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ORIGINAL RESEARCH

Effects of moist ageing on composites of bamboo fiber and montmorillonite/eggshell powder

Mouad Chakkour · Mohamed Ould Moussa · Ismail Khay · Mohamed Balli · Tarak Ben Zineb

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Abstract This paper investigates the effects of adding montmorillonite and eggshell particles on the mechanical, morphological and water absorption properties of bamboo fiber reinforced composites for filler contents ranging from 1wt% to 3wt%. The results show an improvement in the water absorption, the thickness swelling and the mechanical properties of composites with a maximum filler content of 3wt%. Herein, the water absorption was reduced by 37.8 ± 0.29% and 25.7 ± 0.28% the montmorillonite and eggshell powder filled composites, respectively. The thickness swelling was similarly decreased by 36.9 ± 1.3% and 27.8 ± 0.23%, respectively. Under ambient relative humidity, the tensile and bending strengths and modulus of 3wt% montmorillonite and eggshell particle filled composites were found to drastically increase. However, they were slightly enhanced under wet conditions. The swelling, porosity as well as the dispersion quality of particles were analyzed and seemed to reduce the mechanical properties.

M. Chakkour (✉) · M. Ould Moussa (✉) · I. Khay · M. Balli
AMEEC Team, Laboratory of Renewable Energies and Advanced Materials LERMA, College of Engineering and Architecture, International University of Rabat, Salé, Morocco
e-mail: mouad.chakkour@uir.ac.ma

T. Ben Zineb
Université de Lorraine, CNRS, Arts et Métiers ParisTech, LEM3, 54000 Nancy, France

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Introduction

Nowadays, the environmental issues related to the utilization of synthetic fibers (i.e., carbon, glass…) encourage research studies to focus on eco-friendly materials (Gholampour et al. 2020; Faruk et al. 2012). Indeed, lignocellulosic fiber reinforced polymer composites have attracted the attention of researchers due to their interesting mechanical properties (Vigneshwaran et al. 2020), low cost (Awais et al. 2021), partial biodegradability (Rajeshkumar et al. 2020) as well as low environmental impact (Gholampour et al. 2020). Plant fibers such as flax, jute, hemp, kenaf, sisal, banana and bamboo are widely used as reinforcement in polymer composites (Gholampour et al. 2020; Faruk et al. 2012; Bekraoui et al. 2022). Bamboo fibers are commonly considered as "natural glass fibers" because of the alignment of their nanofibrils (low microfibrillar angle) revealing an attractive specific tensile strength (127–1333 vs 480–600 MPa/g.cm^{-3}) and specific elastic modulus (10–53 vs 28 GPa/g.cm^{-3}) values compared to E-glass fibers (Chakkour et al. 2023b; Zakikhani et al. 2014).

However, the major drawbacks of using natural fiber composites remain the water absorption and the poor interfacial adherence due to the incompatibility between the hydrophilic fibers and polymers

(Ramesh et al. 2017; Vigneshwaran et al. 2020). Actually, water vapor molecules diffuse within the polymer matrix through open pores and react with its amine and hydroxyl groups (Chow 2007). They are then attracted by the OH groups of the cellulosic components of fibers leading to a microscopic swelling of the cell walls and the middle lamella (Garat et al. 2020). Afterwards, moisture molecules are accumulated within the lumens and the fiber-matrix interfaces which induces the swelling deformation of composites (Chakkour et al. 2023a). This results in the development of internal stresses and fiber-matrix debonding (Sanjeevi et al. 2021; Chakkour et al. 2023a).

Several attempts have recently been made to decrease the water absorption of plant fiber composites and enhance their interfacial bonding. Many studies showed that the chemical treatments (i.e., alkaline, acetic acid, silane treatments…) considerably reduce the hydroxyl groups of the cellulosic components, increase the roughness of fibers and enhance the fiber-matrix bonding leading to low moisture absorption capacity (Gholampour et al. 2020). However, few research works have investigated the modification of polymer matrices in natural fiber composites. Previous studies revealed that the incorporation of fillers such as Montmorillonite, $CaCO_3$, SiO_2, talc and carbon nanotubes drastically enhances the mechanical, thermal and physical properties of natural fiber/polymer composites as well as their dimensional stability (Chakkour et al. 2023b; Ganesan et al. 2021; Srivabut et al. 2018; Chee et al. 2020). Alamri et al. (2013) reported that adding 1 wt. % of nano clay improves the flexural properties of recycled cellulose hybrid composites. Indeed, it was expected to enhance the fiber-matrix adhesion due to the uniform dispersion of fillers. Ganesan et al. (2021) showed that nano-clay and eggshell waste particles reduce micro-gaps and improve the interfacial bonding between the jute/coir fiber and the polyester matrix. Therefore, a dramatic decrease in the moisture absorption was observed due to the water barrier effect of fillers and the reduction of accumulated water molecules in pores. In addition, the tensile and flexural properties of the composites were significantly improved due to the uniform dispersion of fillers within the matrix leading to a good adhesion and a controlled elasticity of the polyester matrix accordingly (Ganesan et al. 2021). Prasad et al. (2018) revealed that the presence of nano-TiO_2 improves the water absorption capacity and the mechanical properties of flax fiber reinforced composites. This enhancement was explained by the uniform dispersion of fillers which improves the interfacial interaction between fillers, matrix and fibers and restricts the motion of polymer molecules due to the interlocking mechanism (Prasad et al. 2018). Similarly, Mohan et al. (2011) reported that the addition of 3 wt% of nano clay drastically reduces the water absorption of sisal fiber reinforced hybrid composites due to the moisture barrier property of fillers.

Among many bio-composites precursors, montmorillonite (MMT) is the most competitive filler for enhancing the mechanical and physical properties of natural fiber composites due to its wide availability, low cost and large specific surface area (Srivabut et al. 2018; Ganesan et al. 2021). Eggshell powder (ESP) is a suitable reinforcement in polymer composites, a viable and cost-effective alternative (Jannet et al. 2021) for replacing the calcium carbonate particles due to its low density and important specific area compared to the commercial $CaCO_3$ (Jannet et al. 2021; Bang et al. 2012; Tangboriboon et al. 2018). Previous research works focused on the modification of the Epoxy matrix either by including inorganic fillers (Najafabadi et al. 2021) or natural fibers (Chin et al. 2020) as reinforcement, which revealed limited properties. Herein, these two separate approaches are simultaneously used to solve the moisture absorption and the dimensional stability issues as well as the weak interfacial bonding of the bamboo fiber composites. To the best of our knowledge, there are no studies addressing the effect of the modification of the epoxy matrix with MMT or ESP particles on the hygromechanical features of bamboo fiber reinforced composites. Hence, this paper investigates in a comparative way the effects of the most cost-effective fillers with the largest specific surface area (MMT and ESP) on the physical and mechanical properties of the considered bamboo fiber composites at different weight contents. Morphological characterizations (SEM analyses) are performed on the fracture surfaces to figure out the key role of fillers at the fiber-matrix interfaces.

