

Effect of Reinforcing Fillers and Fibres Treatment on Morphological and Mechanical Properties of Typha-Phenolic Resin Composites

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Abstract: This study estimates the potential using of typha australis (*t. australis*) as reinforcing element in composite materials based on plant fibres as way of enhanced for this invasive plant. Composite materials based on *t. australis*, bamboo and rice husk fibres were prepared with phenolic resin and their properties compared in order to evaluate this invasive plant in relation to the commonly used fibres in composite materials. Scanning Electronic Microscopy shows similarity in the morphologic structure of *t. australis* and bamboo fibres. The failure mode is typically the same for all composite materials when fibres or system undergo the same treatment. The 3-point bending tests exhibit mechanical characteristics in the same range for different composites materials, for example the Young modulus for *t. australis*, bamboo and rice husk composites without any modification are estimated at 1.92, 2.04 and 2.00 GPa respectively.

Keywords: *Typha australis*, Composites, Mechanical properties, Morphology, Water uptake

Introduction

Typha australis, one variety of *typha domingensis*, is an aquatic plant, that can reach 3 m in height [1-3]. It is considered a harmful plant [4] because it causes the disappearance of certain species of marine animals and the reduction of agricultural lands. Similarly, there has been an increase in granivorous birds in addition to damage to marine facilities due to the presence of *t. australis*. The proliferation of the *t. australis* on the Senegal river, is due to the construction of the hydroelectric dam of *Diama*, thus affecting the ecosystem on its valley and at the same time the socio-economic activities of the neighbouring populations have been affected too. This expansion of the plant, more than 50.000 ha on both sides of the river, is mainly from to the low fluctuation of the water and its salinity [5]. Thus, the two countries (Senegal and Mauritania) across the river are themselves confronted with an ecological degradation.

The commonly valorization or uses of *t. australis* plants is to transform them into coal for heating and cooking [6,7]. The *t. australis* was not fully studied although there has been few works related the use of its fibres to treat water for removing heavy metal ions from aquatic ecosystems [8,9].

Use of eco-friendly composite materials gains attraction due to its lightweight and moderate strength in the recent years essentially by the low density of the natural fibres compared to the synthetic fibres (glass fibres, carbon fibres, etc...). The composite materials can be regarded as a useful lightweight engineering material [10,11]. Several works indicate how to achieve lightweight and moderate strength [12-17]. The most important thing is to combine great

functionality in addition to the lightweight and the moderate strength. There has been much research like fireproofing materials for building [18,19], for automotive [20,21] and for chemicals [22-24] industries performed in this field.

Phenolic resin composites materials reinforced with natural fibres were fully studied in the last decade and this research provided many results on mechanical and absorption properties [15,25,26]. The phenolic resins are frequently used as commodity and engineered materials in the high technology transportation industry. In fact, phenolic resins have several desirable characteristics, such as great heat-resistant, mechanical strength, and dimensional stability, as well as high chemical resistance against various solvents, acids and water. They resist on flammability and are inherently evolve low smoke upon incineration, which make them a good candidate for lightweight and strength materials combined with a great functionality [27-29].

The SEM micrographs (Figure 1) of *t. australis* and bamboo fibres show similarity in their morphology; both are hallowing like tubes with longitudinal features. *T. australis* fibres present at the external surface some cavity compared to smoother bamboo. Furthermore, bamboo is one of the best natural fibres compared to others such as sisal, jute or ramie [15,26,30-32], used to reinforce materials. They provide good mechanical properties; accordingly, it is a great interest in this work to pay attention on this kind of properties.

