl groups could also occur. When combined with the PLA matrix, several reactions may occur. Yu et al. (2010) proposed on one hand, a reaction between amine groups from APS and acid end groups of PLA leading to the formation of an amide function (Fig. 1 – Scheme 1), and on the other hand, a reaction between epoxy groups from GPS and hydroxyl end groups of PLA occurred leading to the formation of an ether function (Fig. 1 – Scheme 2). Nevertheless the authors did not suggest the possibility of an additional epoxy-acid reaction at the silane/GPS interface (Fig. 1 – Scheme 3).

The interfacial interaction between natural fibre and PLA resin are improved by coupling agent, the mechanical and

Table 1

Silanes used for the natural fibres/polymer composites in the literature.

Silane	Abbreviation	Target matrix	Target fibres	Ref.
γ -aminopropyltriethoxy silane	APS	Polypropylene Poly acid lactic	Luffa Ramie Coconut shell Kenaf Pineapple Microfibrillated cellulose	Demir et al. (2006) Yu et al. (2010) Chun et al. (2012) Huda et al. (2008) Threepopnatkul et al. (2009) Lu et al. (2008)
γ -glycidopropyltrimethoxy silane	GPS	Polycarbonate Epoxy *	Cellulose fibres Ramie Microfibrillated cellulose	Abdelmouleh et al. (2004) Yu et al. (2010) Lu et al. (2008)
γ -Methacryloxypropyltrimethoxy silane	MPS	Polycarbonate Low density polyethylene (LDPE) *	Kenaf Hemp Pineapple Cellulose fibre Cellulose fibres	Sgriccia et al. (2008) Sgriccia et al. (2008) Threepopnatkul et al. (2009) Abdelmouleh et al. (2007) Abdelmouleh et al. (2004)
γ -(trimethoxysilyl)-1-propanethiol silane	TMPS	Polypropylene	Luffa	Demir et al. (2006)
Hexadecyltrimethoxy silane	HTS	Low density polyethylene (LDPE)	Cellulose fibre	Abdelmouleh et al. (2007)
γ -mercaptopropyltrimethoxy silane	MRPS	Low density polyethylene (LDPE) *	Cellulose fibre Cellulose fibres	Abdelmouleh et al. (2007) Abdelmouleh et al. (2004)
Vinyltris (2-methoxy-ethoxy) silane	VMS	Hight density polyethylene (HDPE)	Henequen	Valadez-Gonzalez et al. (1999a,b)
Triethoxy-vinyl silane	TVS	Poly acid lactic	Chopstick	Shih et al. (2010)

* The matrix is not presented in the articles.

oven under vacuum for 6 h to obtain a constant weight (m_2). The weight percent loss (WPL) of husks was calculated from Eq. (1):

$$\text{WPL} = \frac{(m_1 - m_2)}{m_1} \times 100 \quad (1)$$

2.3.2. Silane treatment procedure

1 wt.% of silane (weight percentage compared to the husks) was dissolved in water/ethanol mixture (30/70 w/w). The pH of the solution was adjusted to 4 with acetic acid and stirred continuously during 30 min. Next, the husks were soaked in solution for 3 h, washed by tap water and dried through a two-steps process: (i) highly wet husks were first kept in air for 3 days, and (ii) then husks were oven dried at 60 °C for 24 h.

2.3.3. Procedure for combined alkaline and silane treatments

A combination of alkaline and silane treatments was carried on. In this case before silane treatment, husks were treated by NaOH with a given concentration of 5% for 24 h. Table 2 lists all the treatments that were applied on husks in this study.

2.4. Methods for husks and biocomposites characterizations

2.4.1. Microscopic observations

The husks surfaces before and after treatment were observed by an environmental scanning electron microscope (ESEM) Quanta FEG 200, equipped with an OXFORD Inca 350 energy dispersive X-ray microanalysis (EDX) system. The ESEM operated at an accelerating voltage of 15 kV.

Table 2

Nomenclature used for untreated and treated husks.

Concentration of NaOH (%)	APS	GPS	Abbreviations for Einkorn wheat husk (W) and long-grain rice husk (R)	
0	No	No	W	R
2	No	No	WN2	RN2
5	No	No	WN5	RN5
10	No	No	WN10	RN10
0	Yes	No	WA	RA
5	Yes	No	WNA	RNA
0	No	Yes	WG	RG
5	No	Yes	WNG	RNG

2.4.2. Determination of husks composition

The method to analyze the husk composition was adopted from the work of Bledzki et al. (2008). It can be divided into three steps that are the followings:

1st step: determination of the inorganic compound content (ash)

2 g of dried of husk were put in oven at 600 °C for 8 h and then cooled until room temperature. The weight of ash is w_1 (g), and the ratio of ash in husk was calculated by Eq. (2):

$$\text{Ash (A)(\%)} = \frac{w_1}{2} \times 100 \quad (2)$$

The ash elements composition was determined by ESEM-EDX.

2nd step: determination of the extractable content

5 g of dried husk were introduced in an extraction thimble and then in a Soxhlet extraction unit. A mixture of ethanol and toluene (50/50 v/v) was used as solvent and extraction process continued for 18 h. Then, ethanol/toluene was changed to ethanol 99% and the extraction process continued for 6 h. After extraction, the sample was dried up to constant weight (w_2) at 100 °C. The extractive was calculated by Eq. (3):

$$\text{Extractive (E)(\%)} = \frac{5 - w_2}{5} \times 100 \quad (3)$$

3rd step: determination of lignin and holocellulose contents.

1.5 g of the previously extracted sample was put in a flask with 125 ml of de-ionized water. 1 ml of glacial acetic acid and 1 g of sodium chlorite were added successively. The flask was put in a water bath and heated up to 70 °C for 2 h and 1 ml glacial acetic acid and 1 g of sodium chlorite were introduced. This last addition of acetic acid and sodium chlorite was repeated several times. Finally, the holocellulose was filtered, washed and dried in an oven up to constant weight at 100 °C. The whole process should ideally be repeated until the husk turn white in colour and the weight does not decrease further. The weight of sample at the end of process (w_3) is the weight of holocellulose.

The ratio of lignin in the husk was calculated by Eq. (4):

$$\text{Lignin (L)(\%)} = \frac{(1.5 - w_3)(1 - E)}{1.5} \times 100 - A \quad (4)$$

where A is the ratio of ash in husk calculated by Eq. (2); E is the ratio of wax in husk calculated by Eq. (3).