Methods and materials

Elaboration of composites

Extraction of fibers

Bamboo fibers were extracted using both the water retting and compression methods. First, stem internodes were harvested from the bamboo plant, peeled from the outside and cut into several strips which were then immersed into distilled water at room temperature for three days to be molten. The wet specimens were pressed using a mechanical press (*W.415A FACOM*) with a maximum pressure of 2.2 ± 0.1 kPa. This process was repeated until the separation of fibers which were afterwards washed with distilled water and maintained at 105 °C for 48 h within a *DHG 9053A* air-oven with accuracy of 1 °C in order to remove the adsorbed moisture. The moisture content and the average diameter of bamboo fibers prior to composite manufacturing were 9.4 ± 0.1% and about 500 ± 150 µm, respectively (Average of five replicate measurements for each case).

Processing of MMT/ESP fillers

The pure montmorillonite clay (MMT) was supplied from a local Moroccan company in Casablanca, for a particle size of less than 40 µm (< 40 µm). Eggshell powder (ESP) was prepared from raw chicken eggshell wastes using a milling process. First, eggshell wastes were treated with boiling water to eliminate stuck impurities and exposed to sunlight for 48 h to remove the adsorbed moisture. Afterwards, they were preground using mortar and pestle, placed in a milling machine for fine grinding, then, sifted through a sieve with a mesh size of 40 µm. Figure 1 illustrates the main steps of the eggshell powder preparation.

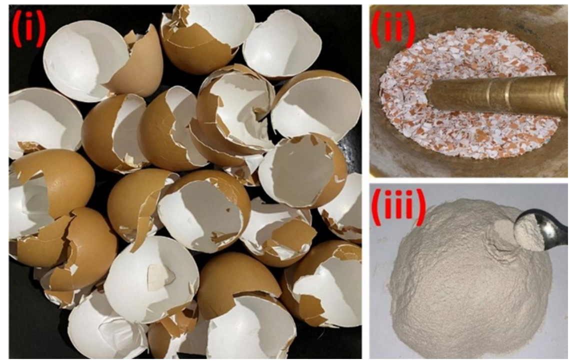

Fig. 1 Eggshell powder preparation process: (i) Raw Eggshell waste free of impurities (ii) Manually pre-ground waste (iii) Obtained powder after milling and sifting

Fabrication of composites

Composites were elaborated using a combination of the hand layup and cold compression molding, that offers low-cost tooling and simple processing, as reported by Chakkour et al. (2023a). Molds with dimensions of 75 × 16 × 4 mm^3 and 120 × 16 × 4 mm^3 were used to manufacture the bamboo fiber composites to carry out tensile and bending tests, respectively.

MMT and ESP fillers were mixed homogeneously with the *Poliep 507* Epoxy resin for 20 min at room temperature and different weight fractions. In addition, 33 ± 0.5 wt% of the Epoxy corresponding hardener was added to the mixture for producing the total weight of the matrix. The used mold was coated with an adhesive tape to ensure an easy demolding of the specimens after the elaboration process. The mixture was added to the fibers which were carefully placed in the mold and manually impregnated with resin using a spatula to remove any involved air bubbles. Finally, a pressure of 5 kPa was applied to the top of the mold using steel bricks and maintained for up to 12 h at room temperature to ensure uniformity of the composite surface. After the compression molding, the specimens were subjected to post-curing at room temperature of 30 °C for 20 days. Experiments' reproducibility was ensured by testing at least three specimens for each configuration, which permits enhancing the

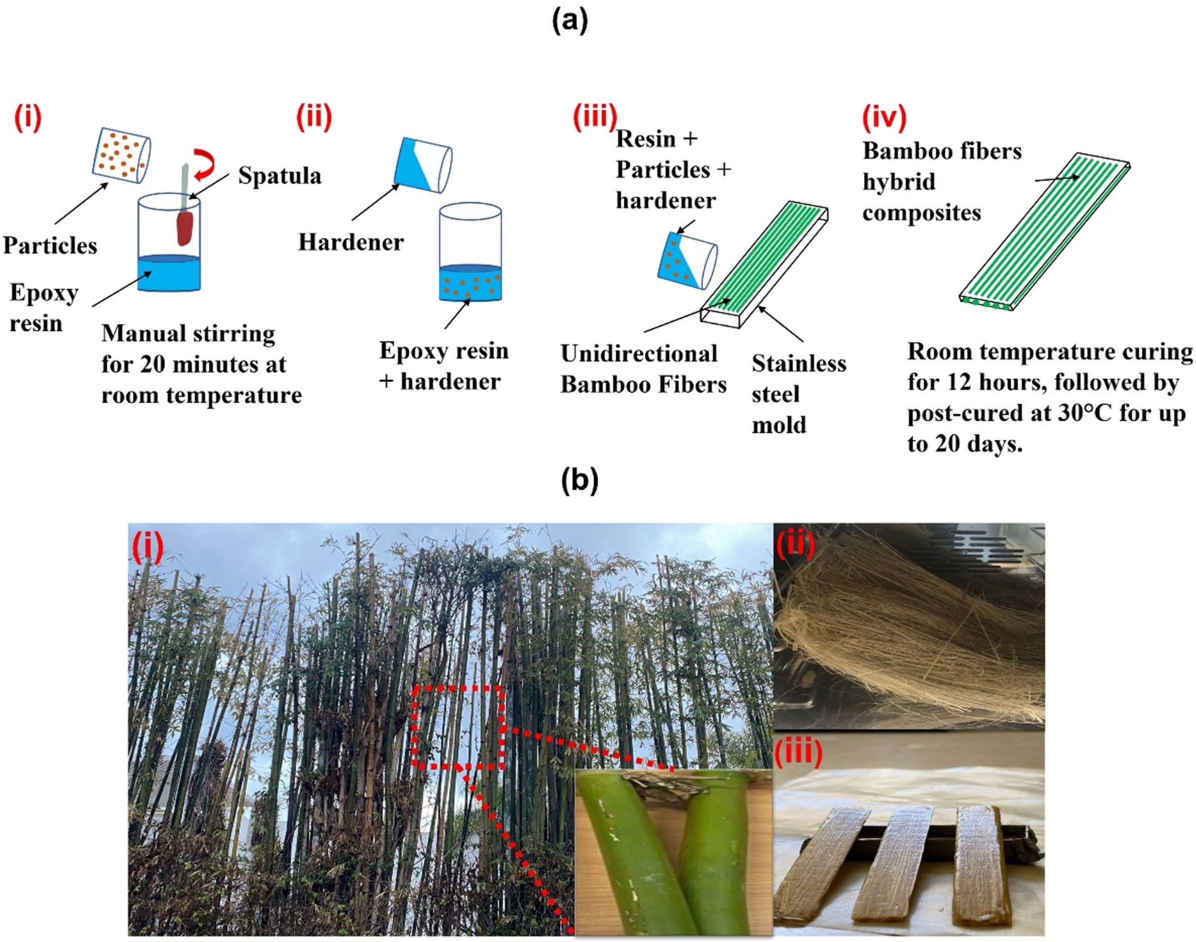

Fig. 2 **a** Illustration of the different steps of the composite elaboration process: (i) Manual stirring of the Epoxy resin and the added particles (ii) Addition of hardener to the mixture (iii) Inserting the fibers into the mold, pouring the final mixture and imposing pressure on the top of the mold (vi) Demolding and post-curing of specimens at 30 °C for 20 days **b** Images showing (i) Bamboo stems (ii) Extracted fibers (iii) Elaborated composites