In this study, the main objective is to produce wood plastic composite materials based on *t. australis* fibres and phenolic resin for their valorisation in various fields. To this end, we focused on morphological and mechanical properties when reinforcing fillers were added or fibres were treated. Additional components were used in the composite formulation like limestone clay to prevent fire retardant, and Citric acid as

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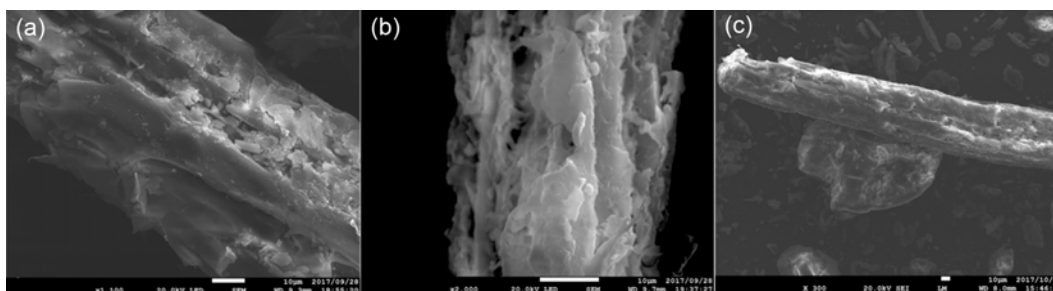


Figure 1. SEM micrographs of fibres; (a) *t. australis*, (b) bamboo, and (c) rice husks.

crosslinker [27,33,34]. The mechanical properties were investigated and compared to commonly use materials reinforced with bamboo fibres [32] or rice husk.

Experimental

Material

Fresh biomass of *t. australis* were collected from the Senegal river and dried in atmospheric air for two (2) weeks, chopped in small pieces and crushed in powder. Before use, the fibres with size smaller than 250 μm were dried again in the woven at 105 $^{\circ}\text{C}$ for 24 h. Bamboo fibres was obtained by partners and husk rice collected in a farm along the Senegal river. They were dried and crushed in powder like *t. australis* fibres. Citric acid is kindly supplied by Aldrich and the limestone clay is a gift from “SOCOCIM” (a Senegalese cement industry). All other chemicals in analytical grade were used as received.

Table 1. Composition of Phenolic composites based on fibres

Fibres variety	Sample	Fibres (%)	Phenolic resin (%)	Clay (%)	Citric acid (%)
Typhaaustralis	TPC400	40.0	60.0	0.0	0.0
	TPC410	39.8	59.7	0.5	0.0
	TPC411	39.6	59.4	1.0	0.0
	TPC412	38.0	57.0	5.0	0.0
	TPC420	39.8	59.7	0.0	0.5
	TPC421	39.6	59.4	0.0	1.0
	TPC441	39.2	59.4	1.0	1.0
Bamboo	BPC400	40.0	60.0	0.0	0.0
	BPC420	39.8	59.7	0.0	0.5
	BPC421	39.6	59.4	0.0	1.0
	BPC422	38.0	57.0	0.0	5.0
	BPC441	39.2	59.4	1.0	1.0
Rice husk	RPC400	40.0	60.0	0.0	0.0
	RPC411	39.6	59.4	1.0	0.0
	RPC412	38.0	57.0	5.0	0.0
	RPC441	39.2	59.4	1.0	1.0

Composites Manufacturing

Before composites manufacturing, phenolic resin, fibres and additives (limestone clay, citric acid) were mixed for 30 min in a Psl-1M ball mill device from Ito Seisakusho. Different composite materials were made by using a hot press machine model AS ONE. The blending powder, around 12 g, was put in floating die and placed between the plates of hot press. After 10 min, 20 MPa pressure was applied during 10 min, then take off for cooling and after sample can be removed to the mould. All composites samples were prepared in a fibre/matrix weight ratio equal to 0.667 or 40 % of fibres and presented in Table 1.

Characterization

A Rigaku diffractometer model Ultima IV was used for the X-ray analysis. All FTIR spectra were obtained by a Michelson Infrared Spectrophotometer equipped with dynamic alignment system from Shimadzu Corp (IRAffinity-1S model). The morphology of fibres and fractured composite materials was observed in a field emission scanning electron microscope JEOL JSM-7610F. For morphological experiments, samples were coated firstly with Gold (Au) for better image quality. The fractured surfaces were observed to reveal the fibres distribution in matrix, the interface between the two part of composites and the macroscopic feature of fracture initiation and propagation.