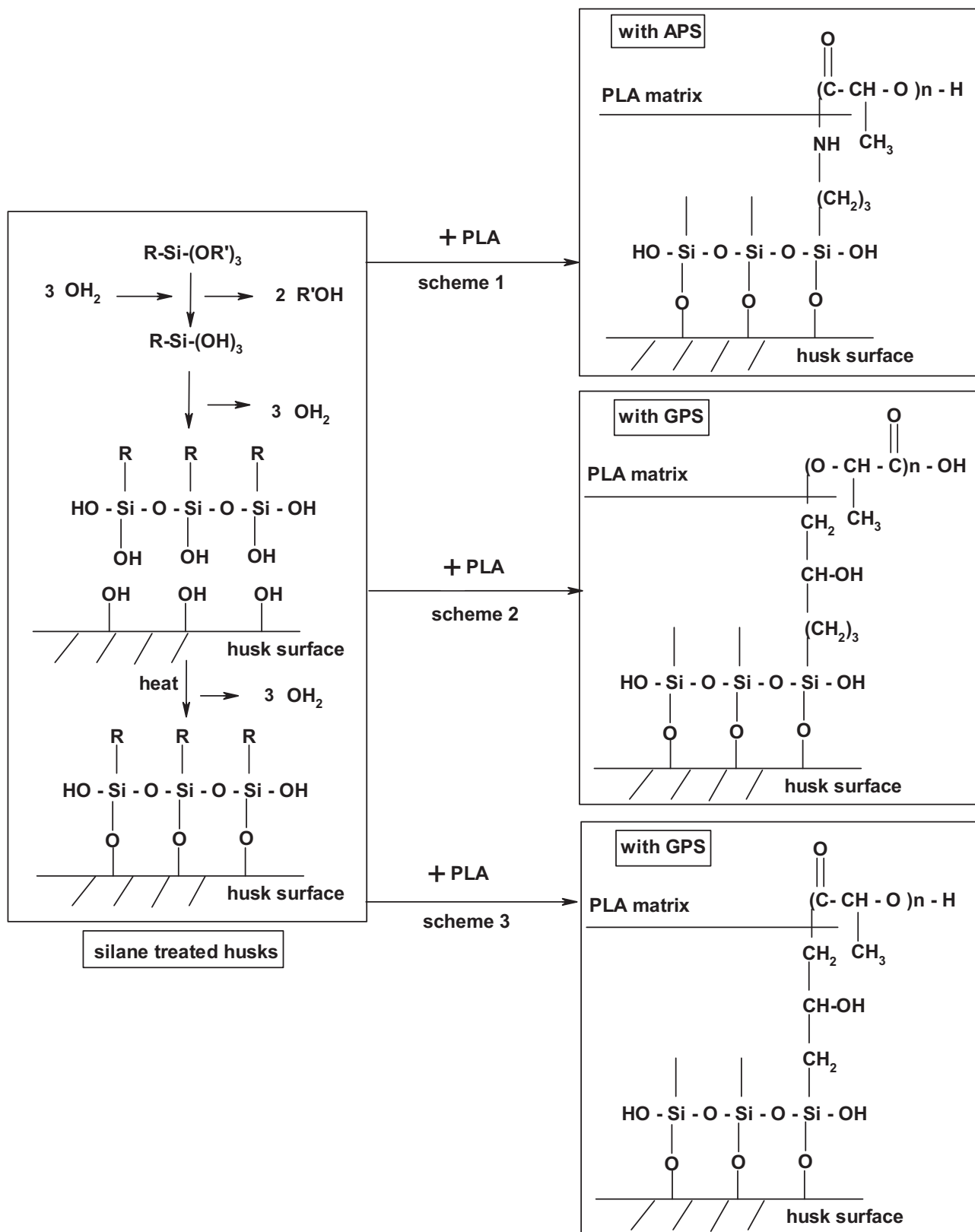


Fig. 1. Chemical mechanisms at the interfacial area between silane (Scheme 1: APS and Schemes 2 and 3: GPS) treated natural fibres and PLA matrix.

The ratio of holocellulose in the husk was calculated by Eq. (5)

$$\text{Holocellulose } (H)(\%) = \frac{(w3)(1-E)}{1.5} \times 100 \quad (5)$$

2.4.3. Surface energy

Contact angles of husks were performed using Digidrop apparatus (GBX Instruments) with an automatic system for the liquid droplet formation. Husks were considered as solids. About 300 mg of husk were compressed under a force 10kN during 5 min to

product a pellet sample with the diameter 13 mm. The wetting liquids used was diiodomethane, formamide and water. For each liquid three measurements were performed. In order to determine the polar and the dispersive components of the surface free energy the approach proposed by Owens et al. and Wendt (1969) has been used (Eq. (6)):

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p} \quad (6)$$

where the subscripts *L* and *S* are related respectively to the liquid and the solid states, and *d* and *p* to the dispersive and polar characters.

2.4.4. Moisture absorption

3 g dried husks were stored at 20 °C 65% RH until the weight was stabilized (w4). The moisture absorption (MA) of husk was calculated by Eq. (7):

$$MA = \frac{w4 - 3}{3} \times 100(\%) \quad (7)$$

2.4.5. FTIR measurements

FTIR was used to determine changes in chemical functional groups of R and W before and after treatment. R and W were grinded to dust and then were mixed with KBr to make a pellet sample concentration in KBr (3 wt.%). Each spectrum was recorded in the MIR range with a Bruker IFS 66 device, at a resolution of 4 cm⁻¹, the scan ranging from 4000 to 500 cm⁻¹ and a total of 32 scans were averaged.

2.4.6. Mechanical properties of composites

Mechanical properties of composites were measured by a Zwick 2010. The samples were stored at room temperature under standard atmospheric conditions (22–24 °C) for 24 h before testing. At least 5 specimens were used for each test to ensure the reproducibility.

Strength tests were measured according to the ISO 572-1 standard (load cell: 2.5 kN; crosshead speed: 50 mm/min for break properties, 1 mm/min for tensile modulus). The specimen had a dog-bone geometry with a 200 mm length and central dimensions of 10 × 4 mm² (Sample 1A according to ISO 527-2).

Three-point-bending tests were followed standard ISO 178:2001. Sample size was 80 × 10 × 4 mm³, load cell was 2.5 kN and the crosshead speed was 2 mm/min.

2.4.7. Thermogravimetric analysis (TGA) experiments

Thermogravimetric analyses were carried out using a Perkin Elmer equipment (Pyris1 TGA) to study the influence of husks surface treatments on the thermal stability of husks themselves and of PLA/husks biocomposites. The samples were scanned from 25 to 600 °C at a heating rate of 10 °C/min in the presence of nitrogen.

3. Results and discussion

3.1. Alkaline treatment of husks

3.1.1. Surface morphology of alkaline treated husks

Husks surfaces before alkaline treatment were observed by ESEM and discussed in a previous paper (Bergeret et al., 2013). It was observed that the outer surface of untreated rice husk was highly ridged and that the ridges included peaks and valleys interlay regularly (Fig. 2a). On the contrary the outer surface of untreated wheat husks was flat and presented tiny knots scattered (Fig. 2e). Further investigations through EDX measurements have showed the presence of silica. For rice husks, a silicon–cellulose membrane is present at the outer surface and formed a natural protective layer against termites and other micro-organisms that may attack on the

paddy (Ndazi et al., 2007). As concerns wheat husks, it was not observed any silicon–cellulose membrane on the outer surface but white knots containing silica near the outer surface were presented.

After NaOH treatment, the surface morphology of both husks is modified. As concerns rice husks, some small holes appear on the outer surface (for a NaOH concentration of 2%) (Fig. 2b). There are more holes and these holes are larger for a NaOH concentration of 5% (Fig. 2c). When using a 10% NaOH solution, rice husks are destroyed (Fig. 2d) and the surfaces has a lot of large holes and breaks. With a NaOH concentration of 2%, the surface of wheat husk appears many little gutter parallel, the knot change to white colour (Fig. 2f). It may be predicted that wheat husk have a very thin film of lignin covering the surface, and this film was dissolved easily by NaOH at low concentrations. When the NaOH concentration increased (5 and 10%), the white knots on the wheat husks surface were smaller and some of them disappeared (Fig. 2g and h).

Therefore, it can be concluded from ESEM observations that NaOH treatment leads to an increase in the surface roughness of the husks that is induced by a partial dissolution of some components of husks and this dissolution seems to be more and more important when the concentration of the NaOH solution increases. Ndazi et al. (2007) also observed that the roughness of outer and inner surfaces of rice husks did not change significantly after an alkaline treatment (2% NaOH), and that changes started to be substantial wearing of asperities on the outer surface and particle cracking only after treated with a NaOH solution at a 4 and 8% concentration. Further investigations will determine the global weight loss of alkaline treated husks and the nature of the dissolved fractions.

