Moisture Effects on the Mechanical Behavior of Fir Wood Flour/Glass Reinforced Epoxy Composite

Camelia Cerbu,[a,]* and Camelia Cosereanu [b]

Fir wood flour may be used as filler in glass reinforced composites due to the lower content of tannins in comparison with oak wood flour (Cerbu *et al.* 2010). This work focuses on the behavior of E-glass / fir wood flour / epoxy hybrid composites in mechanical tests (three-point bending tests, and Charpy impact tests) after immersion in water for 1177, 3048, and 6572 hours. Alternating layers were reinforced either with glass fabric or with fir wood flour. After 3048 hours of immersion, the flexural properties decreased: the modulus of elasticity (MOE) in bending and maximum flexural stress σ decreased by 13.16% and 37.54% respectively, with respect to the values recorded in the case of the dried specimens. The properties recovered a little after saturation because they increased after 6572 hours of immersion: MOE was greater (4.36%), while maximum flexural stress was greater (6.78%) with respect to the values corresponding to the specimens tested after 3048 hours of immersion. In the Charpy test, the impact strength *K* was measured. The damage (cracks developed at matrix-glass interface) caused by water absorption is discussed in order to explain the degradation of the mechanical properties. The adding of the wood flour led to the increasing of the modulus of rigidity E_I in bending and it is proved by comparing with the results obtained in case of glass / epoxy composite without wood flour. Components for outdoor furniture (gardens) could be an application of the hybrid composite analyzed in this paper.

Keywords: Hybrid; Composites; Wood flour; Glass fibers; Moisture degradation; Bending; Impact

*Contact information: a: Department of Mechanical Engineering, Faculty of Mechanical Engineering, Transilvania University of Brasov, 29 Eroilor Avenue, 500036, Brasov, Romania; b: Department of Wood Processing and Wood Products Design, Faculty of Wood Engineering, Transilvania University of Brasov, 29 Eroilor Avenue, 500036, Brasov, Romania; *Corresponding author: cerbu@unitbv.ro*

INTRODUCTION

Hybrid composite materials represent a class of composites that may be reinforced with different kinds of materials in the same layer by using hybrid woven fabrics (*e.g*. carbon / Kevlar fabric). Other hybrid composites are made of different kinds of layers that are reinforced with only one kind of fibers and layers alternate.

The E-glass / fir wood flour / epoxy composites analyzed in this paper were from the last class described above because the layers reinforced with glass fibers alternated with the layers reinforced with fir wood flour. Such a hybrid composite should combine the advantages of wood fibers described below within this section (Klyosov 2007) with the advantages of the glass fibers (Cerbu *et al.* 2009; Zhou *et al.* 2013; Wang *et al.* 2014).

Wood plastic composites (WPC) are widely used (Klyosov 2007) because the addition of the wood flour to plastics may potentially lead to material cost reductions while mechanical characteristics can be improved.

Wood species vary across the world according to geographic area. For example, in the temperate zone, common tree species include fir, oak, beech, hornbeam, poplar, willow, maple, chestnut, bird cherry, and walnut. So there are numerous kinds of wood flour or fiber that may be used as filler for a composite material based on polymer resin.

The use of wood filler in plastic composites has several advantages over inorganic fillers. The use of wood fibers as reinforcing material leads to a weight reduction because the density of wood fibers is lower than glass or carbon fibers (Soler 2014; Müssig and Haag 2015). Wood fibers provide the composite an aspect similar to wood, and thus the composite material may be used for ambient design applications (boards for interior design, furniture parts). The hydrophilic nature of the wood could have a negative effect on performances of the wood–plastic composites (Klyosov 2007). For example, it is well known that wood contains tannins which can form dark color complexes with iron salts (Klyosov 2007) because the tannins are water-soluble phenol and poly-phenol compounds (ferric salts), and fir wood has a lower content of tannins (Klyosov 2007).

During the last few years, significant progress has been made in a new research direction in the field of composite materials, which refers to the use of different materials in order to reduce costs and weight. For instance, such composites may contain either natural fibers (Abdul Khalil *et al.* 2011; Al-Maadeed *et al.* 2014) or recyclable materials (Avila and Duarte 2003; Kamdem *et al.* 2004; Bartl *et al.* 2005; Klyosov 2007; Najafi and Khademi-Eslam 2011; Al-Maadeed *et al.* 2014).

In the case of composite materials reinforced with natural fibers, several studies (Ayensu 2000; Dhakal *et al.* 2007) have reported that the proportional content of the natural fibers plays an important role regarding the mechanical behavior after immersion in water. In the case of hemp/polymer composites, it was shown that a 26% volume ratio of hemp fibers is an optimum value and provides an increase in tensile strength after 30 h of immersion (Dhakal *et al.* 2007). In the case of jute fiber reinforced polymer composites, Ayensu (2000) showed that the flexural strength increased by 45% after 72 h of immersion in water.

Some studies (Kamdem *et al.* 2004; Klyosov 2007) had analyzed the use of wood chips as reinforcements or fillers within plastic composites. The wood chips are obtained during the different stages in wood processing or by recycling the large amounts of wood waste.

It is known that the mechanical properties of the composites made of high-density polyethylene (HDPE) reinforced with fir wood flour as filler, and treated with polypropylene maleate, are improved with respect to high-density polyethylene without wood flour and without polypropylene maleate used as coupling agent (Adhikary *et al.* 2008). Cui *et al.* (2008) showed that both size of the wood chips and wood weight ratio influence the mechanical properties of the composite materials made of post-consumer high density polyethylene filled with wood flour. The smaller wood chips (wood flour) lead to better mechanical properties. Another work (Papanicolaou *et al.* 2012) analyzed the effects of the thermal cycles on the mechanical characteristics of the composite materials made of epoxy resin reinforced with olive pit powder.

Water diffusion (Maggana and Pissis 1999; Boukhoulda *et al.* 2006; Cerbu *et al.* 2009-2010) and the effects of a marine environment (Pomiès *et al.* 1995) on polymer matrix composites reinforced with glass fabrics have been considered in past years. Boukhoulda *et al.* (2006) showed the effects of the fiber orientation angle in glass composite materials on moisture absorption.

A published work of the first author of this study (Cerbu *et al.* 2010) recommends that the oak wood flour used as filler to be replaced with the fir wood flour in the case of glass-reinforced composites that work in a wet environment because oak chips are more hydrophilic in comparison to fir chips. Moreover, the content of tannins is greater in the case of oak wood compared to fir wood.

Within this context, the present work searched for a way to use fir wood waste, in the form of wood flour, to additionally reinforce the polymer composites reinforced with glass woven fabrics in order to reduce material costs and improve the surface aspect of the components made of such a composite material. The main objectives followed by the present paper are to show the advantage of using wood flour as filler in composite materials reinforced with glass fibers and to investigate the durability of the E-glass / fir wood flour / epoxy Epolam 2015 hybrid composite under the effects of the water absorption after the immersion in water for 6572 h.

The results have great applicability. There is a great necessity for components made of wood plastic composites in construction, since such a market is in development (Thompson *et al.* 2010). Wood plastic composites and their variants reinforced with short glass fibers are used in the furniture industry because of the benefits of the technology for obtaining complex geometric designs and the pleasant appearance of wood (Julian *et al.* 2012). Seat-backrest components can be made of fir wood flour/glass/epoxy composite material (Cerbu 2012) for use in indoor or outdoor chairs (furniture for terraces, gardens).