The three-point bending test were performed at room temperature with a Techno graph NMB TG-50 kN quipped with a TU3D-10 kN load cell model. The crosshead speed was fixed at 0.5 mm/min and the length (L) of the support span was 60 mm. All composite sample were tested three (3) times and the average are presented as the result. The flexural strength (σ_f), and the flexural modulus (E_f) were calculated using the following equation (1) and (2).

$$\sigma_f = \frac{3FL}{2we^2} \quad (1)$$

$$E_f = \frac{L^3 m}{4we^3} \quad (2)$$

F : load at fracture

L : support span length

w : width

e : thickness

m : gradient/slope of the initial straight line portion of load/deflection curve

The water absorption of composite material was performed by soaking samples in distilled water as following: (i) firstly, sample was weighed and recorded as the weight of non-swelling sample (M_0); (ii) secondly, the sample was immersed in distilled water, (iii) finally, the sample was removed from the solution, weighed again after wiping of the excess water and recorded as the weight of swelling sample at t time (M_t). Prior to soaking into water, samples were oven dried at 120 for 30 min then weighed. The swelling rate w_t (%) at t of different samples was calculated using the following

equation (3):

$$w_t(\%) = \frac{M_t - M_0}{M_0} \times 100 \quad (3)$$

Results and Discussion

X-ray and FTIR Analysis

The IR spectrum of *t. australis* is similar to what is usually observed on natural fibres like bamboo, wood, etc. Absorption bands of free hydroxyls (OH) groups and C-O elongation of ether from β -1,4 polysaccharide linkages are found respectively around 3500 and 1200 cm^{-1} . The band observed at 1500 cm^{-1} (Figure 2) is probably related to the presence of impurities because they do not correspond to any functional groups present in plant polysaccharides. The *t. australis* is an aquatic plant, the impurities in the proliferation medium can be embedded in its structure. However, an X-ray and SEM-EDS analysis of *t. australis* fibres (Figure 2) revealed the presence of atoms such as Potassium, Chlorine and Nickel, and Nitrogen in its structure. Consequently, this absorption band may correspond to C-N type bonds. These analysis shows also that fiber is composed in entirely by cellulose II with characteristics picks at 2θ on 18°, 20° and 22°; the maximum observed at 20°.

Morphology and Mechanical Properties

The fractured surface in Figure 3, showed a good dispersion of fibres into the matrix. In the micrograph of sample without clay content (TPC400), fibres pull out and

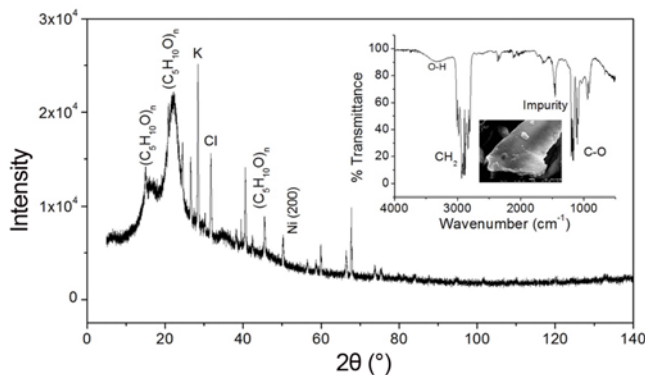


Figure 2. XRD of *t. australis* fibres (inside: FTIR spectra spectra and SEM-EDS micrograph).