3.1.2. Global weight loss of husks after alkaline treatments

Natural fibres are mainly composed of cellulose, hemicellulose, lignin and wax. Hemicellulose corresponds to several sugar molecules which are soluble in water or alkaline solutions. The structure of lignin is similar to that of unsaturated aromatic polymers and it may be soluble in an alkaline solution (Nguyen Tri Phuong et al., 2010). Therefore hemicellulose and lignin may partially dissolve during an alkaline treatment, leading to a decrease in husks weights. Fig. 3a shows the influence of alkaline concentration on rice and wheat husks weight loss after treatment duration of 24 h at room temperature. Results show that the greater the alkaline concentration, the higher the weight loss and that the alkaline concentration have more influence on wheat than on rice husk. It is worthy to note that the weight loss of wheat husk is higher than that of rice husk at 5 and 10% NaOH concentration. Fig. 3b shows the influence of alkaline treatment time on the weight loss of husks for a given NaOH concentration (5%). It was found that the weight loss increases significantly during the first 18 h of treatment, and then the change in weight loss was not significant. This results are agreement with the results of Sun et al. (1995), that showed that wheat straw weight loss is about 40% for an alkaline treatment at a NaOH concentration of 1.5% at 20 °C for about 18–24 h, and then, the weight of wheat straw did not change. Nguyen Tri Phuong et al. (2010) found also that weight percent loss of bamboo fibres treated by a 0.5 M alkaline solution increased significantly during the first 15 h and then began to stabilize after treatment. However, the maximum weight percent loss of bamboo fibres is only about 12%, nearly three times lower than that of rice husk, wheat husk and wheat straw. This result may be explained by the high cellulose content of bamboo fibres.

3.1.3. Chemical composition of husks after the alkaline treatment

Table 3 shows the repartition of inorganic compound, hemicellulose, lignin and wax within the different alkaline treated husks for 24 h. Before treatment, wheat and rice husks contain about 2% of waxes that help the husk to be waterproofed and protect the grains. After alkaline treatment, waxes are removed. Untreated rice husks

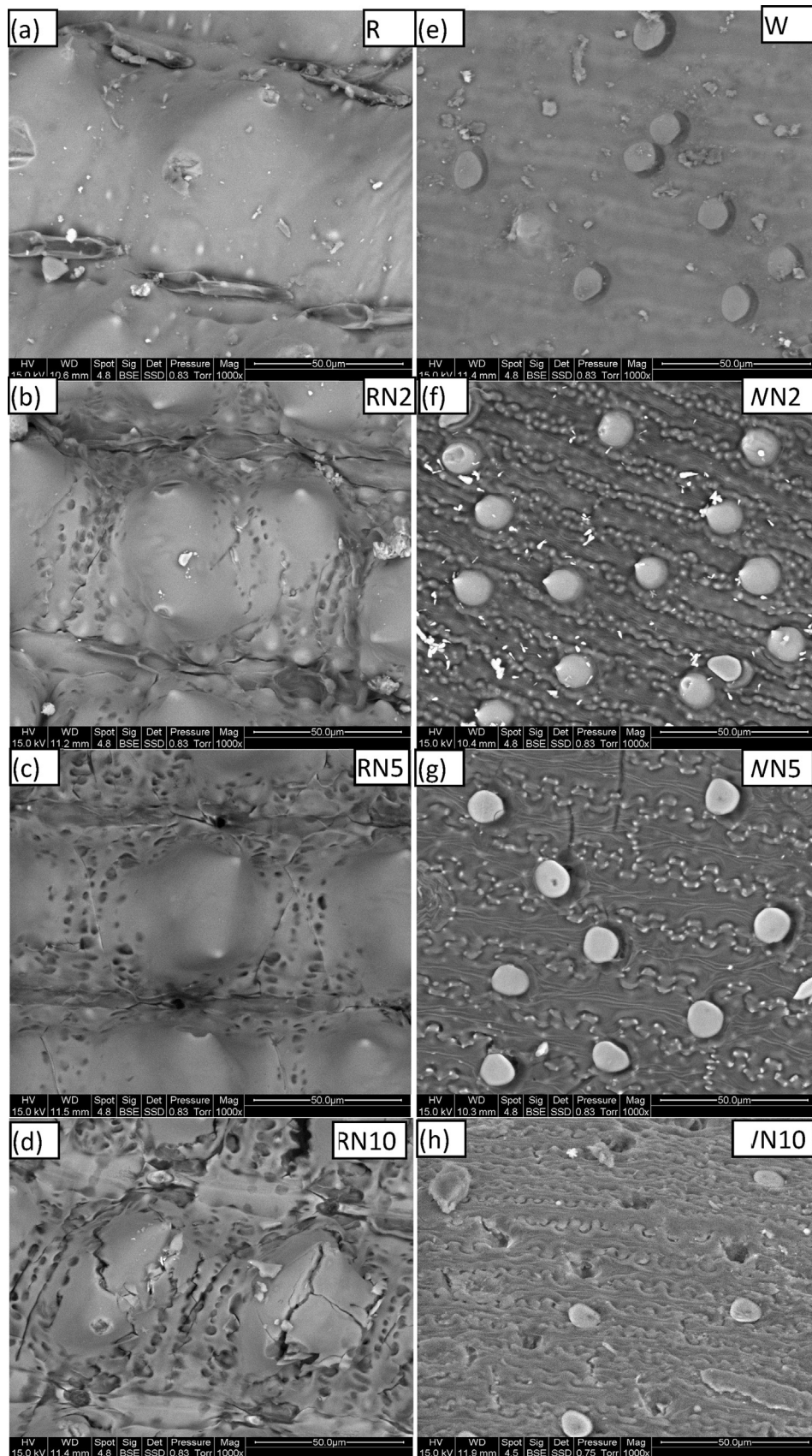


Fig. 2. Surfaces morphology of husks before and after treatment by NaOH: (a) untreated rice husk; (b)–(d) treated rice husk with NaOH concentration of 2%, 5% and 10%, respectively; (e) untreated wheat husk; (f)–(h) treated wheat husk with NaOH concentration of 2%, 5% and 10%, respectively.

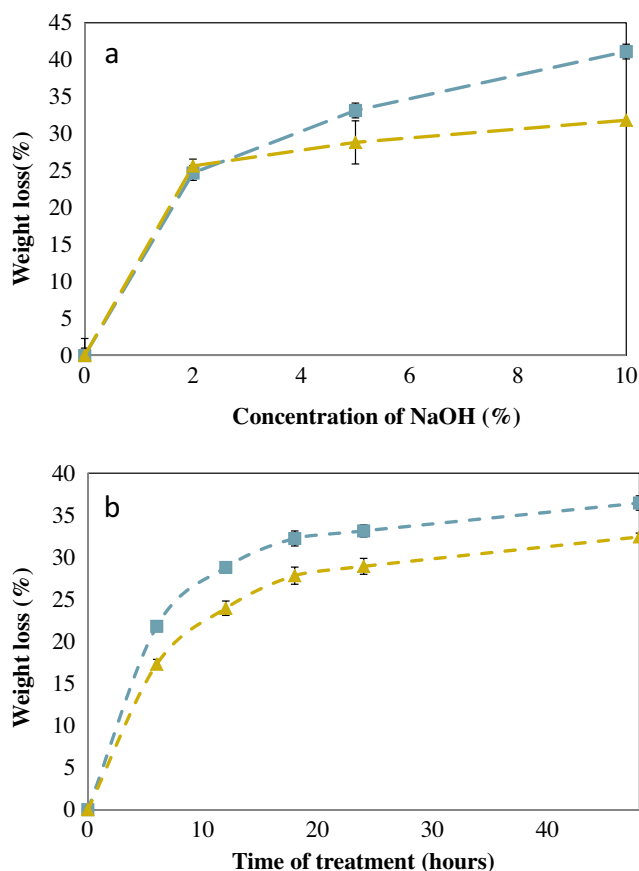


Fig. 3. Weight loss of Einkorn wheat and rice husks as a function of the alkaline treatment conditions: (a) influence of the alkaline concentration for a 24 h treatment and of (b) the treatment time with an alkaline concentration of 5%.