E-glass / fir wood flour / epoxy Epolam 2015 could be also used to manufacture panels for constructions or acoustic protection of human habitations located along busy roads or expressways. Such acoustic barriers or panels are exposed to the effects of aggressive environments (humidity, thermal cycles, and so on). Additionally, these panels are often subjected to damage caused by rocks thrown up from the road by high speed vehicles. Therefore, it is very important that such barriers be able to withstand impact.

EXPERIMENTAL

Materials

The E-glass woven fabric was produced by AeroGlass, Niederlenz (Switzerland) and it contains 50 wt.% warp and 50 wt.%. weft (Certificate of WE200 glass woven fabrics 2010). Yarns made of E-glass fibers are the same type on both warp direction and weft direction.

The particles of fir wood flour had dimensions smaller than 200 μm and were obtained by recycling the waste which resulted from the processing of fir wood structures. Wastes of fir wood were finely milled, and laboratory sieving equipment was used to separate the wood chips by size.

According to the Certificate of Epolam 2015, epoxy resin (provided by Axson Technologies, 2006), the epoxy resin is widely used for manufacturing the laminated composite materials by handing lay-up technology, injection with low pressure, and filament wrapping. This kind of resin works well for the impregnation of timber and within a wet environment according to the certificate of Epolam 2015 epoxy resin. The physical and chemical characteristics of the epoxy resin in the liquid state are shown in Table 1, while the mechanical characteristics of the cured epoxy resin without the reinforcements are shown in Table 2 (Certificate of Epolam 2015 epoxy resin 2006).

Table 1. Physical and Chemical Characteristics of the Epolam 2015 Epoxy Resin, in Liquid State (Certificate of Epolam 2015 epoxy resin 2006)

Characteristic	Value	Unit of measure	Method
Density, 25 °C	1.15	g/cm3	EN ISO 1675: 1985
Viscosity, 25 °C	1550	mPa·s	Brookfield LVT
Mixture ratio with hardener agent	32 (weight ratio) 38 (volume ratio)	%	-
Gel-time, at 23 °C (100 g resin + 32 g hardener)	2.5	Hours	-
Manipulation time (100 g resin + 32 g hardener)	60	Minutes	-
Glass transition temperature	80	°C	EN ISO 11359: 2002°C9188

Table 2. Mechanical Characteristics of the Epolam 2015 Epoxy Resin (with hardener) without Reinforcing (Certificate of Epolam 2015 epoxy resin 2006)

Characteristic	Value	Unit of measure	Method
Tensile stress in tension	70	MPa	EN ISO 527: 1993
Flexural stress	120	MPa	EN ISO 178: 2001
Modulus of elasticity E	3100	MPa	EN ISO 178 :2001
Impact strength - Charpy (unnotch specimen)	40	kJ/m2	EN ISO 179
Elongation in tensile test	5	%	EN ISO 527: 1993
Hardness	83	Shore D15	EN ISO 868: 2003

In order to show the advantages of the fir wood flour used as filler, the mechanical properties of the E-glass / fir wood flour / epoxy Epolam 2015 are compared with the properties corresponding to the similar glass composite material without filler. To evaluate the durability of the E-glass / fir wood flour / epoxy Epolam 2015 under water absorption, the changes of some properties were measured in mechanical tests (bending test, Charpy impact test) after different times of immersion in distilled water (1177 h, 3048 h, 6572 h). The properties recorded for the wet specimens were compared with the properties recorded for the dried specimens.

Finally, the results of the present study were compared with the results published by the authors in another work that analyzed the effects of the wood species on the mechanical characteristics in the case of some glass composite materials filled with wood flour (Cerbu *et al.* 2010). The comparison shows that a lower content of the wood flour leads to the decreasing of the water content at saturation and to a greater stability of the bending properties (flexural modulus E; maximum flexural stress σ_{max}).

Manufacturing Technology

A laminated composite plate having a thickness equal to 5.8 mm was manufactured using E-glass woven fabric (200 g/m^2) to reinforce Epolam 2015 epoxy resin mixed with fir wood flour. The structure of the hybrid laminated composite material is illustrated within Fig. 1. It contains seven layers of E-glass woven fabric.

The wood chips whose size was smaller than 200 μm were dried at 30 °C in a drying stove for 24 h before to incorporate in the epoxy Epolam system (epoxy Epolam 2015 resin

and Epolam 2014 hardner). To initiate and accelerate the polymerization process, the hardener agent Epolam 2014 (manufactured by Axson Technologies) was mixed with the Epolam 2015 epoxy resin before adding the wood flour. The mixture of wood flour and epoxy resin was continuously mixed by using a laboratory mixer for 3 to 4 min at 24 °C temperature, in order to ensure the homogeneity.

Finally, the hybrid composite contained: 9.42 wt.% fir wood flour; 14.73 wt.% E-glass woven fabric; 75.85 wt.% mixture between Epolam 2015 epoxy resin and hardener agent Epolam 2014.

A lower forming pressure was used to manufacture the plates by using hand lay-up technology. Vacuum equipment was finally used to eliminate the air gaps. After manufacturing, all the specimens were dried for 3 days at 40 °C by using a drying chamber before immersion.

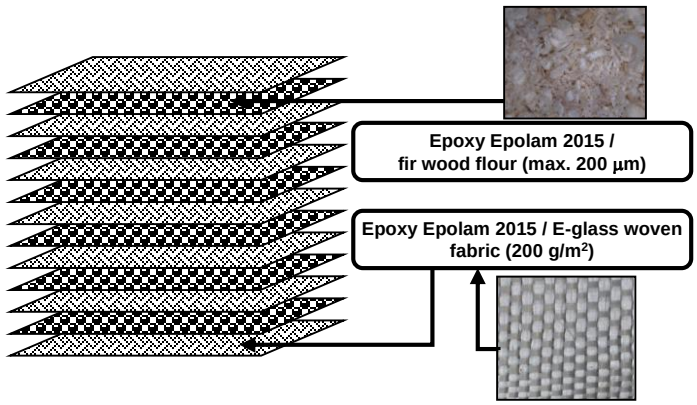
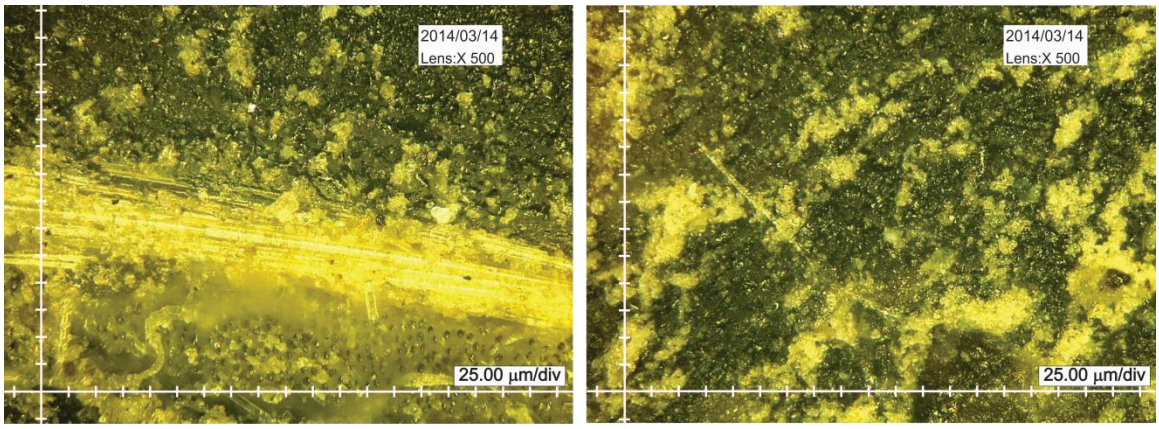


Fig. 1. Structure of the laminated hybrid composite material



a. b.