Table 1 Hybrid composite configurations and their designations

Designation	Bamboo (wt%)	MMT (wt%)	ESP (wt%)	Epoxy (wt%)
S0F	0	0	0	100
S30F	30 ± 0.1	0	0	70 ± 0.3
S1M	30 ± 0.1	1 ± 0.01	0	69 ± 0.3
S3M	30 ± 0.1	3 ± 0.01	0	67 ± 0.3
S1E	30 ± 0.1	0	1 ± 0.01	69 ± 0.3
S3E	30 ± 0.1	0	3 ± 0.01	67 ± 0.3

data reliability and accounting for likely effects of the natural structure gradient of the bamboo stems. Figure 2a gives images of the extracted bamboo fibers and the corresponding hybrid composites. Figure 2b shows a schematic illustration of the composites' elaboration process and the corresponding formulations are given in Table 1. The proposed fiber content in the current study is about 30 ± 0.1 wt%, which is found to be the optimal fraction for maximum mechanical properties of bamboo fiber epoxy composites, as reported by Chakkour et al. (2023a).

Density and void content

The density of fibers was estimated using Archimedes' principle according to ASTM D8171-18. This method consists of measuring the weight of specimens in air and after immersion in a liquid at 23 °C. The apparent loss in weight corresponds to the weight of the displaced liquid. In fact, canola oil and gasoline with densities of 0.914 g/cm^3 and 0.74 g/cm^3 were used as immersion liquids, respectively. Experimental data unveiled that the bamboo fibers float on the liquid surface, revealing that their density is lower than the liquid one. Then, it is estimated to be 0.7 g/cm^3 since it was found to range between 0.6 g/cm^3 and 1.1 g/cm^3 according to previous works (Chakkour et al. 2023a). In a similar vein, the density of eggshell waste (five reproducible experiments) was measured using canola oil as an immersion liquid according to Eq. (1) and found to be 2.17 ± 0.09 g/cm^3, while the density of MMT particles was collected from previous works (Ganesan et al. 2021).

$$\rho_{\text{eggshell}} = \frac{m_{\text{air}} - m_{\text{immersed}}}{m_{\text{immersed}}} \rho_{\text{liquid}} \tag{1}$$

where m_{air} and $m_{immersed}$ correspond to the mass (g) of specimens in air and when immersed in canola oil while ρ_{liquid} refers to the density of the used liquid (g/cm^3), respectively.

The apparent density of the epoxy matrix and composites was calculated according to Eq. (2) using five reproducible (five samples in each case) experimental measurements.

$$\rho_{measured}\left(\frac{g}{cm^3}\right) = \frac{m}{V} \tag{2}$$

where m and V represents the mass and volume (length × width × thickness) of specimens measured by using *OHAUS analytical* balance with 0.0001 g of accuracy and a manual caliper, respectively.

The measured and theoretical densities were used in analytical formulas to determine the void content in bamboo fiber reinforced composites following the ASTM-D-2734–94 standards and according to the Eq. (3):

$$\text{Void content } (\%) = \frac{\rho_{\text{theoretical}} - \rho_{\text{measured}}}{\rho_{\text{measured}}} \times 100 \tag{3}$$

The theoretical density was calculated using Eq. (4):

$$\rho_{\text{theoretical}}\left(g/cm^3\right) = \frac{1}{\frac{M_f}{\rho_f} + \frac{M_m}{\rho_m} + \frac{M_a}{\rho_a}} \tag{4}$$

M and ρ are the weight fraction and the density (g/cm^3), respectively. The subscripts f, m and a refer to the fibers, matrix and additives, respectively.

Water absorption and thickness swelling

Moisture absorption analysis was performed according to the ASTM D 570 standards. The composite specimens were placed in a *DHG 9053A* air oven at 70 °C for 70 h, then, were immersed in distilled water at room temperature. At regular intervals of 24 h, the specimens were wiped using absorbent paper and weighted by means of an *OHAUS analytical* balance with an accuracy of 10^{-4} g. The equilibrium state has been reached when the weight change was no more than 0.1% (Venkatesha et al. 2021).

Dimensional stability analysis was performed according to the ASTM D 570 standards. The thickness of composite specimens was recorded using a manual caliper with an accuracy of 0.1 mm before and after immersion in water.

The water absorption (M_t) and thickness swelling (T.S) of the specimens were calculated according to Eqs. (5) and (6) and based on three reproducible experimental weight and thickness measurements, respectively.

$$M_t = \frac{W_2 - W_1}{W_1} \tag{5}$$

$$T.S = \frac{T_2 - T_1}{T_1} \tag{6}$$

where W_i, T_i correspond to the weight (g) and thickness (mm) of specimens while subscripts i (=1) and i (=2) indicate the dry and wet states of specimens, respectively.

Mechanical characterizations

Tensile tests were performed according to the ISO 6892–1 standard at room temperature and for a displacement rate of 2 mm/min, using a Tinius Olsen machine with a maximum load of 50kN. A contact extensometer (Doli extensometer) with a gauge length of 12 mm was used to measure the engineering strain.

Bending tests were performed according to the ASTM D 790 standard at room temperature, using a Lloyd machine with a maximum load of 30kN. The used support span and displacement rate were 32 ± 0.5 mm and 2 mm/min, respectively.

The tensile and bending properties of the moisture saturated montmorillonite/eggshell powder filled bamboo fiber composites were investigated at different filler contents (1 wt% and 3 wt%), then, compared to similar specimens stored under a relative humidity of 80 RH% at 25 °C. Experiments' reproducibility was ensured by testing three flat rectangular specimens with dimensions of 75 mm × 16 mm × 1.5 mm and 120 mm × 16 mm × 2 mm for the tensile and bending tests, respectively.

Morphological analysis

A *FEI FEG 450* scanning electron microscope (SEM) was used to analyze the fiber–matrix interface of the fractured specimens as well as the dispersion quality of particles. The working voltage was 10 kV in the high vacuum mode (HV) and the corresponding distance ranges between 10 and 20 mm. The specimens with 5 mm of height were cut from the fracture surfaces of the composites and were used for imaging.