Table 3
Husks compositions (%) as a function of the NaOH concentration for an alkaline treatment duration of 24 h.

Husk composition	R	RN2	RN5	RN10
Wax	2.2 ± 0.9	0.8 ± 0.4	0.7 ± 0.6	0.5 ± 0.4
Lignin	37.1 ± 2.7	38.2 ± 1.4	39.9 ± 0.4	27.4 ± 1.3
Holocellulose	46.3 ± 1.4	49.8 ± 0.8	52.0 ± 0.2	65.1 ± 0.6
Inorganic (ash)	14.3 ± 0.2	11.2 ± 0.2	7.5 ± 0.1	6.9 ± 0.0

Husk composition	W	WN2	WN5	WN10
Wax	2.0 ± 0.0	0.8 ± 0.7	1.3 ± 1.2	1.2 ± 1.1
Lignin	28.3 ± 0.8	22.9 ± 0.9	17.8 ± 0.9	16.2 ± 1.3
Holocellulose	63.0 ± 1.0	72.0 ± 0.5	76.5 ± 0.6	78.2 ± 0.6
Inorganic (ash)	6.7 ± 1.4	4.3 ± 0.1	4.5 ± 0.2	4.4 ± 0.0

contain about 46% of holocellulose that is much lower than that of untreated wheat husks (about 63%). After alkaline treatment, this amount is increased. The increase in the holocellulose content of RN10 is about 19% compared to R and those of WN10 is about 15% compared to W. As concerns lignin and inorganic components such as silica, a decrease is observed. According to literature it can be assumed that silica in raw rice husks is bonded to organic material (Huda et al., 2006), so that when the lignin was dissolved, silica was removed also.

The ash content of rice husk decreased a half from $14.3 \pm 0.2\%$ to $7.5 \pm 0.1\%$ for RN5, and then it decreased slightly for RN10. The NaOH concentrations do not have much influence on the ash content of wheat husk. This results reveal that the alkaline solution dissolve more inorganic components of rice husk than of wheat husk.

Table 4
Atomic composition of husk ashes (%).

Element	R	RN2	RN5	RN10
Carbon (C)	3.44 ± 0.37	3.92 ± 0.58	3.75 ± 1.46	3.15 ± 0.22
Oxygen (O)	52.75 ± 0.01	51.94 ± 0.42	51.34 ± 0.17	51.57 ± 0.32
Sodium (Na)	0.38 ± 0.26	2.77 ± 0.06	3.82 ± 0.25	4.10 ± 0.04
Silicon (Si)	37.47 ± 0.84	32.68 ± 0.03	31.00 ± 1.10	31.63 ± 0.62
Calcium (Ca)	1.79 ± 0.14	6.42 ± 0.09	7.83 ± 0.06	7.58 ± 0.43

Element	W	WN2	WN5	WN10
Carbon (C)	3.96 ± 0.24	4.40 ± 0.24	4.77 ± 0.02	5.24 ± 0.26
Oxygen (O)	52.38 ± 0.01	48.40 ± 0.02	49.05 ± 0.21	49.02 ± 0.02
Sodium (Na)	0.00	9.64 ± 0.36	9.23 ± 0.18	18.42 ± 0.08
Silicon (Si)	35.77 ± 0.75	28.20 ± 0.41	27.38 ± 0.33	17.22 ± 0.28
Calcium (Ca)	2.31 ± 0.04	6.17 ± 0.28	6.72 ± 0.15	7.60 ± 0.15

The ash of husks consists in inorganic components, which are not degradable at 600 °C for 18 h. The atomic compositions of ashes are listed in Table 4. High amounts of silicon (35–38%) in ashes were found whatever the untreated husk considered. This amount is reduced with the increase of NaOH concentration (about –16% for rice husk and –52% for wheat husk for a NaOH concentration of 10%). These differences could be explained by the previously description of the husk surface morphology after alkaline treatment (Fig. 2). Indeed for rice husks, the surfaces have a lot of large holes however the silicon–cellulose membrane still exists. On the opposite, the wheat husks surfaces have tiny holes that replaced white knots of silica.

As concerns the other atoms it can be observed no significant variations in carbon and oxygen whatever the NaOH concentration and husk nature. A slight increase in sodium and calcium quantity after alkaline treatment is observed. It is well known that alkaline treatment have an effect on the cellulose structure, the crystallinity and the polymorphic transformation (from cellulose type I to cellulose type II) (Oh et al., 2005a,b). During an alkaline treatment process, sodium goes deeply into the structure of cellulose. It can be assumed that the washing process only removes sodium on the husk surface, and not sodium deep inside the structure of the husk. It causes the increase of sodium quantity in husk ash after any alkaline treatment. Absorption of calcium from carbonates of water can also be supposed. Wheat husk always absorbs more sodium and in mean proportion calcium than rice husk, may be due to the content of holocellulose of wheat husk which is always higher than those of rice husk.

3.1.4. FTIR analysis of alkaline treated husks

3.1.4.1. Comparison of untreated wheat and rice husks. The various chemical constituents present in untreated and alkali treated rice husk and Einkorn wheat husk were analyzed by FTIR (Fig. 4). It can be observed that rice husk (R spectrum) and wheat husk (W spectrum) have similar FTIR spectra because of equivalent chemical composition. The hydrophilic tendency of both R and W husks was reflected in the broad absorption band ($3100\text{--}3700\text{ cm}^{-1}$), which was ascribed to the strong hydrogen-bonded OH stretching present in aliphatic or aromatic alcohols and present in their main components. The two peaks at about 2920 cm^{-1} are due to the C–H stretching from aliphatic saturated compounds, i.e. aliphatic moieties in cellulose and hemicellulose. The shoulder peak at about 1735 cm^{-1} is assigned to the stretching vibrations of the C=O function of the acetyl and ester group of hemicellulose or waxes and natural fatty components (Seki, 2009). The peak at about 1650 cm^{-1} is assigned to H–O–H bending of absorbed water (Sun et al., 1995). The most characteristic infrared bands of lignin are found at about 1510 cm^{-1} representing the C=C aromatic skeletal vibrations (Abdelmouleh et al., 2007; Shih et al., 2010; Valadez-Gonzalez et al., 1999a,b). The bands in the