Fig. 2. Photos (500x) of: (a) section within the structure containing glass fibres and epoxy resin, and (b) section within the structure showing the mixture of the fir wood flour with the epoxy resin

Another laminated composite panel having a thickness equal to 3.6 mm was made of the same Epolam 2015 resin reinforced only with the same E-glass woven fabric (200 g/m^2). This composite material contained 7 glass layers (the same like the previous composite) and the content of the glass fibers was equal to 40 wt.%.

Figure 2 shows a photo of the cross-section of the laminated composite material by using a digital microscope (500x). Figure 2a shows a glass reinforced ply located between two layers reinforced with fir wood flour. Figure 2b shows only the layer obtained by

mixture of the fir wood flour with both the Epolam 2015 epoxy resin and hardener agent Epolam 2014. This microscopic photo indicates that the fir wood flour was uniformly distributed inside the resin because there are not agglomerations of wood fibers that are non-homogenized in the layer made of epoxy resin reinforced with fir wood flour.

The specimens, for the three-point bending tests and Charpy impact tests were cut from the panel made of E200-glass / fir wood flour / epoxy Epolam 2015 composite. By considering the recommendations of the European standards, the specimens had parallelepiped shapes. The specimen dimensions were 120 mm x 15 mm x 6 mm for the three-point bending tests (EN ISO 14125 1998), and 80 mm x 10 mm x 6 mm for Charpy impact tests according to (EN ISO 179-1 2001).

On the other hand, another set of specimens for bending test was prepared from the composite panel reinforced only with E200-glass woven fabric.

Characterization Methods

Immersion in water

The two kinds of specimens (bending specimens and Charpy specimens) made of E200-glass / fir wood flour / epoxy Epolam 2015 composite, were divided into four sets. A set of specimens was kept dried in a desiccator until they were to be mechanically tested. The other three sets of specimens were immersed in distilled water at room temperature, prior to the mechanical testing, for different time periods: for 1177 h (1 month and 19 days); for 3048 h (4 months and 7 days); for 6572 h (9 months and 4 days). The water tanks were covered to minimize evaporation. To keep the immersion conditions constant, the water was changed every two weeks. To monitor the uptake of water, quantified by the content m of the water absorbed, the specimens were periodically removed from the tanks, dried superficially with absorbing paper, and weighed by using an electronic analytical balance (maximum mass 250 g), accurate within ±0.0001 g. The electronic analytical balance SI-234A is manufactured by Denver Instrument.

The moisture absorbed m of the specimens, expressed in percentage (%), was computed according to the British Standard (EN ISO 62 2008) by using the following relationship (Eq. 1),

$$m = \frac{m_w - m_d}{m_d} \cdot 100(\%) \quad (1)$$

where m_w is the mass of the wet specimen after a known immersion time t while m_d represents the mass of the dried specimen that are called blank samples.

The curve of the absorbed moisture m versus the square root of time $\sqrt{t}$ is expected to obey Fick's law in case of the composite material involved in this study after immersion in distilled water; such a relationship has been reported in studies dealing with moisture absorption in fiber-reinforced plastics (Shen and Springer 1976; Springer 1988; Dhakal *et al.* 2007; Boukhoulda *et al.* 2006; Naceri 2009). Therefore, by using Fick's law the diffusion coefficient denoted with D is defined as the slope of the normalized mass uptake against $\sqrt{t}$ and has the relationship (Eq. 2),

$$D = \pi\left(\frac{h}{4M_m}\right)^2 \cdot \mathrm{tg}^2\alpha, \quad (2)$$

where h is the thickness of the composite specimen immersed; M_m is the equilibrium absorbed distilled water inside the composite material at saturation, expressed in percentages; $\mathrm{tg}\alpha$ represents the initial slope of the curve of the absorbed moisture $m(t)$ versus the square root of time $\sqrt{t}$ (Shen *et al.* 1976; Boukhoulda *et al.* 2006; Naceri 2009). The initial slope of the linear portion may be computed by using the following relationship (Eq. 3),

$$\mathrm{tg}\alpha = \mathrm{slope} = \frac{m_2 - m_1}{\sqrt{t_2} - \sqrt{t_1}}, \quad (3)$$

where $\left(m_1, \sqrt{t_1}\right)$ and $\left(m_2, \sqrt{t_2}\right)$ are the coordinates of the two arbitrary points located on the linear portion of the plotted absorption curve $\left(m_1 < m_2, t_1 < t_2\right)$.

Mechanical testing

After immersion, both dried and wet specimens made of E200-glass / fir wood flour / epoxy Epolam 2015 composite were subjected to the bending test (or flexural test) by using a three point bending test setup (EN ISO 14125 1998).

The flexural specimens made of E200-glass / epoxy Epolam 2015, were also subjected to the bending test. Finally, the results recorded for this set of specimen were used to compare with the ones corresponding with the hybrid composite materials filled with fir wood flour.

The LR5K Plus machine manufactured by LLOYD Instruments (West Sussex, United Kingdom) was used for three-point bending test. The maximum load capacity is ±15 kN. The flexural specimen was simply supported at its ends during testing and the span between the supports was equal to 96 mm. The crosshead speed was 1.5 mm/min according with standard (EN ISO 14125 1998).

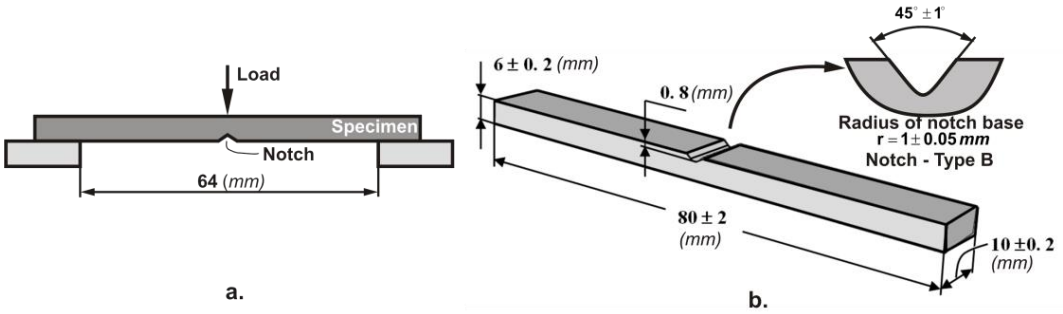


Fig. 3. Specimen used for Charpy test
(a) Scheme of loading; (b) Shape and dimensions of the specimen

With respect to the Charpy test, Fig. 3a shows the scheme of loading used in this mechanical test, while the dimensions of the specimen are shown in Fig. 3b (EN ISO 179-1 2001). The notch is introduced on the material specimen in order to produce a stress concentration and thus to promote failure (EN ISO 179-1 2001). Herein, the notch of type B (EN ISO 179-1 2001) was considered (Fig. 3b). Moreover, the notch may be used to align the Charpy specimen with respect to the simple supports of the Charpy pendulum such that the pendulum hammer hits the specimen on the opposite side of the notch.

A pendulum impact tester HIT50P whose maximum impact energy is equal to 50J, manufactured by Zwick/Roell (Ulm, Germany), was used for the Charpy impact test. The dimensions of the cross-section were recorded for each specimen before the impact testing.

The failure energy U was measured and recorded automatically by the testing equipment, in case of each specimen tested. Finally, the impact strength K (also called resilience) of each specimen was computed by using the following formula (Eq. 4),

$$K = \frac{U}{A}, \quad (4)$$

where A represents the area of the specimen cross-section where the notch is positioned.