Table 2 Theoretical and experimental densities as well as void contents within the considered bamboo fiber reinforced hybrid composites

Designation	Measured density 10^{-2} (g/cm^3)	Calculated density 10^{-2} (g/cm^3)	Void fraction (%)
S0F	1.03 ± 0.10	–	–
S30F	87.12 ± 0.43	93.39	7.19 ± 0.47
S1M	88.75 ± 0.50	93.73	5.61 ± 0.45
S3M	92.76 ± 0.24	94.42	1.78 ± 0.29
S1E	88.08 ± 0.49	93.79	6.48 ± 0.54
S3E	90.98 ± 0.32	94.60	3.98 ± 0.40

Results and discussion

Density and void content

Table 2 shows the experimental and theoretical densities as well as the void fraction of the hybrid composites. The findings reveal that the addition of bamboo fibers contributes to the lightening of the material and leads to reduce the density from 1.03 ± 0.01 g/cm^3 to 0.87 ± 0.004 g/cm^3 when compared to the neat epoxy matrix (S0F). However, the measured densities are found to be lower than the theoretical ones due to the potential formation of air bubbles during the hand layup elaboration process. In addition, raw bamboo fibers are characterized by a low roughness due to the presence of waxes, fats and impurities on their surfaces which may lead to weak fiber-matrix interfaces inducing an important void fraction.

The percentages of voids in the different hybrid composites are presented in Table 2. Results show that the addition of MMT and ESP fillers decreases the void content within the manufactured composites. The specimen S30F exhibits the highest void fraction of 7.19 ± 0.47% while the specimen S3M displays the lowest value of 1.78 ± 0.29%. The incorporation of fillers allows to fill the generated gaps during the elaboration process and the interfacial voids depending on their sizes that can range from micron to nano scale (Ganesan et al. 2021). Effectively, 3 wt% of MMT and ESP fillers are found to significantly decrease the void content within the composites to 1.78 ± 0.29–3.98 ± 0.4%, respectively. However, the void fraction of the MMT filled hybrid composites is found to be lower than that of the ESP filled ones due to the important surface area of the montmorillonite fillers. Indeed, previous works reported that the specific surface area of the eggshell powder is about 7.8 m^2/g (Tangboriboon et al. 2018) while that of the montmorillonite particles reaches almost 24 m^2/g (Tertre 2005).

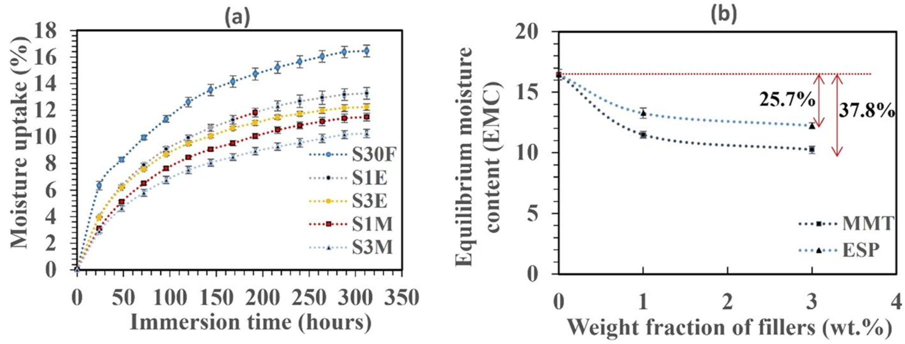

Fig. 3 **a** Water absorption induced moisture content versus immersion time curves of Montmorillonite/Eggshell powder filled bamboo fiber hybrid composites at room temperature **b** Evolution of the equilibrium moisture content of the hybrid composites with respect of the filler content

Water absorption

The moisture absorption analysis is carried out to investigate the effect of MMT/ESP fillers on the equilibrium moisture content of the considered hybrid composites. Figure 3a shows the moisture absorption kinetics of the hybrid composites with different types of fillers (montmorillonite and eggshell) at different weight contents (1 wt% and 3 wt%) with respect of time at room temperature. The results reveal that the moisture gain dramatically increases during the first 96 h, then, saturates after 316 h of water immersion. The maximum moisture absorption values are obtained for the S30F composites and reach 16.46 ± 0.43% due to the presence of only hydrophilic fibers that present a high affinity for moisture absorption (Chakkour et al. 2023a). Besides, water molecules first diffuse into epoxy matrix through open pores and voids and interact with its amine and hydroxyl functional groups (Chow 2007). Afterwards, the bound water molecules are attracted by the hydroxyl groups of the cellulosic components (amorphous cellulose and hemicellulose) and the carboxyls of pectins thanks to hydrogen bonds (Garat et al. 2020). Finally, free water molecules continue to spread towards the fiber lumen, pores and especially through the fiber-matrix interfaces until the ambient vapor pressure is reached (Sanjeevi et al. 2021).

Figure 3b shows that the equilibrium moisture content (EMC) of the hybrid composites decreases with respect of the filler content and the maximum reduction was observed for the 3 wt% MMT filled hybrid composites. In fact, the moisture absorption was dropped by 19.44 ± 0.34%, 25.7 ± 0.28%, 30.25 ± 0.37% and 37.8 ± 0.29% reaching 13.26 ± 0.43%, 12.23 ± 0.25%, 11.48 ± 0.28% and 10.24 ± 0.34% for S1E, S3E, S1M and S3M composites when compared to S30F ones, respectively.

Montmorillonite and eggshell particles obviously play an important role in decreasing the moisture absorption of the considered hybrid composites by introducing a tortuous path for water molecules to diffuse (Alamri et al. 2013). Indeed, they act as water barriers and restrict water molecules to penetrate the fiber lumen (see Fig. 4). The low moisture absorption capacity of the filled hybrid composites could be due to the uniform dispersion of montmorillonite and eggshell fillers within the epoxy matrix. Moreover, the

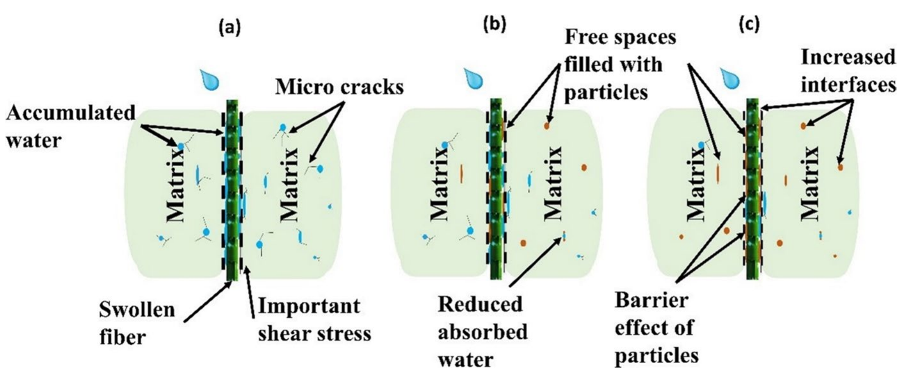

Fig. 4 Schematic illustration showing the physical effects of moisture on **a** unfilled composites **b** 1 wt% and **c** 3 wt% MMT/ESP filled hybrid composites

addition of fillers tends to fill the generated gaps during the hand layup elaboration process and improves the interfacial adhesion by decreasing the void content (see Fig. 4).