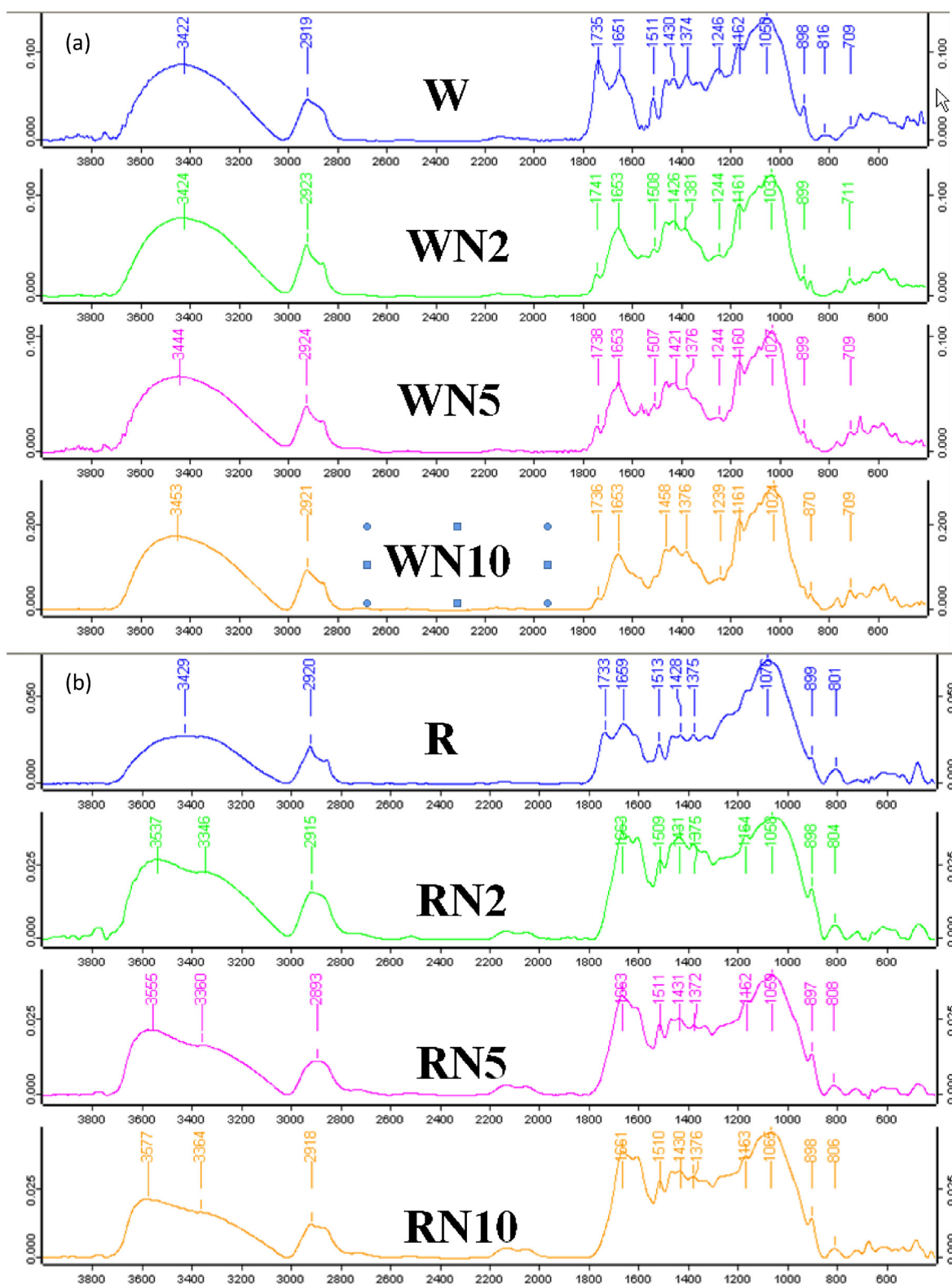


Fig. 4. FTIR spectra of untreated and alkaline treated wheat husk (a) and rice husk (b) at different NaOH concentrations (2, 5 and 10%).

range of $1430\text{--}1460\text{ cm}^{-1}$ were distributed to C–H deformation (asymmetric) and aromatic skeletal vibration (Sun et al., 1995) and the bands in the range of $1375\text{--}1350\text{ cm}^{-1}$ were assigned to the symmetric and asymmetric C–H deformations in methyl and phenolic alcohol or C–H rocking in alkanes (Bledzki et al., 2012, 2014). The peak at about 1245 cm^{-1} is ascribed to C–O deformation in

secondary alcohol and aliphatic ether. The large band in the range $1160\text{--}900\text{ cm}^{-1}$ is attributed to asymmetric and symmetric Si–O–C and Si–O–Si stretching bonds corresponding to silica present in cereal husks used in this study. The absorbance bands at about 800 cm^{-1} are commonly ascribed to the stretching vibrations of the Si–C bonds.

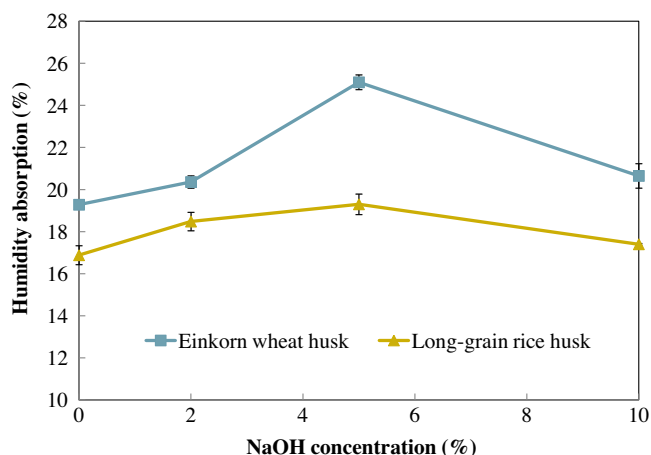


Fig. 5. Moisture absorption of wheat husk and rice husk as a function of the NaOH concentration.

3.1.4.2. Influence of the NaOH concentration. For wheat husk treated at different NaOH concentrations (WN2, WN5 and WN10), the large peak assigned to hydrogen-bonded OH stretching is shifted to higher wavenumbers (from 3420 for W to 3453 cm^{-1} for WN10) at higher NaOH concentrations as shown in Fig. 4a. For rice husk treated at different NaOH concentrations (RN2, RN5 and RN10), the shape this large peak is changed and two peaks located at around 3550 cm^{-1} and 3360 cm^{-1} can be distinguished. This difference may be due to different lignin contents between both husks. Moreover these two peaks are shifted towards higher wavenumbers when the NaOH concentration increased in relation with the variations in the lignin content (Table 3). (Oh et al., 2005a,b). For both rice and wheat husks, the absorption band at about 1735 cm^{-1} decreases after any alkaline treatment. This peak was corresponding to waxes and natural fatty components that are removed after the alkaline treatment as observed from chemical composition analyses (Table 3) (Ndazi et al., 2007). And the band about 1650 cm^{-1} assigned to H-O-H bending of absorbed water seems to grow up, which agreed with the increased moisture absorption of both rice and wheat husk after alkaline treatment (Fig. 4). The absorption band located at about 1510 cm^{-1} (C=C phenolic vibrations) and in the range 1160–900 cm^{-1} (Si–O–C and Si–O–Si stretching bands) decreases both with increased concentrations of NaOH for wheat husks, as they remain at the same wavelengths for rice husks. This result is in agreement with the lignin and silica content measurements (Table 4) that show a higher residual content of lignin and silica for rice husks than for wheat husk. The absorbance band at about 800 cm^{-1} ascribed to the Si–C stretching vibrations (Enescu et al., 2009) disappears after alkaline treatment for wheat husk. This is another evidence of the possibility for NaOH to react with silica on the surface wheat husk. On the contrary these peaks remains in the case of rice husks showing that the silica amount on the surface of rice husk is greater than that of wheat husk, so that, alkaline treatments cannot dissolve completely silica on the rice husk surface. These results are also in agreement with ESEM observations.

3.1.5. Moisture absorption of alkaline treated husks

Fig. 5 shows the influence of alkaline treatment on the moisture absorption of the husk.