Microscopic analysis of the degraded material

To explain the change in the mechanical properties, the damage mechanism had to be studied both at the level of the resin matrix and at the level of the fiber. The equipment used consists of a digital microscope Keyence-VHX600 (Japan), whose magnification is up to 5000x. It has an adjustable lighting system (adjustable slit), and image processing. This allows the measurement of the surfaces, angles, perimeters, and allows the construction of 3D images by depth scanning. As far as acquisition, processing, and measuring digital images, it is completely computerized.

RESULTS AND DISCUSSION

Absorption Data

The absorption data recorded for the hybrid composite material analyzed is shown in Fig. 4. The average value of the absorbed water was equal to: 1.25% after 1177 h (1 month and 19 days), 1.81% after 3048 hours (4 months and 7 days) of immersion, and 1.90% after 6,572 h (9 months and 4 days) of immersion.

Since the water uptake behavior followed Fick's law (Fig. 4) in case of the E-glass / fir wood flour / epoxy composite tested, both absorption properties were experimentally determinate: diffusion coefficient D and moisture content M_m at saturation.

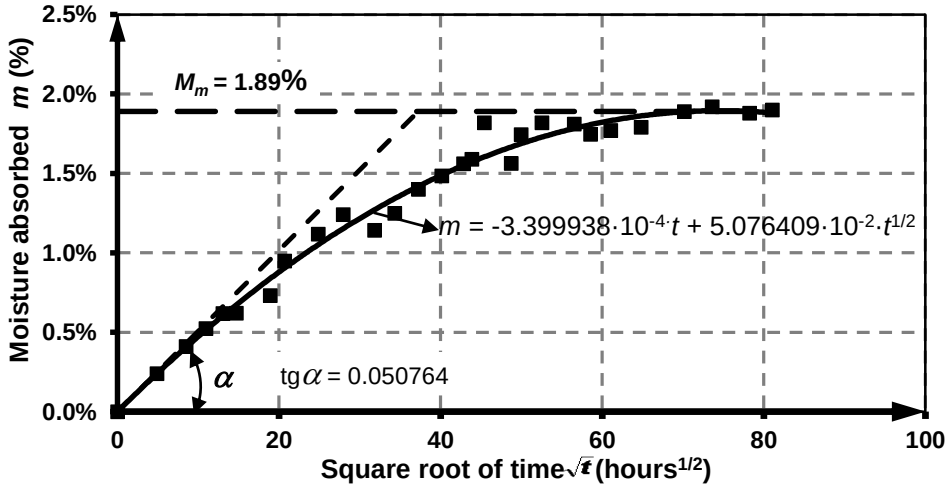


Fig. 4. Absorption data during 6,572 h of immersion in water

Analyzing Fig. 4, it may be noted that after approximately 4900 h of immersion in distilled water, the absorption curve plotted approached asymptotically the equilibrium absorbed water $M_m = 1.90\%$. The initial portion of the absorption curve (Fig. 4) was approximated with a linear function graphically drawn by a line. The initial slope of the Ficks's absorption curve was $\mathrm{tg}\alpha = 0.050764$ and it was used to compute the diffusion coefficient D by using the relationship (Eq. 5):

$$D = \pi\left(\frac{5.8}{4 \cdot 1.89}\right)^2 \cdot 0.050764^2 = 47.6512 \cdot 10^{-4}\ \frac{mm^2}{hours} = 1.3236 \cdot 10^{-6}\ \frac{mm^2}{s}. \quad (5)$$

Several of the analyzed specimens had black spots on the cut edges after 6.572 hours of immersion in water. Since there was no spot before immersion in water, it might be assumed that either the oxidation of the resin or the degradation of the wood flour particles could be one of the causes of the black spot appearance.

Immersion-time Dependence of the Flexural Mechanical Characteristics

Experimental results (force-displacement - $F - \mathrm{v}$ curves) recorded during the three-point bending tests could be graphically drawn by using $\sigma - \varepsilon$ coordinates where: σ represents the flexural stress and ε denotes the strain, corresponding to the points located on the bottom edge of the rectangular cross-section of the specimen located to the middle of span between supports. Figure 5 comparatively shows $\sigma - \varepsilon$ curves recorded in case of: both dried specimens and wet specimens made of E200-glass / fir wood flour / epoxy composite; dried specimens made of E200-glass / epoxy (composite without filler material). The $\sigma - \varepsilon$ curves are drawn only until the maximum flexural stress (*i.e.* max. force) by taking into account the assumption that the Hooke's law remains valid up to the failure of the first layer of the composite materials tested in bending. It is known that the maximum force corresponds to the failure of the first layer. In practice, it is known the composites reinforced with glass fibers are characterized by elastically behavior combined with plastically behavior until the breaking of the specimens in bending.

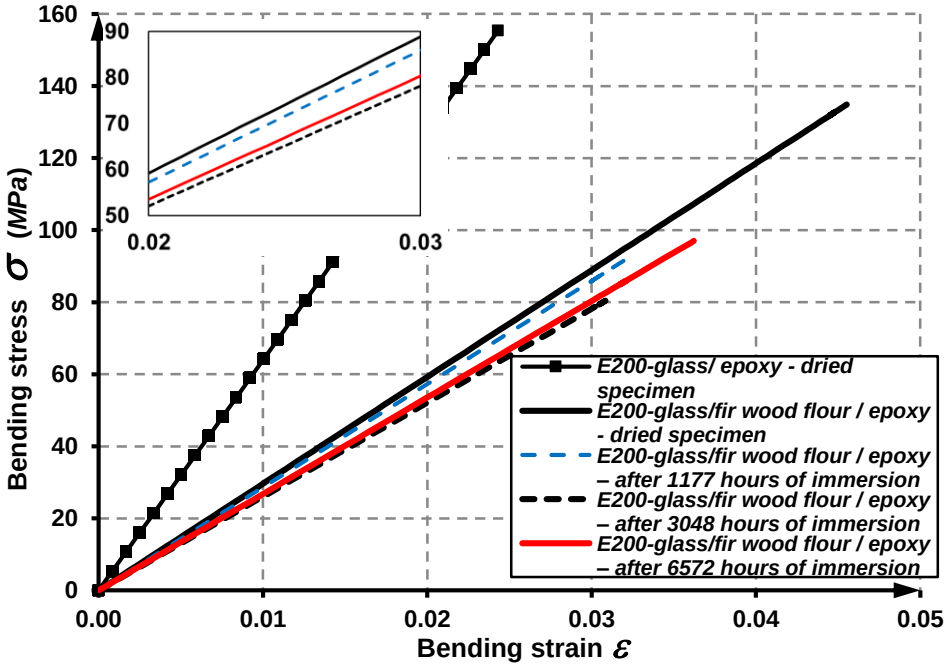


Fig. 5. Stress-strain $\sigma - \varepsilon$ curves recorded in flexural tests in case of both dried and wet specimens

Figure 5 shows only a representative $\sigma - \varepsilon$ curve in the case of each set of specimens tested in bending. The chosen $\sigma - \varepsilon$ curve had an initial slope approximately equal to the average value of the flexural modulus E recorded in case of that set of specimens.

In Fig. 5 it is shown that the slope corresponding to the $\sigma - \varepsilon$ curve recorded in case of the E200-glass / epoxy composite, was greater than the slope corresponding to any $\sigma - \varepsilon$ curve recorded in case of E200-glass / fir wood flour / epoxy composite. This means that the greatest value of the flexural modulus E was recorded in case of the composite reinforced only with the glass woven fabric (without fir wood flour).