Findings show that the addition of MMT particles considerably reduces the moisture absorption of the hybrid composites when compared to ESP ones. This could be attributed to the reported high specific surface area of montmorillonite compared to the eggshell powder (Tangboriboon et al. 2018; Tertre 2005). Indeed, particles with good aspect ratio fill more pores in composites and lead to a limited deposit of free water molecules in the interfacial voids resulting in low water absorption capabilities. Similar findings are reported in (Mohan et al. 2011; Alamri et al. 2013; Ganesan et al. 2021). Mohan et al. (2011) showed that the addition of 3 wt% of nano clay dramatically reduces the water absorption of sisal fiber reinforced epoxy hybrid composites from 62.1–15.8%, explaining that fillers act as water barriers and stop the water flow within the fiber lumen. Alamri et al. (2013) investigated effects of the incorporation of nano-clay at different weight contents on the water absorption capacity of recycled cellulose reinforced epoxy composites. Their results revealed that the addition of 3 wt% and 5 wt% of nano-clay reduces the moisture absorption from 23.28–17.04% and 15.39% when compared to unfilled composites, respectively. Ganesan et al. (2021) showed that the incorporation of 3 wt% of nano-clay and eggshell powder considerably decreases the void content within jute/coir fiber reinforced polyester composites leading to low moisture absorption capacity.

Thickness swelling

Analysis of dimensional stability is carried out to investigate the effect of MMT/ESP fillers at different weight contents on the thickness swelling of the considered hybrid composites under wet conditions. Figure 5a shows the evolution of thickness swelling with respect of water immersion time at room temperature. Results show a dramatic increase in the thickness swelling during the first 24 h, followed by a progressive increase until reaching the saturated state. The maximum swelling value is found to reach 8.46 ± 0.11% for the S30F composites. This could be attributed to the large volume of voids within the unfilled composites in addition to the presence of only hydrophilic bamboo fibers which are characterized by their weak dimensional stability. In fact, the H-bonded water molecules are attracted by the hydroxyl groups of the cellulosic components and the carboxyls of pectins located at the middle lamella and the cell walls of bamboo fibers inducing then a microscopic swelling. The macroscopic changes in dimensions of composites are due to the accumulated free water molecules within micro-voids, the fiber lumen as well as the fiber-matrix interfaces (Sanjeevi et al. 2021; Garat et al. 2020).

Figure 5b shows that the thickness swelling of the hybrid composites decreases when the filler content increases. As expected, the maximum decrease in swelling is observed for the 3 wt% MMT filled hybrid composites. In addition, the thickness swelling decreased by 24.11 ± 0.52%, 27.8 ± 0.23%, 29.66 ± 0.55% and 36.9 ± 1.3% reaching 6.42 ± 0.15%, 6.16 ± 0.11%, 5.94 ± 0.4% and 5.34 ± 0.44% for 1 wt% ESP, 3 wt% ESP, 1 wt% MMT and 3 wt% MMT filled composites when compared to the unfilled ones, respectively. The low swelling of the filled

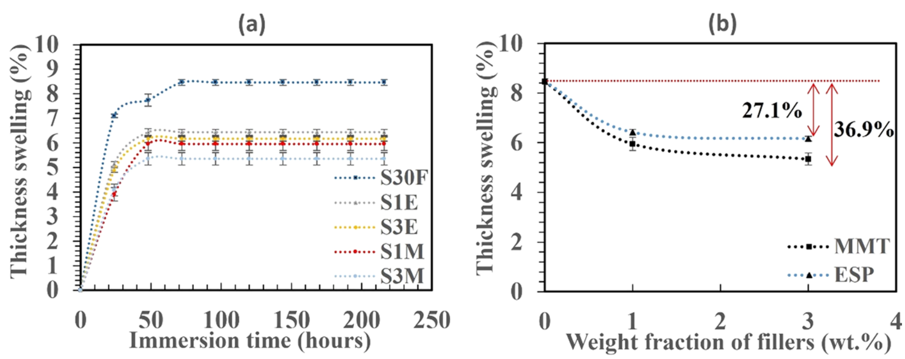

Fig. 5 **a** Thickness swelling versus immersion time curves of the considered hybrid composites at room temperature **b** Evolution of the thickness swelling of the hybrid composites with respect of the filler content

composites is directly attributed to their low absorbed moisture which could be due to the uniform dispersion of additives (Reddy et al. 2020; Chee et al. 2020). Indeed, fillers reduce the free water flow through the fiber lumen and the fiber-matrix interfaces resulting in low dimensional changes of the filled composites. Besides, the thickness swelling values of the MMT filled composites are smaller than those of the ESP filled ones. This is due to the low moisture absorption capacity of the MMT filled composites which results in small values of swelling.

Similar findings are reported by Garat et al. (2020) who studied the effect of water immersion at room temperature of 23 °C on the morphological and structural properties of flax and hemp bundles from various botanical origins. They first observed a microscopic swelling due to the bound water H-linked to the cell walls, followed by a macroscopic one related to the formation of free water through the lumen and pores inducing anisotropic deformations of bundles. Chee et al. (2020) revealed that the addition of 1 wt% of montmorillonite reduces the thickness swelling of kenaf/bamboo fiber reinforced hybrid composites from 8.86% for neat composites to 6.19%, which is explained by the ability of additives to fill the pores in addition to their moisture barrier property that eventually leads to limit the weight and thickness changes.