Wheat husks have higher moisture absorption rate than rice husks. This can be explained by the higher holocellulose content of wheat husks compared to rice husks. Both husks reach to maximum absorption after treatment for a NaOH concentration of 5%. This evolution could be related to two consecutive phenomena occurring according to the alkaline concentration. For low NaOH

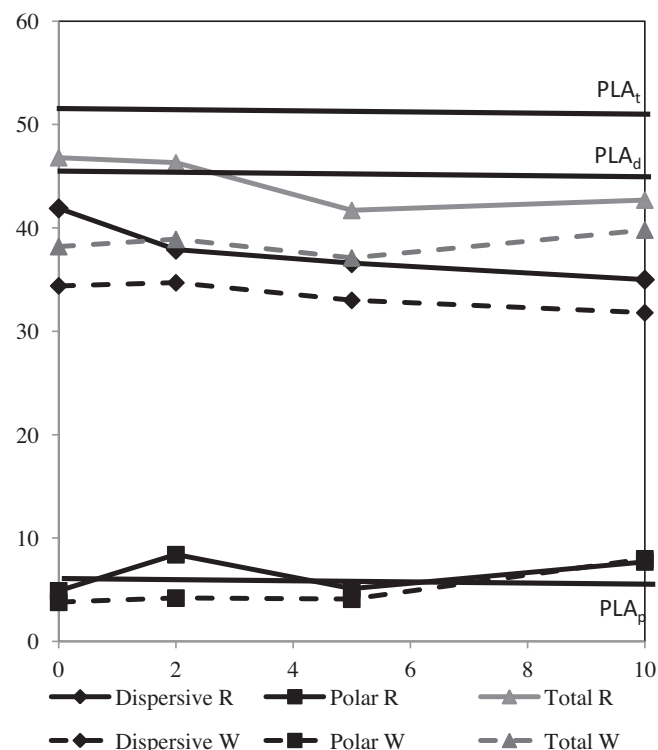


Fig. 6. Surface energy and its polar and dispersive components of rice and wheat husks as a function of the NaOH concentration.

concentrations, a partial removal of lignin and waxes may occur leading to an activation of hydroxyl surface groups and therefore an increase in the moisture absorption. For high NaOH concentrations, alkaline treatments may mainly modify the crystallinity and polymorphic transformation (from cellulose type I to cellulose type II) (Oh et al., 2005a,b) so that the husk surface is less polar and the moisture absorption rate slightly decreases.

3.1.6. Surface energy of alkaline treated husks

Fig. 6 shows the influence of different alkaline treatments on the dispersive and polar components of the surface energy of the husks in comparison to PLA. For PLA, polar and dispersive components are 5.7 and 45.1 mJ/m^2 , respectively. The corresponding values are 4.9 and 41.9 mJ/m^2 for untreated rice husk (R) and 3.8 and 34.4 mJ/m^2 for untreated wheat husk (W). As the polar and dispersive components of R are closer to those of PLA than those of W, it can be said that the R/PLA interfacial adhesion is better compared to W/PLA. Moreover as the difference between the surface free energy of the husks and of the PLA is greater for the W than for the R, it can be concluded that the wetting by PLA is better for W than for R. Nevertheless a previous study (Bergeret et al., 2013) has shown no significant difference in mechanical properties according to the husk nature when untreated.

It can be seen a reduction in the dispersive component of the surface energy of both husks when the NaOH concentration increased. Alkaline treatment seems to have more influence on the dispersive component of the rice husks (decrease by –16% between R and R20) than of the wheat husks (decrease by –7% between W and W20). For wheat husks an increase in the polar component is observed as a discontinuous evolution is obtained for rice husks. As a result an increase by 10% in the surface energy is revealed for wheat husks as no significant variation is given in evidence for rice husks.

It is well known that the dispersive component is related to the ability for creating Van der Waals interfacial interactions at the solid surface and the polar component to the ability for settling acid–base

interfacial interactions at the solid surface. Wax and lignin include hydrophobic and aromatic groups. As alkaline treatment removes wax and lignin, the number of hydroxyl groups may increase, leading to an increase in the polar component and a decrease in the dispersive component of the surface energy. [Gassan and Gutowski \(2000\)](#) observed also an increase in the polar components of jute fibres after corona and UV treatments.

3.1.7. Conclusion on alkaline treatments

This first part showed that after an alkaline treatment, some components of rice and wheat husks have been removed such as waxes, lignin and silica. On the opposite, an increase in the holocellulose content was observed. A global higher weight loss was obtained for wheat husk compared to rice husk with a quite stabilization for NaOH concentration over 5% and a treatment duration of 24 h (for a NaOH concentration of 5%). The increase in holocellulose content induced a greater water sensibility after alkaline treatment especially at low NaOH concentration with a maximum point for a NaOH concentration of 5%. The alkaline treatment resulted also in variations in the surface energy properties with a decrease in the dispersive component and an increase in the polar component leading to a global decrease in total surface energy so that an improvement of the wetting by PLA is expected. This evolution is more effective for rice husk.

3.2. Silane treatment of husks

As already shown, the major components of husks include cellulose, hemicellulose, lignin and wax. Cellulose is resistant to strong alkali but is easily hydrolyzed by acid. Hemicellulose is very hydrophilic, soluble in alkali and easily hydrolyzed in acids. Lignin is not hydrolyzed by acids, but soluble in hot alkali, readily oxidized and easily condensable with phenol ([John et al. and Thomas, 2008](#)). In the second step of this paper, the husks were treated by 1 wt.% of silane dissolved in a water/ethanol mixture (30/70 w/w). This solution cannot dissolve cellulose, hemicelluloses and lignin, may be only remove the waxes from the surface of the husk. Therefore the morphology of the husk surface and the chemical component of husks did not change after a silane treatment. So that, the results of this part are only focused on the modification of the husks surface energy of the moisture absorption and of the colour of the husks after silane treatments.

3.2.1. FTIR analysis of silane treated husks

FTIR spectra of APS and GPS are presented in [Fig. 7](#), both APS and GPS present three peaks at about 2975, 2945 and 2840 cm^{-1} that are corresponding to C–H symmetric and asymmetric stretching vibrations. The bands in the range 1000–1200 cm^{-1} (1167 and 1080 cm^{-1} for APS and 1194 and 1087 cm^{-1} for GPS) are clearly attributed to Si–O–Si vibrations. The peaks at 957 cm^{-1} for APS and 910 cm^{-1} for GPS are assigned to silanol groups produced in the silane hydrolysis ([Lu et al., 2008](#)). Finally the peaks at 790 cm^{-1} for APS and 822 cm^{-1} for GPS are related to stretching vibrations of the Si–C bonds ([Chun et al., 2012](#)).

The spectrum of APS presents also a small peak at 3377 cm^{-1} revealing a C–NH₂ bond according to [Threepopnatkul et al. \(2009\)](#). Weak bands at 1560 and 1443 cm^{-1} are typical of the amine group that are strongly hydrogen bonded to the hydroxyl groups of silanols in agreement with the study of [Lu et al. \(2008\)](#). Spectra of silane treated rice and wheat husks are presented in [Fig. 7b](#) and [c](#), respectively. As rice husk and wheat husk contain 14.5% and 6.6% respectively of silica ([Table 4](#)) it will hide bands assigned to the stretching of the Si–O–Cellulose bands demonstrating that a reaction occurred between silane agents and the husk surface. Moreover the bands related to both silanes overlap with those of

husks so that characteristic peaks of APS and GPS could not be detected by IR.

Wheat husk after silane treatment present a peak at 711 cm^{-1} for WA and WG and 708 cm^{-1} for WNA and WNG. This peak is also higher sharper for WNA and WNG, it reveals that pre-treatment by alkaline promote silanes react with the husks. The FTIR spectra of RNA and RNG presented small peaks at 667 and 668 cm^{-1} , these peaks could be assigned to Si–C stretching.