In the case of the hybrid composite material, a small decrease of the slope of $\sigma - \varepsilon$ curve was recorded in the case of the wet specimens, comparatively with the slope recorded in the case of the dried specimens. It may be noted that flexural modulus E was computed for the data points located on the linear portion of the F–v curve (Fig. 5) for v = 1÷4.5 mm according to the standard (EN ISO 14125 1998). In the case of the hybrid composite material (E200-glass / fir wood flour / epoxy), the changes to some mechanical properties were graphically analyzed after immersion in water for 1177 h, 3048 h, and 6572 h, respectively: flexural modulus E (Fig. 6); maximum flexural stress σ_{max} (Fig. 7); mechanical work W done to maximum force F_{max} (Fig. 8) in bending test.

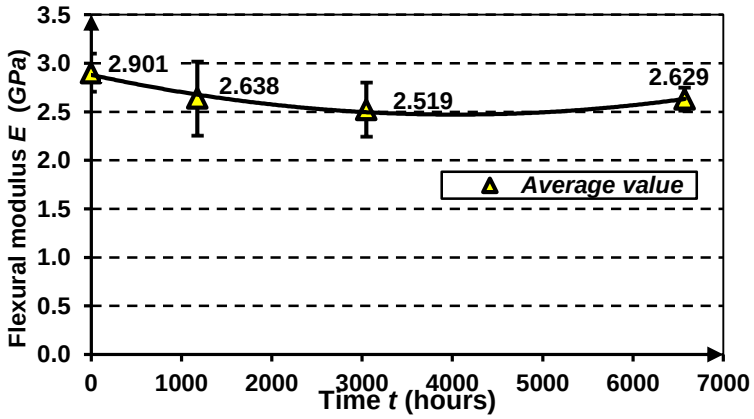


Fig. 6. Immersion-time dependence of flexural modulus *E* (MOE)

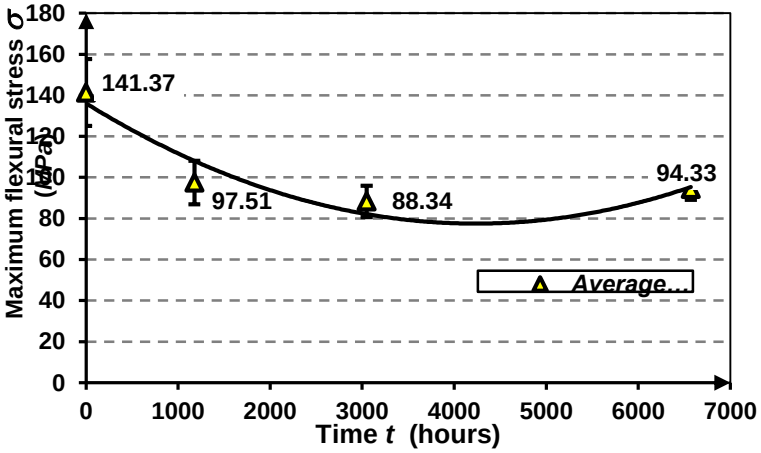


Fig. 7. Immersion-time dependence of the maximum flexural stress σ_{max}

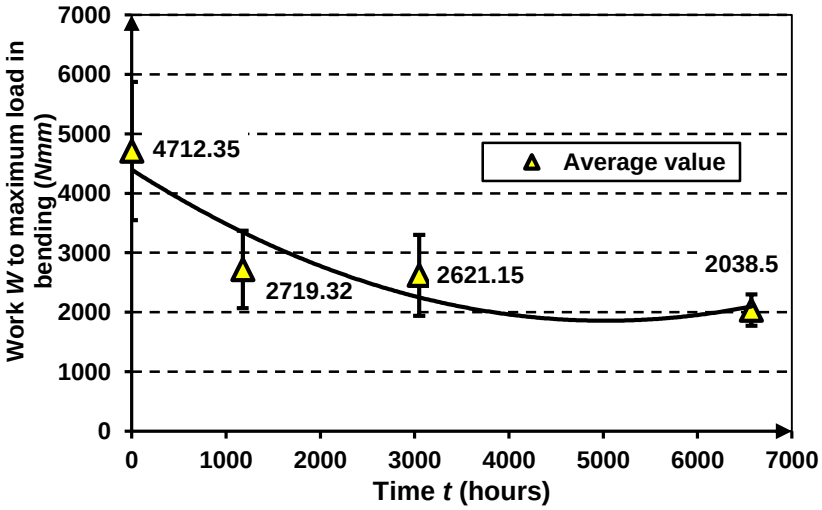


Fig. 8. Immersion-time dependence of the mechanical work *W* to maximum load

One may observe that the flexural modulus *E* (Fig. 6) decreased from 2.901 GPa to 2.637 GPa (with 9.07%) after 1177 h of immersion in water, and then decreased to 2.519 GPa (with 13.16%) after 3048 h of immersion; it decreased to 2.629 GPa (with 9.37%) after 6572 h of immersion.

The change of the average values of the flexural modulus *E* could be approximated by a polynomial function of the 2nd degree, as it follows in Eq. 6,

$$E(t)=3\cdot10^{-8}\cdot t^2-0.203\cdot10^{-3}t+2.8813 \quad (GPa), \tag{6}$$

where *t* represents the immersion time. The above function shows the immersion-time dependence of this quantity. The trend line of that polynomial function was graphically drawn in Fig. 6.

In the same manner, Fig. 7 shows that the maximum flexural stress σ_{max} decreased with 31.03% from 141.37 MPa to 97.5 MPa after 1177 h of immersion in water. It also decreased to 88.30 MPa (with 37.54%) after 3048 h of immersion while it had decreased to 94.33 MPa (with 33.27%) after 6572 h of immersion.

To show the immersion-time dependence of the maximum flexural stress σ_{max}, the variation of the average values of this quantity could be also approximated by a polynomial function of degree 2 (Fig. 7) as follows (Eq. 7):

$$\sigma(t)=3\cdot10^{-6}t^2-0.0276\cdot t+136.06 \quad (MPa). \tag{7}$$

Analyzing Fig. 8, one could observe that the average value of the mechanical work W, done until the maximum force, also recorded a decrease from the value 4712.35 N·mm to 2719.32 N·mm (with 42.29%) after 1177 h of immersion and to 2038.49 N·mm (with 56.74%) after 6572 h of immersion, respectively. In the same manner presented above, the immersion-time dependence of this quantity could be expressed by using the following function (Eq. 8) graphically illustrated in Fig. 8:

$$W(t)=0.0001\cdot t^2-1.0105\cdot t+4396.4 \quad (N\cdot mm), \tag{8}$$

The polynomial functions (Eq. 6 to 8) corresponding to the trend curves (Figs. 6 to 8) may be used to estimate the mechanical properties corresponding to the E-glass /fir wood / flour composite after different immersion periods up to 6572 h of immersion. The accuracy values of the properties lead to the good results in modeling of the material in strength calculus. Safety coefficients could be computed in order to take into account the degradation caused by the absorption of water.

There was a small difference between the degradation of the mechanical characteristics in the case of specimens immersed for 3048 h in water with respect to the degradation recorded in the case of specimens immersed for 6572 h.

Minor increases of the mechanical characteristics near saturation (Figs. 6 to 8) lead to the conclusion that other mechanisms could take place inside the hybrid composite material. Similar remarks have been reported in the case of the hemp fiber reinforced composites (Dhakal *et al.* 2007) and jute fiber reinforced polymer composites (Karmakar *et al.* 1994; Ayensu 2000). Thus, it was shown that a higher volume ratio (26%) of hemp fibers leads to the increase of tensile strength after 30 h of immersion, in the case of hemp/polymer composites (Dhakal *et al.* 2007).