Tensile properties

Tensile tests are carried out on the hybrid composites to estimate their tensile properties and assess the contribution of montmorillonite and eggshell waste particles under different environmental conditions. Figure 6a shows the tensile strength of the hybrid composites under ambient relative humidity 80 RH% and wet conditions (water immersion). It is observed that the presence of the bamboo fibers significantly improves the tensile strength of the composites when compared to the neat epoxy matrix, achieving 154.5 ± 3.5 MPa. Moreover, the strength is found to increase with increasing the filler fraction reaching 170.3 ± 4.89 MPa, 192.3 ± 1.4 MPa, 162 ± 7.6 MPa and 177.33 ± 7.2 MPa for the S1M, S3M, S1E and S3E composites under ambient relative humidity, respectively. In fact, pores and micro-gaps act as stress concentration zones and cause premature failure during loading in the case of the unfilled composites (Alamri et al., 2013). Obviously, the ability of fillers to fill pores and the interfacial voids improves

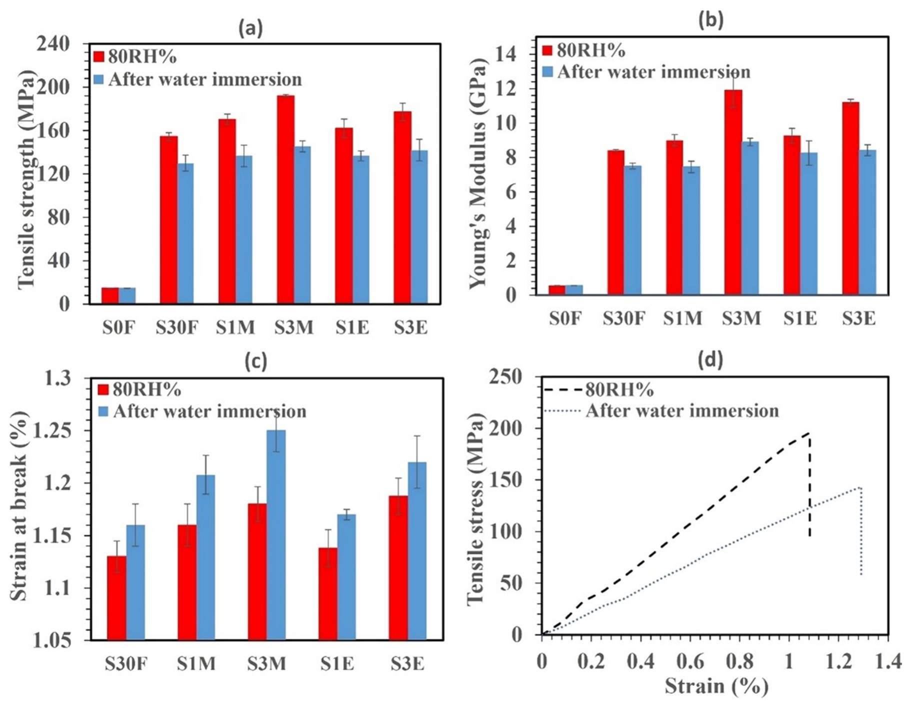

Fig. 6 Evolution of **a** Tensile strength **b** Young's Modulus **c** Strain at break of the hybrid composites under ambient relative humidity 80 RH% and wet conditions **d** Typical tensile stress–strain curves of the S3M configuration under ambient relative humidity 80 RH% and wet conditions at room temperature

the stress transfer between fibers and matrix resulting in an enhanced tensile strength.

However, the tensile strength of the composites significantly decreases by 15.85 ± 1.2%, 19.75 ± 0.85%, 24.42 ± 1.11%, 15.65 ± 0.8% and 19.91 ± 1.08% for the S30F, S1M, S3M, S1E and S3E under wet conditions compared to dry ones, respectively. This significant reduction is mainly due to the swelling of the bamboo fibers that induces important shear stresses across the interfaces and causes fiber-matrix debonding (Sanjeevi et al. 2021). In addition, the incorporation of fillers generates more interfaces (see Fig. 6a) which are the most favorable regions for the nucleation of the water absorption-induced degradation. The presence of montmorillonite and eggshell particles slightly enhances the maximum stress of the water-immersed hybrid composites (Alamri et al. 2013). However, the crucial decrease in the tensile strength of the MMT filled composites could be related to the microscopic swelling of montmorillonite that generates additional internal stresses and leads to the nucleation and propagation of cracks.

Values of Young's modulus of the hybrid composites under dry (80 RH%) and wet conditions are shown in the Fig. 6b. The presence of the bamboo fibers shows a tremendous effect on the longitudinal Young's modulus of the material that rises from 0.55 ± 0.04 GPa for the neat Epoxy matrix to 8.42 ± 0.05 GPa for the bamboo fiber composites. Under dry conditions, the addition of montmorillonite and eggshell fillers increases Young's modulus of the composites reaching 9 ± 0.33 GPa, 11.9 ± 1.05 GPa, 9.26 ± 0.43 GPa and 11.22 ± 0.17 GPa for 1 wt% MMT, 3 wt% MMT, 1 wt% ESP and 3 wt% ESP filled composites, respectively. This enhancement is due to the improved fiber-matrix interfaces and may be attributed to the exfoliation/intercalation of fillers in the Epoxy matrix which restricts the mobility of polymer chains under loadings (Alamri et al. 2013; Mohan et al. 2011). Actually, the orientation of particle platelets and polymer chains along the loading direction would contribute to the strengthening and stiffening effects. In addition, the exposure to moisture causes a considerable drop in the longitudinal Young's modulus (see Fig. 6b) that decreases by 10.97 ± 1.03%, 15.72 ± 0.35%, 27.4 ± 1.84%, 12.1 ± 1.26% and 24.95 ± 1.1% for the S30F, S1MMT, S3MMT, S1ESP and S3ESP wet composites compared to the dry ones, respectively. This tendency may be attributed to the increased ductility of composites due to water absorption (Mohan et al. 2011). The incorporation of fillers leads to a slightly improvement of Young's modulus of the composites.

Figure 6c shows that the addition of MMT and ESP particles allows to increase the strain at break of the hybrid composites leading to values of 1.16 ± 0.02%, 1.18 ± 0.01%, 1.13 ± 0.01% and 1.18 ± 0.01% for the S1M, S3M, S1E and S3E dry composites, respectively. However, Fig. 6d shows that the addition of MMT fillers does not change the failure nature that remains ductile under dry and wet conditions. In fact, montmorillonite and eggshell particles act as crack stoppers and induce some deformation mechanisms such as fiber-matrix

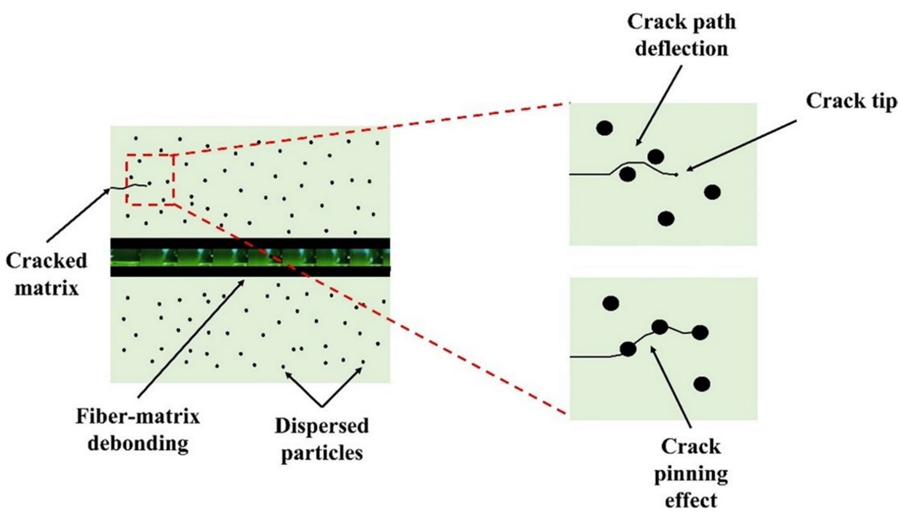

Fig. 7 Schematic illustration of the involved deformation mechanisms in bamboo fiber reinforced hybrid composites

debonding, crack pinning and deflection leading to composites' failure (Mohan et al. 2011) (see Fig. 7). Likewise, the strain at break is found to obviously increase due to the moisture absorption. This improvement is mainly attributed to water molecules that act as plasticizing agents in the composites and lead to enhance the materials ductility, as reported in (Mohan et al. 2011; Ganesan