3.2.2. Moisture absorption of silane treated husks

The influence of surface treatments on the moisture absorption of husks is showed in [Fig. 8](#). In a previous paper on untreated husks ([Bergeret et al., 2013](#)) it was shown that the higher the lignin content the higher the hydrophobicity that explain the difference between untreated rice and wheat husks. When husks were treated by APS and GPS no change in the moisture absorption was observed for wheat husks as a slight decrease for rice husks. After an alkaline pre-treatment an increase in the moisture absorption was obtained. This moisture absorption decreased when husks are treated with silane agents. The silane treatments have more influence on wheat husk than on rice husk. The decrease of moisture absorption of husk after silane treatment may be explained by the chemical reaction in [Fig. 1](#). Indeed silanes react with the hydroxyl group on the glucose units of the cellulose molecules in the husks cell-wall, so that the ability absorption of husk is decreased. As wheat husk contain more holocellulose than rice husk, and as alkaline treatment removes more lignin and silica on the surface of wheat husk than rice husk. A greater number of hydroxyl groups are present on the wheat husk surface and then reaction the silanes are emphasized.

3.2.3. Surface energy of silane treated husks

[Fig. 9](#) shows the influence of silanes treatment on the polar and dispersive components of the surface energy of the husks. It can be observed that silane treatment increased the dispersive component (+31% for APS and +28% for GPS) of the surface energy of wheat husk. As concerns rice husk just a slight increase (+3%) is obtained for APS and a slight decrease (–4%) for GPS so that it can be concluded that both silanes have negligible influence on the dispersive component. Because of the low values of the polar components it is difficult to conclude about their variations. As a result, no variation in the surface energy is observed for rice husk as an increase is given in evidence for wheat husk (+27% for APS and +20% for GPS). The differences between rice and wheat husks may be due to a greater number of hydroxyl groups present on the wheat husk surface because of higher contents of lignin and silica removed from the surface after the alkaline pre-treatment. Differences between APS and GPS may be due to a more effective reactivity of APS towards cellulose than GPS.

3.3. Properties of biocomposites

3.3.1. Mechanical properties

[Table 5](#) shows the influence of different surface treatments on the mechanical properties of PLA reinforced by rice husks and Einkorn wheat husks.

The results show that the husks treated with only the NaOH aqueous solution does not improve the flexural and tensile strength (reduction by 50–60% and 35–40% for bending and tensile strengths, respectively). [Gomes et al. \(2007\)](#) reported also that the tensile strength of 10 wt% alkaline treated curaua fibres is much lower than that of untreated fibres. This lost in strength after an alkaline treatment may be due to a lower interfacial adhesion between PLA and alkaline treated husks that can be confirmed by the dispersive components of W5 and R5 that is less close from PLA than W and R ([Fig. 6](#)).

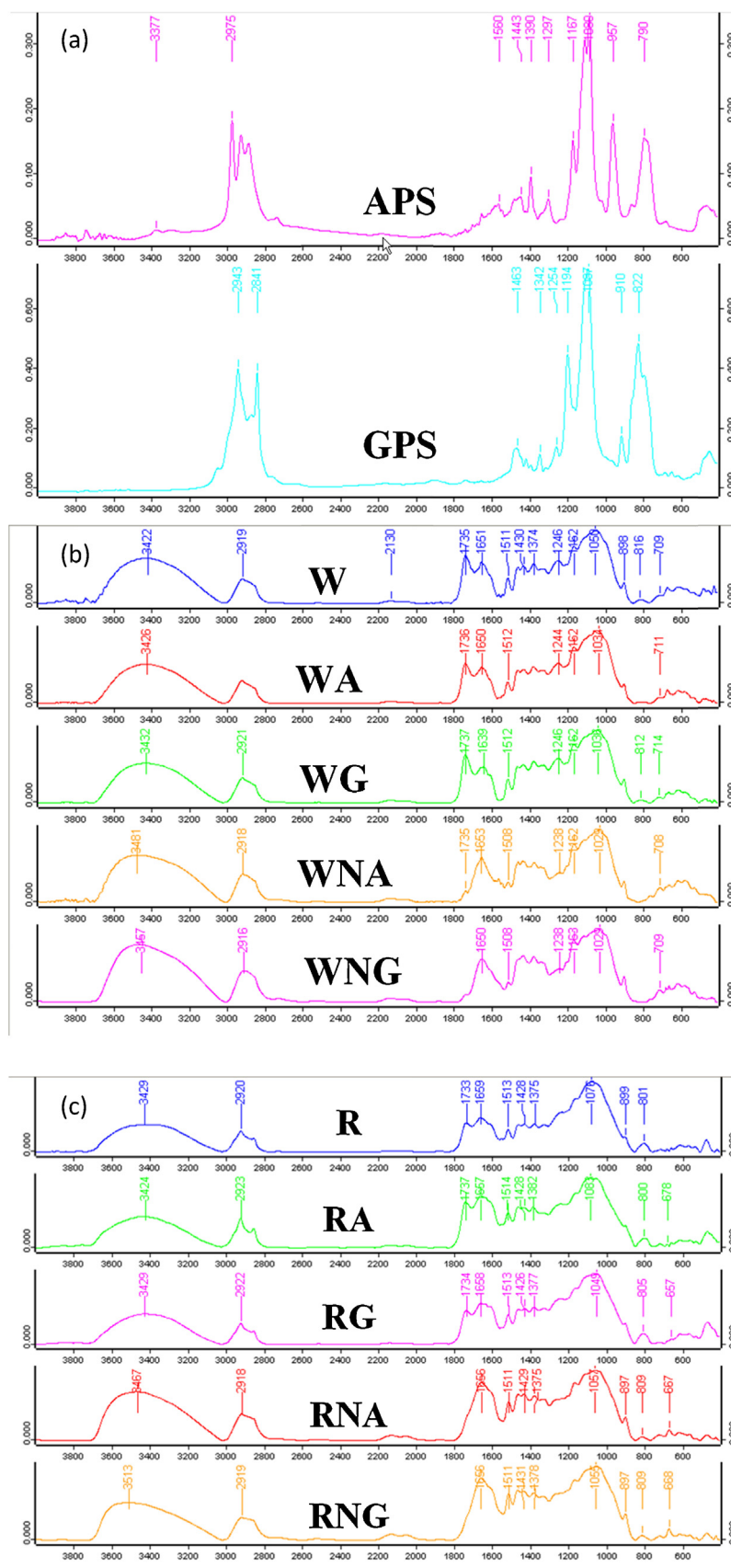


Fig. 7. FTIR spectra of pure APS and GPS (a), untreated and silane treated wheat husk (b) and rice husk (c).

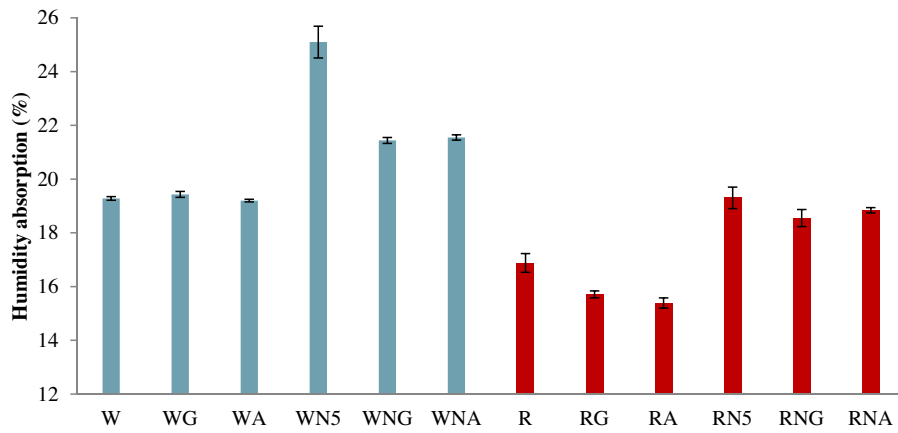


Fig. 8. Moisture absorption of silane treated husks (20 °C, 65% R.H).