The cause of the increase in the mechanical characteristics near saturation (Figs. 6 to 8) could be the additional swelling of the wood chips similar to the hemp fibers (Dhakal *et al.* 2007) and the jute fibers (Ayensu 2000). Thus, after swelling, the wood fibers better fill the possible gaps located at the interface between resin and glass fibers. Consequently, an improvement of the resin-fiber interface could lead to a slight improvement in behavior

in bending test near to the saturation (see the absorption curve, Fig. 4). It had been also proven that the flexural strength of jute fiber reinforced polymer composites increased by 45% after 72 h of immersion in water (Ayensu 2000).

Immersion-time Dependence of the Mechanical Characteristics in Charpy Tests

To easily analyze the values obtained for the impact strength *K* (or resilience), Fig. 9 illustrates the values of this quantity recorded for the specimens tested. The average value of the impact strength *K* for dried specimens was equal to 117.60 kJ/m^2 and one could remark that this value was greater than the value 40 kJ/m^2 that characterize the Epolam 2015 epoxy resin with hardener without reinforcing (Table 2).

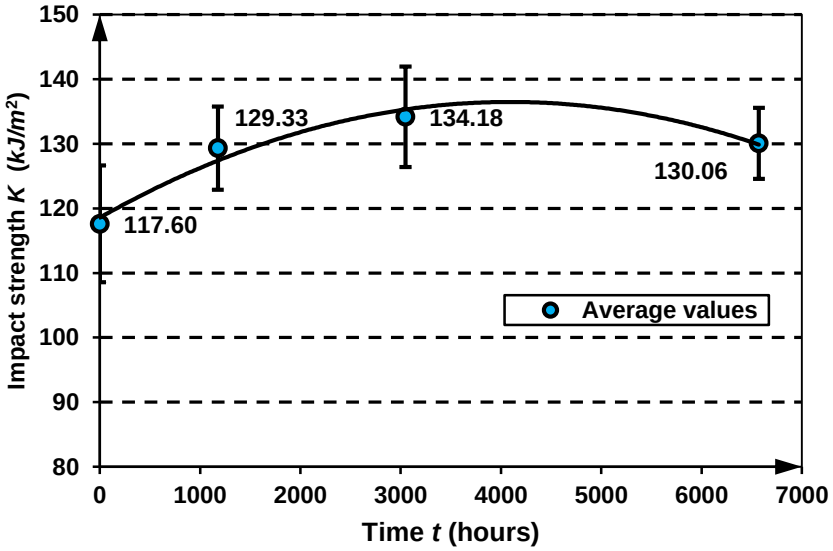


Fig. 9. Immersion-time dependence of the impact strength *K* in Charpy test

The impact strength *K* increased from the value 117.60 kJ/m^2 to 129.33kJ/m^2 (with 9.97%) after 1177 h of immersion, to 134.18 kJ/m^2 (with 14.10%) after 3048 h of immersion, and to 130.06 kJ/m^2 (with 10.59%) after 6572 h of immersion.

The immersion-time dependence of the impact strength could be expressed by using the following function (Eq. 9) graphically illustrated in Fig. 9:

$$K(t) = -1.0711 \cdot 10^{-6} \cdot t^2 + 8.7584 \cdot 10^{-3} \cdot t + 118.58 \quad (kJ/m^2). \qquad (9)$$

Failure Areas of the Specimens

Eventually, the failure areas of the damaged specimens during the flexural tests were analyzed. For this purpose, Fig. 10 represents a microscopic photo (500x) of a damaged specimen within flexural test, after 6572 h of immersion in water, acquired by using the digital microscope. It could be observed that only two to three layers were completely broken in bending.

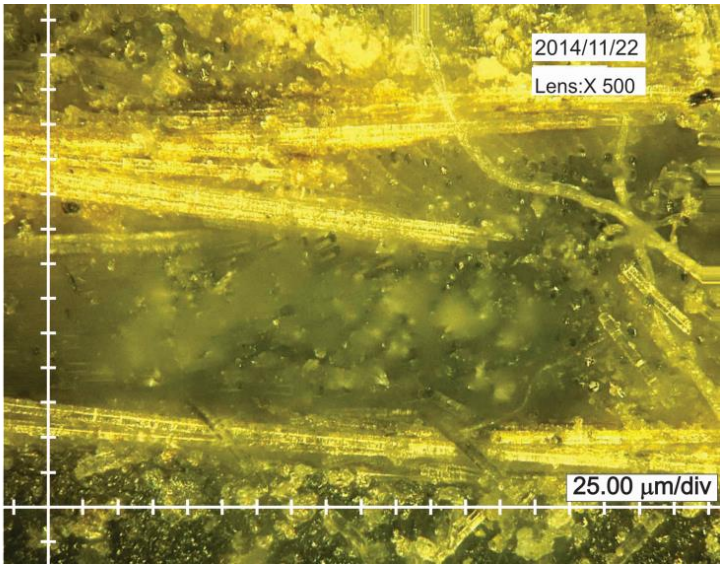


Fig. 10. Failure area (500x) of a specimen subjected to the flexural test (after 6572 h aged)

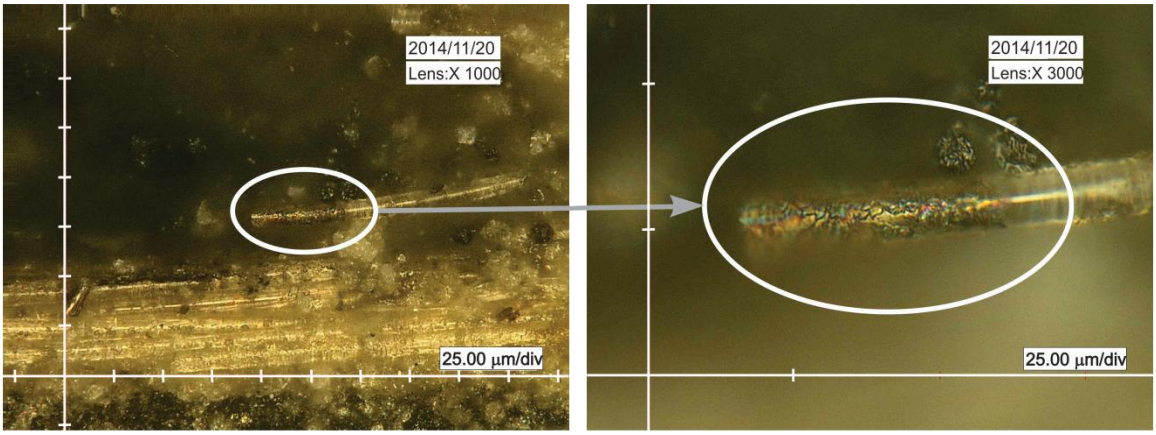


Fig. 11. Degraded areas at the surface of the glass fibers (after 6572 h aged)