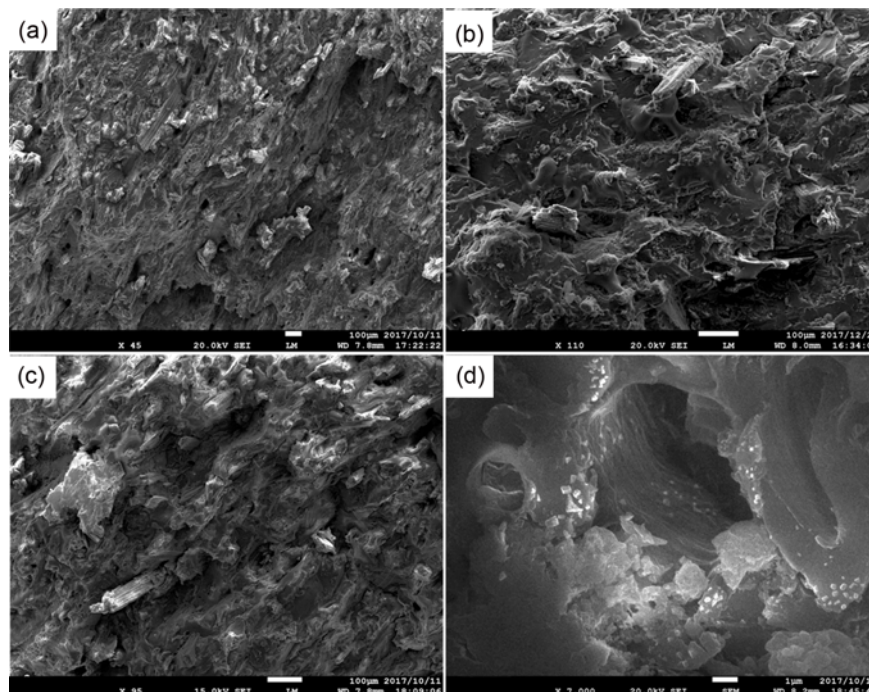


Figure 3. Micrographs SEM of composite materials (clay effect) at the fractured surfaces; (a) TPC400, (b) TPC411, and (c-d) TPC412.

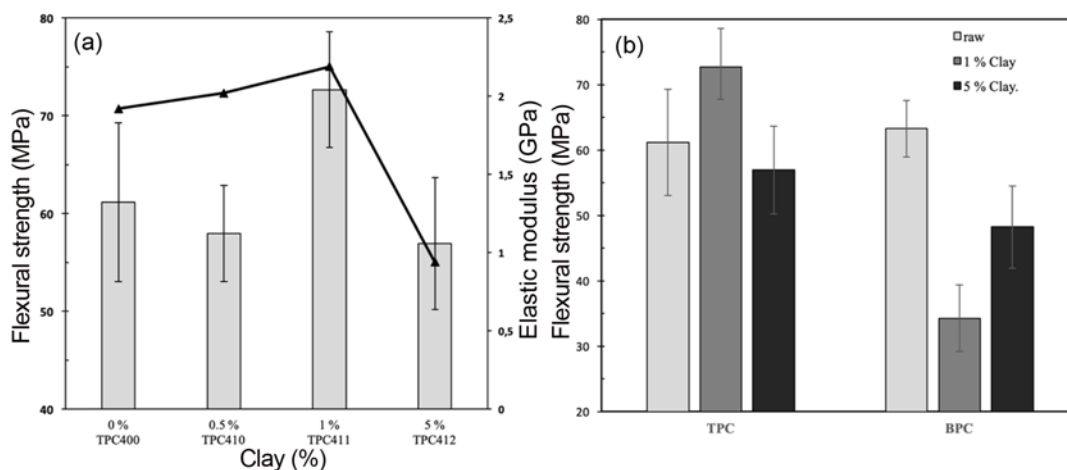


Figure 4. Evolution of flexural strength and elastic modulus on typha and rice husk composites with clay.

the fibres-matrix interface can be found distinctly. In the other micrographs, the clay hasn't impacted the dispersion of fibres at low clay (1%) content but at 5% fissure and void appear at the fractured surface Figure 3(c). The clay particles are found in the cavity at the fibres-matrix interface (Figure 3(d)) which reduces the wettability of polymer, consequently the flexural strength and the elastic modulus drop as shown in Figure 4.