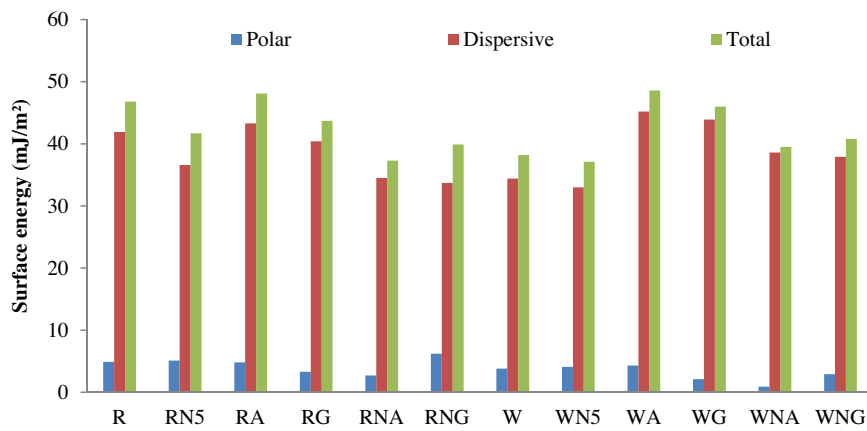


Fig. 9. Surface energy and its polar and dispersive components of rice and wheat husks as a function of the silane treatment.

Table 5
Comparison of the mechanical properties of PLA reinforced by different treated husks. Values are calculated in % compared to values obtained for untreated husks (+ = increase, – = decrease).

	Bending modulus		Bending strength		Tensile strength	
	Wheat husk	Rice husk	Wheat husk	Rice husk	Wheat husk	Rice husk
WN5/RN5	+6.4	+5.7	–58.4	–50.7	–36.0	–38.5
WA/RA	+7.5	–3.9	+8.4	+8.4	–1.6	–6.5
WNA/RNA	+8.0	–5.7	+20.1	+10.9	+9.7	+6.6
WG/RG	+8.0	–3.0	+11.0	+5.7	+1.8	–3.7
WNG/RNG	+7.7	–2.8	+17.8	+10.5	+5.8	+4.7

Higher bending strengths are obtained for husks treated with APS (+8.4% for both RA and WA husks) and GPS (+11% and +5.7% for WG and RG respectively) that confirms the occurring of interfacial reaction such as those described in Fig. 9. As wheat husks contain a higher quantity of holocellulose than rice husks, a greater surface reactivity with silanes may be in agreement with the higher increase obtained for wheat husks compared to rice husk. Opposite phenomena were observed by Huda et al. (2008). These authors obtained a decrease by 60% of the flexural strength of the PLA/kenaf fibres biocomposites with the addition 40 wt.% of kenaf fibres, but an increase by 50% when kenaf fibres are treated by APS. The bending modulus of biocomposites containing treated wheat husk increases by about 7–8%, while those of treated rice husk decrease by about 3–5% whatever the silane used.

It is worth noting that the combination of both alkaline and silane treatments gives the highest performances compared to individual treatments. It may be explained by the fact that, after the

alkaline treatment, the hydrogen bonding network within the cellulose structure may be broken and the hydroxyl groups of cellulose may become more active and therefore improve the hydrophilic of the husks as well as their compatibility with the silane agents.

3.3.2. Thermal properties of biocomposites

The thermal stability of neat PLA and PLA reinforced with untreated and treated husks was investigated by TGA. Results for rice husks and wheat husks are similar, so that only the results for rice husk are shown in Fig. 10. Thermal degradation of PLA involved a single step degradation mechanism occurring at 360 °C. Biocomposite with untreated rice husks shows a lower degradation temperature (340 °C) than PLA due to a decrease of average molecular weight of PLA when biocomposites are processed by extrusion as shown in a previous study (Bergeret et al., 2013).

Thermal degradation temperatures of the biocomposites reinforced by silane treated husks (RA, RG) and by alkaline then

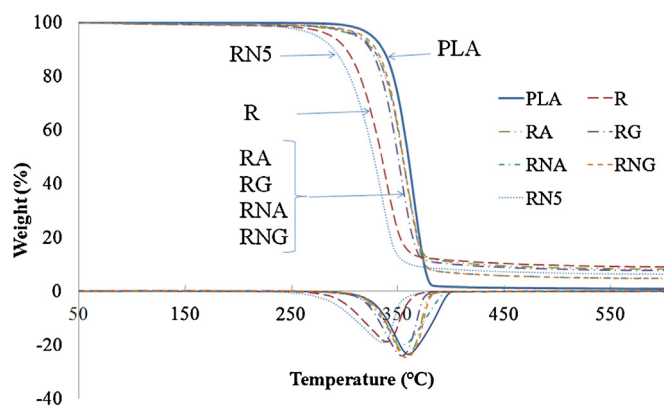


Fig. 10. Thermogravimetric curves of the neat PLA and biocomposites with untreated and treated rice husk.

silane treated husks (RNA, RNG) increase to about 354–357 °C. This temperature is only slightly lower than that of neat PLA, and significantly higher than that of the biocomposite with untreated husks. The chemical bond between PLA matrix and the husk could enhance the interfacial adhesion and the thermal degradation temperature increases consequently (Lee et al. and Wang, 2006; Yu et al., 2010). However, the thermal degradable temperature of the composites with alkaline treated rice husks (336 °C) is lower than that of the composites with silane treated husks. It may be indicated that the stability of the interface bond between alkaline treated husks and PLA is less effective than that of the interface bond between silane treated husks and PLA (Yu et al., 2010). This phenomenon is in agreement with the loss of mechanical properties of biocomposites in Section 3.3.1.

4. Conclusion

Different surface treatments including alkaline treatments with NaOH solutions at different concentrations and silane agents (γ -aminopropyltriethoxysilane (APS) and γ -glycidoxypolytrimethoxysilane (GPS)) on the characteristics of rice and wheat husks were investigated.

It is observed that alkaline treatments dissolved wax, lignin and silica. Husks after alkaline treatments have a higher sensitivity to moisture, and lower surface energies. Nevertheless alkaline treatments did not improve the mechanical properties of biocomposites.

When husks are treated with silane agents, results show a decrease in the moisture absorption compared to untreated and alkaline treated husks. An increase in the energy surface of husks and in the mechanical properties and the thermal stability of biocomposites were obtained. Better results were obtained with APS agent compared to GPS agent because of a higher reactivity, the group amine of APS shows more effect on PLA than group epoxy of GPS.

When silane treatments are combined with an alkaline pretreatment, biocomposites have higher mechanical properties and thermal stability than biocomposites with only silane treated. Alkali treatment cleans the surface of husk and active the hydroxyl groups. These active hydroxyl groups react with the silanes more easily than the hydroxyl group on the surface of untreated husks.

It is also given in evidence that wheat husks (with higher cellulose content) lead to better performances when they are incorporated within PLA than rice husks.

The future works may be focus on the influence of the treatment surface on the aged resistance of biocomposite.

Acknowledgement

The authors would like to thank the Vietnamese Government (Governmental project N.322) for financial support of this work.

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