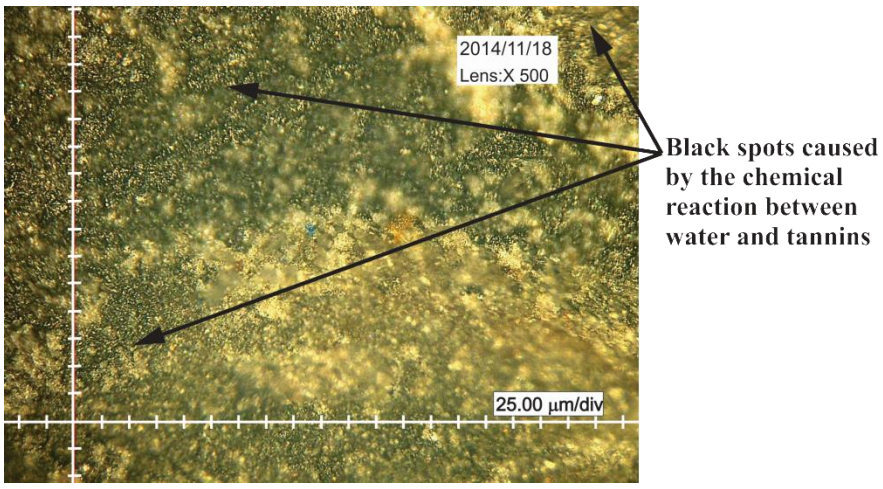


Fig. 12. Degraded areas caused by oxidation of the resin in the layer made of fir wood flour / epoxy (after 6572 h aged)

Regarding the damaged areas caused by the effects of the water, both resin matrix and glass fibers were analyzed by using the digital microscope (Figs. 11 and 12). Figure 11a shows a microscopic photo (1000x) of glass fibers damaged because of the water absorbed after 6572 h of immersion. A detailed microscopic photo (3000x) of an isolated glass fiber (Fig. 11b) shows cracks developed on the glass fiber. The damaged areas alternate with the shiny areas that characterize glass fibers.

It is known that the main components of the wood fibers are cellulose, lignin, and hemicelluloses. Lignin is a photosensitive material, and its color changes from brownish to grey once exposed to UV and water (Fig. 12) (Klyosov 2007). Cellulose and hemicelluloses are polysaccharides, and these contain many hydroxyl groups (–OH) that facilitate the formation of the hydrogen bonds with the polymer structure (Klyosov 2007). The presence of hydroxyl groups explains the hydrophilic nature of the wood fibers (Klyosov 2007). On the other hand, hydrogen bonding formed between the water molecules and cellulose structure could be the cause of the degradation of the mechanical characteristics in the case of the glass/wood flour/epoxy composite material after long-time immersion in water. Water molecules are absorbed inside the hybrid composite and then these plasticize the polymer because of the chemical bonding that takes place (Maggana and Pissis 1999). In addition, the water molecules form hydrogen bonds with the cellulose structure (Dhakal *et al.* 2007). Therefore, both the cellulose structure and the polymer structure were damaged. Furthermore, the interface between epoxy resin and glass fibers was affected (Fig. 11b). Thus, damages of the interface between the glass fibers and epoxy resin are characterized by the developing of cracks and the deposition of the oxides at this level (Fig. 11).

Finally, the damages described above show mechanical degradation as a result of extended immersion in water, as demonstrated in previous sections.

Comparison with Similar Composite Materials

This section compares the mechanical properties recorded in bending in the case of the dried specimens made of E200-glass / fir wood flour / epoxy Epolam 2015 and the properties corresponding to the E200-glass / epoxy Epolam 2015 without fir wood flour (filler). Regarding the durability of the E200-glass / fir wood flour / epoxy composite under the effects of the water absorbed by immersion, the bending properties of two similar composite materials (EWR145–glass / fir wood flour / polyester Copoly 7233; EWR145 – glass / oak wood flour / polyester Copoly 7233) are compared; they are analyzed by the first author of this study within another work published (Cerbu *et al.* 2010).

Table 3. Comparison of the Absorption Data with those of Similar Composite Materials

Composite material	Reference	Immersion time (hours)	Time up to saturation (hours)	Initial slope to Fick's curve $\mathrm{tg}\alpha$	Moisture content M_m at saturation (%)	Diffusity coefficient D $(\cdot 10^{-6}\ mm^2 \cdot s^{-1})$
E200-glass, 7 layers (14.73 wt.%)/ fir wood flour (9.42 wt.%) / epoxy Epolam 2015	This work	6572	4921	0.05076	1.89	1.324

EWR145–glass (10.12 wt.%) / fir wood flour (15.23 wt.%) / polyester Copoly 7233	(Cerbu *et al.* 2010)	5612	3437	0.25098	8.00	3.436
EWR145–glass (10.12 wt.%) / oak wood flour (15.23 wt.%) / polyester Copoly 7233	(Cerbu *et al.* 2010)	5863	4328	0.26149	10.60	2.1244

EWR145-glass is a flat bidirectional glass fabric whose mesh size equals 5 mm and it is usually used in construction to reinforce the layer of plaster. Colpoly 7233 polyester resin is recommended for fiberglass reinforced applications (boats, pools, tanks for the chemical industry) that work in environments with high level of humidity (Cerbu *et al.* 2010).

Table 3 shows the comparison of absorption properties, experimentally determined, of the three composite materials analyzed. The moisture content M_m = 1.89% at saturation of the composite material involved in this study is lower than the corresponding value M_m = 8% recorded in the case of the EWR145–glass / fir wood flour / polyester composite. The greater content of moisture of the composite filled with oak wood flour is caused by more pronounced hydrophilic character of oak chips compared to the fir chips.

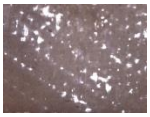
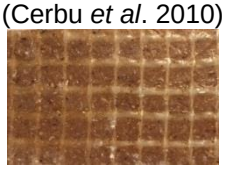
Table 4 comparatively shows the properties measured in the bending test of the composite materials involved in this study and in the case of the other two similar composite materials. The moment of inertia of the cross-section, denoted with I , was used to compute the modulus of rigidity E_I in bending according to the relationship (Eq. 10),

$$E_I = EI = E\frac{bh^3}{12}, \quad (10)$$

where b represents the width of the specimen cross-section; h is the height of the cross-section or thickness of the composite plate from which the flexural specimens were cut.

The composite materials were compared by multi-criteria analysis (Table 4). Marks (A to F) were assigned to each type of composite material for each flexural property (Table 4). The E200-glass / epoxy Epolam 2015 composite was found to be the best composite structure both in terms of the flexural modulus E and the maximum flexural stress (σ_{max}).

Table 4. Comparison of the Bending Properties with those of Similar Composite Materials

Composite material	Reference / Photo of the material	Type of specimens		Flexural modulus E ($\cdot 10^{-3}$ GPa)		Max. flexural stress σ_{max} (MPa)		Modulus of rigidity E_I in bending ($\cdot 10^4$ N·mm^2)
E200-glass, 7 layers (40wt.%)/ epoxy Epolam 2015	This work:  Aspect: shiny and transparent	Dried specimens		6155.4 (±386.7)	A	158.4 (±28.6)	A	35.898 C
E200-glass, 7 layers (14.73 wt.%) / fir wood flour (9.42 wt.%) / epoxy Epolam 2015	This work: 	Dried specimens		2901.0 (±194.6)	B	141.4 (±16.2)	B	70.752 A
		After immersion in water	1177 h	2637.9 (±377.5)	C	97.5 (±10.6)	C	64.336 B
			3048 h	2519.2 (±275.9)	C	88.3 (±7.7)	C	61.441 B
			6572 h	2629.1 (±115.3)	C	94.3 (±5.3)	C	64.121 B
EWR145–glass (10.12 wt.%) / fir wood flour (15.23 wt.%) / polyester Copoly 7233	(Cerbu *et al.* 2010) 	Dried specimens		601.1 (±98.1)	D	27.7 (±8.4)	D	38.470 C
		After immersion in water	5612 h	356.2 (±49.2)	E	15.98 (±2.4)	E	22.797 D
EWR145–glass (10.12 wt.%) / oak wood flour (15.23 wt.%) / polyester Copoly 7233	(Cerbu *et al*. 2010) 	Dried specimens		215.0 (±45.9)	F	20.98 (±1.1)	D	5.805 E
		After immersion in water	861 h	606.9 (±78.7)	D	22.5 (±0.76)	D	16.386 F
			5853 h	500.9 (±118.8)	D	24.99 (±2.7)	D	13.524 F

Taking into account the criterion of the rigidity of the composite structure in bending (*i.e.* modulus of rigidity E_I), it may be noted that the E200-glass / fir wood flour / epoxy Epolam 2015 composite was the best (Table 4). Both composites contained 7 layers of E200-glass woven fabric. In summary, the adding of the fir wood flour as filler in glass composites led to the increase of the modulus of rigidity E_I in bending. Consequently, the deformations were lower when the wood chips are used as filler.