Figure 4(a) showed an elastic modulus improvement when the clay content increase in typha-phenolic resin composites. Beyond 1% of clay, the depletion of elastic modulus can be associated to the augmentation of the number of cavities resulting from the propagation of fissure was easier. The fractured surface of rice-phenolic resin composites with clay presents the same damage but the mechanical result is different at 1% of filler. However, many factors can explain this phenomenon including the difference of the fiber nature, a lack of mixing when preparing rice sample. In any case, the rice composite materials with 1 and 5% of clay exhibits a 3-point bending results lower than compared composite materials with *t. australis* Figure 4(b).

Generally, the mechanical properties can be enhanced in composite materials when a crosslink between fibres and matrix was achieved. The characteristics of the of fibre-matrix interface on composite play an important role in its mechanical properties as the load transfer from the matrix to the fibres occurs through the interface and generally the fibres and matrix adhesion is so poor. The surface modification of natural fibres received vast research interest to solve these imperfections. Several treatments are suggested in the literature to modify the fibres surface and intensify the fibre-matrix adhesion. However, the modification must involve, at least partially, reagents obtained from renewable sources to not invalidate the use of vegetable fibres as reinforcement [31]. Therefore, according to Berglund [35], strong mechanical properties (Young's modulus, tensile strength, and heat

distortion temperature) in bio-composite were achieved at very low clay content. Because the combination of fine dispersion of individual clay silicate layers of high aspect ratio, preferred orientation of silicate layers and polymer molecules, as well as silicate layer effects on molecular mobility and morphology of the matrix. Usually, clay fillers were used to reduce the flammability of materials [23,36-41] and all improvement on mechanical properties by using clay are just beneficial.

For making a better fibres-matrix interface, the presence of polar hydroxyl groups in both the phenolic resin and in the main components of the lignocellulosic fibres was exploited by adding citric acid as coupling agent. The three functional carboxyl groups present in citric acid can make strong linkage with hydroxyl groups to favour the fibre-matrix adhesion. Natural fibres components are complex macromolecules similar to phenolic resin, that represents another possibility to improve the interaction between fiber and phenolic polymer matrix [31]. Nevertheless, the results presented in Figure 5 show a depletion of mechanical properties of bamboo-phenolic resin composites. Probably, citric acid increases the reticulation of polymer chains of resin and then the phenolic matrix becomes more brittle. Because there is competition between the hydroxyl groups; those from phenolic resins are more accessible thus more reactive than others from fibres. Consequently, the crosslinking reaction takes place between polymer chains and increases the reticulation of resin that becomes more brittle. In fact, when using citric acid for coupling agent, the best way should be treated fibres separately before preparing the material with phenolic matrix, if making linkage between fibres and coupling agent is needed.

The mechanical behaviour of *t. australis* materials was more affected by the presence of citric acid than bamboo composites. The *t. australis* materials lose on their flexural strength 53% and 47% compared to bamboo composites