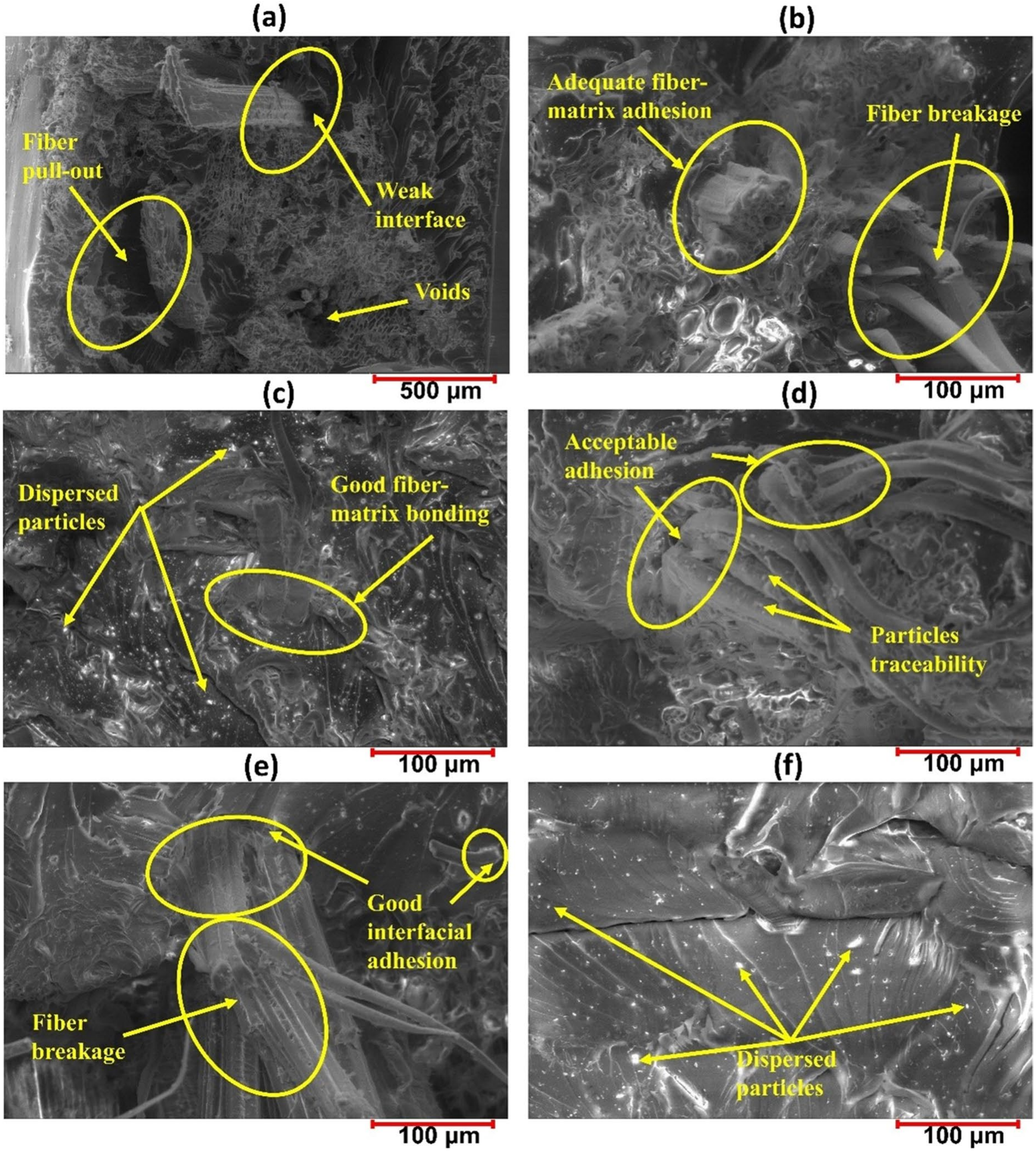

Fig. 8 SEM images showing the tensile fracture surface of **a** unfilled composites **b** 1 wt. % MMT **c** 3 wt. % MMT **d** 1 wt% ESP **e, f** 3 wt% ESP filled bamboo fiber composites

et al. 2021). Mohan et al. (2011) studied the effect of nano clay fillers on the mechanical properties of sisal fiber reinforced composites and revealed that the incorporation of 3 wt% of Cloisite 30B considerably enhances the tensile strength and modulus of these composites. Herein, the improved mechanical properties are obtained thanks to the uniform dispersion of fillers, the adequate fiber-matrix adhesion as well as the good intercalation of clay platelets within the polymer chains. Ganesan et al. (2021) demonstrated that the addition of 3 wt% of nano clay improves the mechanical properties of jute/coir fiber reinforced composites compared to the case of using eggshell powder which was explained by the low void fraction within nano-clay filled composites.

SEM observations of fracture surfaces

The tensile fracture surfaces are analyzed in order to evaluate the contribution of montmorillonite and eggshell particles on the fiber-matrix adhesion. Figure 8 shows the fracture surfaces of the considered unfilled and MMT/ESP filled hybrid composites for different filler contents. From Fig. 8a, it is obvious that the fiber-matrix interface in the case of the unfilled composites shows a weak adhesion that leads to fiber pull-out resulting in small values of strength. Figures 8b c d e and f reveal that the incorporation of MMT and ESP fillers with weight fractions ranging from 1 wt% to 3 wt% improves the fiber-matrix bonding. Therefore, this strong interfacial adhesion ensures an adequate load transfer from matrix to fibers, induces more fibers' breakage (see Fig. 8b c and e) and enhances the stress amplitude at break (Khan et al. 2020). In fact, the uniform dispersion of intercalated particles/matrix as well as their large specific surface area create a strong bonding between fibers and matrix and limit the motion of polymer chains.