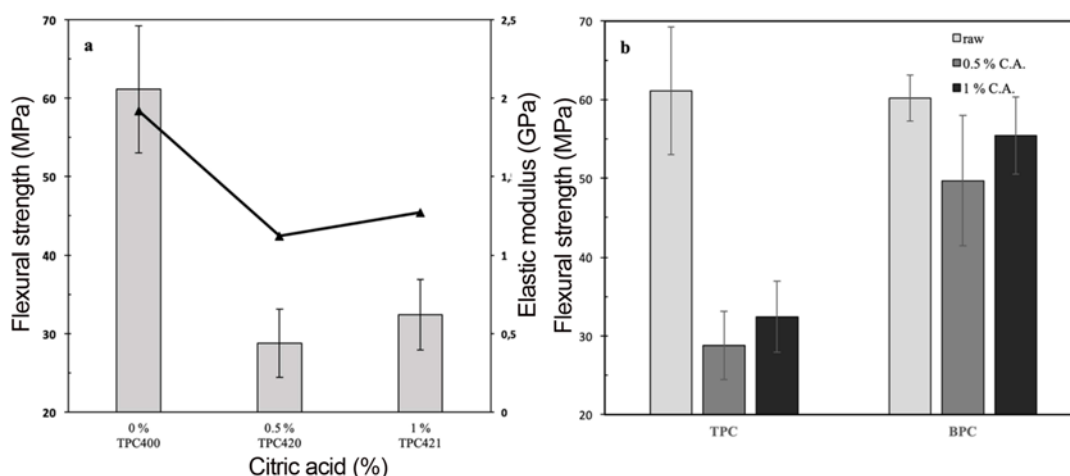


Figure 5. Evolution of flexural strength and elastic modulus of typha and bamboo composites with citric acid; (a) typha composites and (b) comparison flexural strength of typha and bamboo composites.

17 % and 8 % for 0.5 % and 1 % of citric acid respectively. Furthermore, from 0.5 % to 1 %, all composites gained around 12 % on their flexural strength.

The fracture behaviour investigated by scanning electron microscopy (SEM) (Figure 5), showed that many cracking in the bulk of matrix and extensive fiber pull-out mechanism was revealed at the tension side of phenolic resin composites reinforced by *t. australis* or bamboo. The failure mode of composite with citric acid compared to other materials was changed. In high percentage of citric acid (5 %), the SEM micrograph of Figure 5(c) shows more fissures on the matrix than fibres pull-out. The same effect was observed on typha-phenolic resin composites (TPC420-0.5 %) at the SEM micrograph Figure 5(d).

The combined effect of clay (1 % w) and citric acid (1 % w) decreases the flexural strength et the elastic modulus of typha phenolic resin composite. The results summarized in Table 2 exhibit for TPC400 and TPC441 a loss for around 56 % on flexural strength and 46 % on Young modulus. The expected increase by adding 1 %w of clay was probably cancelled out by the negative effect of citric acid by the same reason mentioned previously. All samples made with citric acid, lose their mechanical properties compared to referential materials (TPC400, BPC400 and RPC400). The bamboo composite (BPC441) and the rice husk composite (RPC441) with clay and citric acid present the same results as the typha's. All mechanicals characteristics by three-point bending tests are reported on Table 2.

Furthermore, Figure 6 exhibits four (4) different SEM micrographs at the fractured surfaces of composite materials with 1 % of clay and 1 % of citric acid (b, c and d). The combined effect of fillers is really harmful to all studied materials, intern cracks appear in the bulk material but focused on the polymer, fibres seem to stick well to the matrix. Generally, the mechanical properties of composite

Table 2. Mechanicals properties of phenolic composites by 3-point bending test

Fibres variety	Samples	Flexural strength (MPa)	Elastic modulus (GPa)
<i>T. australis</i>	TPC400	61.15±8.11	1.92±0.26
	TPC410	57.96±4.90	2.03±0.20
	TPC411	72.67±5.91	2.19±0.25
	TPC412	56.94±6.72	0.94±0.31
	TPC420	28.81±4.34	1.12±0.09
	TPC421	32.46±4.51	1.27±0.23
	TPC441	26.53±8.90	1.02±0.22
Bamboo	BPC400	60.21± 2.94	2.04±0.19
	BPC420	49.69±8.32	1.93±0.20
	BPC421	55.41±4.90	1.58±0.21
	BPC441	36.88±8.90	1.46±0.22
Rice husk	RPC400	63.26±4.34	2.00±0.12
	RPC411	34.25±1.09	1.34±0.19
	RPC412	48.24±6.28	2.01±0.26
	RPC441	30.00±8.90	1.19±0.22

materials are managed by the reinforcing elements but in the case of study, short natural fibres do not have significant strength for supporting the charge, they are governed or supported by the matrix. The SEM micrographs on Figure 7 confirm mechanical properties reported in Table 2.

Water Uptake

Clay Effect

The presence of clay under 1% (w/w) resulted a decrease in the swelling of *t. australis* composite materials samples (Figure 8(a)) and beyond that point an upward trend was

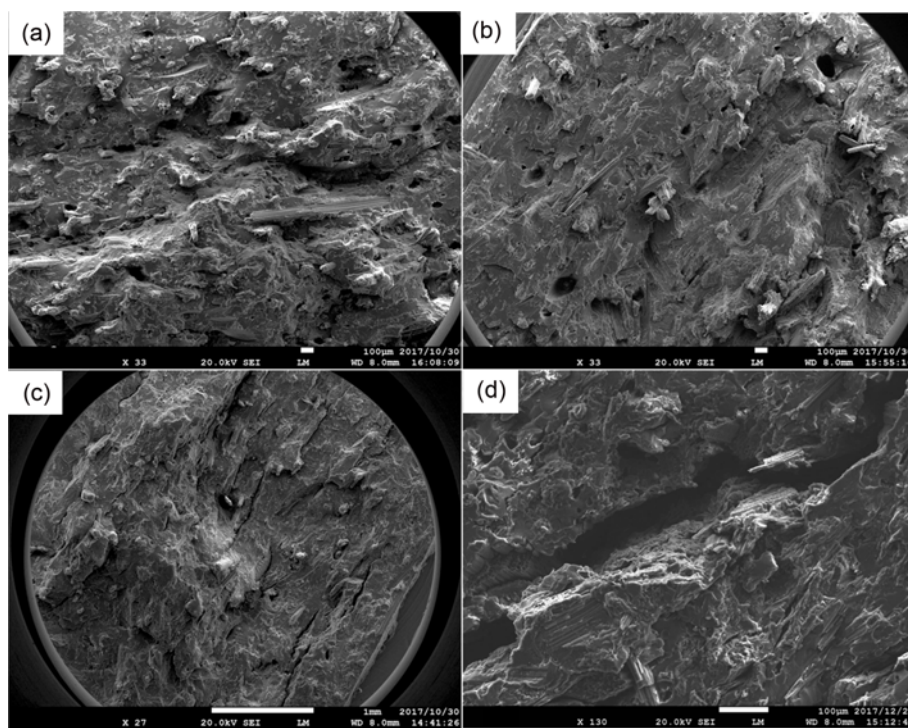


Figure 6. SEM Micrographs of composite materials (citric acid effect) at fractured surfaces; (a) BPC400, (b) BPC420, (c) BPC422, and (d) TPC420.

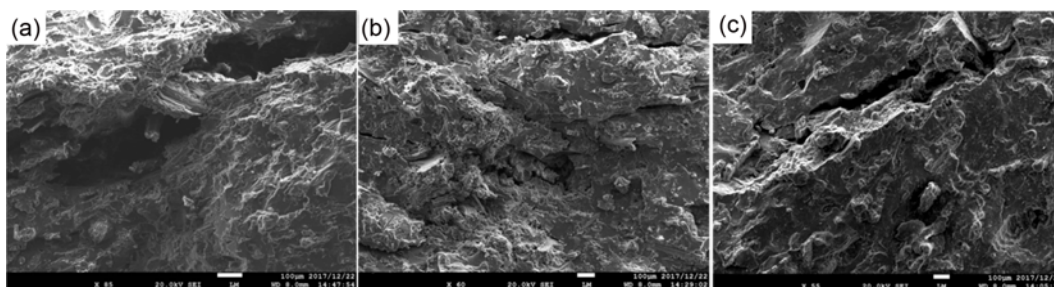


Figure 7. SEM micrographs of composite materials (combined effect of clay and citric acid) at the fractured surfaces; (a) TPC441, (b) BPC441, and (c) RPC441.

observed. The increase of water absorption with the clay percentage is probably due to the augmentation of cracks observed on Figure 3. Small quantity of clay gave better effect on absorption properties, same thing was found on mechanical properties when the material contains clay in small amount. The rice husk materials identical to those *t. australis* present a different behaviour, the water absorption increases with the augmentation of clay. In fact, increasing of water absorption has not a good effect on composite materials but the results given by absorption tests are very weak to affect the composite materials.