Flexural properties

Three-point bending tests are carried out on the different hybrid composites in order to investigate the influence of including montmorillonite and eggshell waste particles within the epoxy matrix. Figure 9a shows the flexural strength of the hybrid composites under ambient relative humidity 80 RH% and wet conditions (water immersion). Results replicate

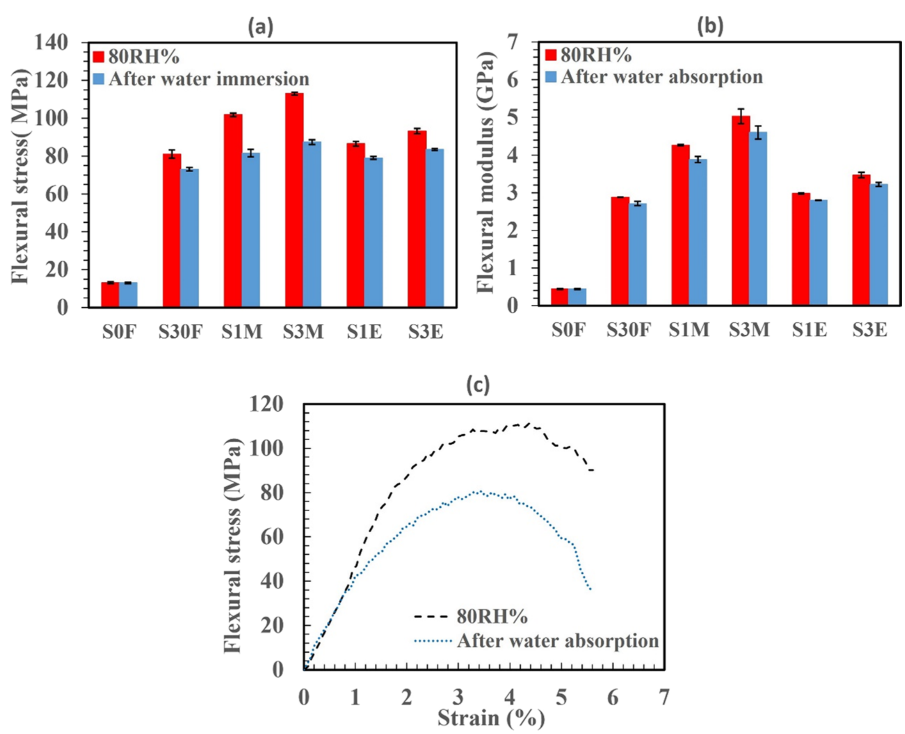

Fig. 9 **a** Flexural strength **b** Flexural modulus of the hybrid composites under ambient relative humidity 80 RH% and wet conditions **c** Typical flexural stress–strain curves of the S3M configuration under ambient relative humidity 80 RH% and wet conditions at room temperature

similar advantages of the MMT/ESP filled bamboo fiber hybrid composites revealing a significant increase in the flexural strength and modulus when the filler content increases. Under a relative humidity of 80 RH%, the flexural strength of the bamboo fiber composites grows up by 621.54 ± 4.26% compared to the neat epoxy matrix. This is clearly due to the ability of fibers to withstand the bending loading of composites. Interestingly, the addition of MMT and ESP particles into the epoxy matrix leads to a certain improvement in the flexural strength of the hybrid composites with values of 113.04 ± 0.72 MPa and 93.19 ± 1.36 MPa for 3 wt. % MMT and ESP filled composites, respectively. This enhancement may be attributed to the strong filler-matrix interaction due to the formation of hydrogen bonds that enhance the interfacial adhesion resulting in a delay of the crack nucleation and propagation (Prasad et al. 2018). In wet conditions, the flexural strength decreases by 9.87 ± 0.84%, 19.89 ± 0.83%, 22.7 ± 0.22%, 8.69 ± 0.34% and 10.29 ± 0.51% for the S30F, S1M, S3M, S1E and S1E composites compared to the dry specimens, respectively. As early discussed, this drop is due to the presence of moisture which degrades the fiber-matrix interface and results then in a poor load transmission from matrix to reinforcement. Moreover, the swelling of montmorillonite clays generates additional internal stresses leading to a severe drop in the flexural strength after water absorption. Finally, the presence of MMT and ESP fillers slightly enhances the flexural strength of the wet specimens.

Figure 9b shows that the flexural modulus of the composites increases with increasing the filler content where the highest obtained values are about 5.03 ± 0.2 GPa and 3.47 ± 0.07 GPa for 3 wt. % MMT and ESP filled composites, respectively. This enhancement results from the uniform dispersion of particles within the epoxy matrix and the involved motion limitation of the polymer chains. However, the decrease in the flexural modulus after water immersion is attributed to the presence of water molecules that act as plasticizers and induce the ductile failure of composites (see Fig. 9c).

Similarly, the flexural strength and modulus of various natural fiber composites were found to increase with the addition of Cloisite 30B, MMT/ESP and titanium TiO_2 fillers, respectively (Alamri et al. 2013; Ganesan et al. 2021; Prasad et al. 2018).

Conclusion

This study was carried out to investigate the influence of montmorillonite and eggshell particles on the physical, morphological and mechanical properties of bamboo fiber reinforced composites, under dry and wet conditions at different filler contents. The results reveal a remarkable improvement in the water absorption capacity and thickness swelling of all filled composites which is due to the uniform dispersion of fillers and the closure of the interfacial voids. The lowest water absorption and thickness swelling values are obtained by adding 3 wt. % of montmorillonite and eggshell particles. Regarding mechanical properties, the tensile and flexural strengths increase when the filler content increases due to the enhanced load transmission from the matrix to the fibers. Similarly, the incorporation of fillers increases the tensile and flexural modulus due to the limited motion of polymer molecules which may refer to the uniform dispersion of particles in the matrix, clearly observed through SEM images. Likewise, the addition of fillers increases the strain at break due to the introduction of various deformation mechanisms such as crack pinning and deflection that delay the composite failure. Herein, the maximum weight percentage of fillers for excellent mechanical properties is 3 wt%. Under wet conditions, the incorporation of particles slightly enhances the tensile / flexural strengths and modulus. However, a significant increase in the strain at break is observed for all composites due to the plasticizing effect of water molecules.

The current findings show that the 3 wt% MMT filled composite can be a viable alternative, lightweight and eco-friendly material for relevant and exigent outdoor applications such as building, automotive, aerospace and wind turbine blades applications. Future works will focus on the evaluation of the dynamic and thermal properties of the MMT/ESP filled bamboo fiber hybrid composites under accelerated ageing.

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T. Ben Zineb, Software: MC, MOM and TBZ, Ressources: MB, Data curation: MC, Writing original draft: MC, Writing review: MOM, IK, MB, TBZ, Visualization: MC, MOM, IK, MB and TBZ, Supervision: MOM, IK, MB and TBZ, Funding acquisition: MOM, MB. All authors have read and agreed to the published version of the manuscript.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethics approval and consent to participate Informed consent was obtained from all individual participants included in the study.

Consent for publication All authors mutually agree to submit this manuscript to your journal.

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