Citric Acid Effect

On typha composites, two effects were noticed (Figure 8(a)): at 0.5 % of CA, the water absorption increase strongly and at 1 % (CA) the amount of water absorbed is close to the

unmodified sample. The fractured surface of sample with 0.5 % of citric acid (Figure 5(d)) shows more cracks than 1 %, cause for which water absorption was more significant at 0.5 than 1 % and 5 %. The bamboo composites present different behaviour on water absorption compared to *t. australis* composite materials. At low citric acid content (0.5 %), composite samples absorbed small quantity and at 1 % of coupling agent an increase of swelling was observed. According to micrographs (b) and (c) of fractured surface (Figure 5), bamboo composite sample with 1 % of citric acid have more cavities and voids by fibres pull-out, reason why they soak up more water. Citric acid is more hydrophilic compare to limestone clay and according to Sung and Kim [42], hydrophilic filler increase the cavity and pores diameters and hydrophobic decrease it.

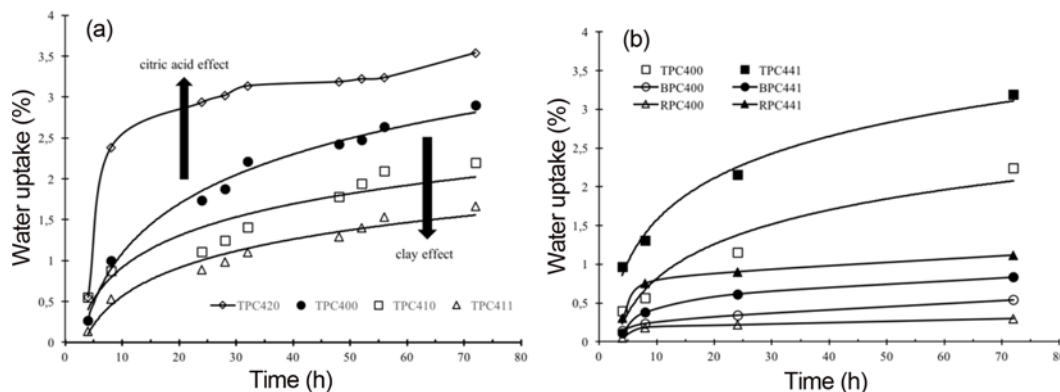


Figure 8. Water uptake of composite materials; (a) individual effect of clay and citric acid and (b) clay and citric acid combined effect.

Clay and Citric Acid Combined Effect

The combined effect of clay and citric acid increases the water absorption of all composite materials reinforced by *t. australis*, bamboo and rice husk (Figure 8(b)). The rice composite materials present the most important absorption (+350 %) compared to typha composites (+87 %) at the stabilization point (8 hours). However, the *t. australis* composites swell more among them. Water absorption of all composite materials is done fairly quickly in the first eight hours, beyond that point the swelling rate is relatively minor. The Figure 8(b) shows that unlike other composite materials, those reinforced by *t. australis* does not reach the saturation after 72 hours in distilled water.

Moreover, according to results presented in previous individual parts on clay and citric effects, the behaviour of composite materials in relation to water are opposed. The presence of clay at 1 % decreases their water uptake while citric acid at same condition increases it. The combined effect onto composite materials go to increase the water absorption, therefore the acid effect has a predominant impact on material than clay.

Conclusion

The *t. australis* fibres used as reinforced element in phenolic resin for making composite materials presents similar behaviour to bamboo and rice husk. According to the mechanical properties of their composite materials *t. australis* fibres can be used for composite materials as reinforcement. The absorption properties are affected when others elements (limestone clay, citric acid) were added but the variation is not really important to affect the mechanical properties. Small quantity of clay (lower than 1 % on weight) improve the flexural strength and the elastic modulus from 61.15 to 72.67 MPa and 1.98 to 2.19 GPa respectively. However, low quantity of citric acid decrease these mechanical properties to 28.81 MPa and 1.19 GPa. At quantity up to 0.5 % of citric acid, many cracks in the bulk material are observed at the fractured surface resulting that

phenolic resin become more brittle with the reagent.

Acknowledgments

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