CONCLUSIONS

1. The damage that occurred at the interface between the epoxy resin / wood flour mixture and the glass fibers (Fig. 11) is an additional cause of the decrease of both modulus of elasticity E (MOE) in bending and maximum flexural stress σ_{max}.
2. It is well known that complete immersion in water may be considered a process of artificial accelerated ageing (Pomiès *et al.* 1995; Abdul Khalil *et al.* 2011). Taking into account the acute degradation of the maximum flexural stress σ_{max} (*e.g.*, decreasing 33.27% comparatively with the value recorded in the case of the dried specimen) after

6572 h of immersion in water, it is recommended to avoid the use of such hybrid composite material for applications in long-term wet environments.

3. However, taking into account the good values of mechanical characteristics (flexural modulus $E \cong 2901$ MPa; maximum flexural stress $\sigma_{max} \cong 141$ MPa; impact strength $K = 117.6$ kJ/m^2) recorded for the dried specimens and the recycling necessity of the large quantity of the wood wastes, this hybrid composite material may be recommended for design boards in building construction, furniture ornaments, carcasses, and so on.
4. It is recommended to use wood chips as filler in glass / epoxy composite materials to improve the rigidity of such composite structures. In this context, the results are applicable in case of the parts made of such composites was a high rigidity is required.

ACKNOWLEDGMENTS

The authors are grateful for the support of the project PNII – IDEI 733. The authors hereby acknowledge the structural founds project PRO-DD (POS-CCE, O.2.2.1., ID 123, SMIS 2637, ctr. No 11/2009) and Transilvania University of Brasov for providing the infrastructure used in this work.

REFERENCES CITED

Abdul Khalil, H. P. S., Jawaid, M., and Abu Bakar, A. (2011). "Woven hybrid composites: Water absorption and thickness swelling behaviors," *BioResources* 6(2), 1043-1052. DOI: 10.15376/biores.6.2.1043-1052

Adhikary, K. B., Pang, S., and Staiger, M. P. (2008). "Dimensional stability and mechanical behaviour of wood–plastic composites based on recycled and virgin high-density polyethylene (HDPE)," *Composites Part B: Engineering* 39(5), 807-815. DOI:10.1016/j.compositesb.2007.10.005

Al-Maadeed, M. A., Nógellová, Z., Micušík, M., Novák, I., and Krupa, I. (2014). "Mechanical, sorption and adhesive properties of composites based on low density polyethylene filled with date palm wood powder," *Materials and Design* 53, 29-37. DOI: 10.1016/j.matdes.2013.05.093.

Al-Maadeed, M. A., Shabana, Y. M., and Khanam, P. N. (2014). "Processing, characterization and modeling of recycled polypropylene/glass fibre/wood flour composites," *Materials and Design* 58, 374-380. DOI:10.1016/j.matdes.2014.02.044

Avila, A. F., and Duarte, M. V. (2003). "A mechanical analysis on recycled PET/HDPE composites," *Polymer Degradation and Stability* 80 (2), 373-382. DOI:10.1016/S0141-3910(03)00025-9

Axson Technologies. (2006). Certificate of Epolam 2015 Epoxy Resin.

AeroGlass. (2010). Certificate of WE200 Glass Woven Fabrics.

Ayensu, A. (2000). "Interfacial debonding of natural fibre reinforced composites," *Quarterly Science Vision* V 6(1), 25-34.

Bartl, A., Hackl, A., Mihalyi, B., Wistuba, M., and Marini, I. (2005). "Recycling of fibre materials," *Process Safety and Environmental Protection* 83(4), 351-358. DOI:10.1205/psep.04392

Boukhoulda, B. F., Adda-Bedia, E., and Madani, K. (2006). "The effect of fiber orientation angle in composite materials on moisture absorption and material degradation after hygrothermal ageing," *Composite Structures* 74, 406-418. DOI:10.1016/j.compstruct.2005.04.032.

Cerbu, C. (2012). "Analysis of the states of stresses and strains in furniture components made of composite materials," *AGIR* 16(1), 78-81. http://www.agir.ro/buletine/1254.pdf

Cerbu, C., Ciofoaia, V., Curtu, I., and Vişan, A. (2009). "The effects of the immersion time on the mechanical behaviour in case of the composite materials reinforced with E-glass woven fabrics," *Mat. Plast.* 46(2), 201-205.

Cerbu, C., Curtu, I., Ciofoaia, V., Roșca, I. C., and Hanganu, L. C. (2010). "Effects of the wood species on the mechanical characteristics in case of some E-glass fibres/wood flour/polyester composite materials," *Mat. Plast*. 47(1), 109-114.

Cui, Y., Lee, S., Noruziaan, B., Cheung, M., and Tao, J. (2008). "Fabrication and interfacial modification of wood/recycled plastic composite materials," *Composites Part A: Applied Science and Manufacturing* 39(4), 655-661. DOI: 10.1016/j.compositesa.2007.10.017.

Dhakal, H. N., Zhang, Z. Y., and Richardson, M. O. W. (2007). "Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites," *Composites Science and Technology* 67(7-8), 1674-1683. DOI: 10.1016/j.compscitech.2006.06.019

ISO 14125. (1998). "Fibre-reinforced plastic composites - Determination of flexural properties," International Standards Organization, Geneva, Switzerland.

ISO 179-1. (2001). "Plastics materials, Determination of the properties in Charpy test Part 1: Uninstrumentally dynamic test - Determination of the characteristics of the materials under Charpy test," International Standards Organization, Geneva, Switzerland.

ISO 62. (2008). "Plastics. Determination of water absorption," International Standards Organization, Geneva, Switzerland.

Julian, F., Méndez, J. A., Espinach, F. X., Verdaguer, N., Mutje, P., and Vilaseca, F. (2012). "Bio-based composites from stone groundwood applied to new product development," *BioResources* 7(4), 5829-5842. DOI: 10.15376/biores.7.4.5829-5842

Kamdem, D. P., Jiang, H., Cui, W., Freed, J., and Matuana, L. M. (2004). "Properties of wood plastic composites made of recycled HDPE and wood flour from CCA-treated wood removed from service," *Composites Part A: Applied Science and Manufacturing* 35(3), 347-355. DOI: 10.1016/j.compositesa.2003.09.013.

Karmakar, A.C., Hoffmann, A., and Hinrichsen, G. (1994). "Influence of water uptake on the mechanical properties of jute fibre reinforced polypropylene," *J. Appl. Polym. Sci*. 54(12), 1803-1807. DOI: 10.1002/app.1994.070541203

Klyosov, A. A. (2007). "Composition of wood-plastic composites: Cellulose and lignocellulose fillers," in: *Wood-plastic Composites*, John Wiley & Sons Publishing, Hoboken, New Jersey, pp. 75-122.

Maggana, C., and Pissis, P. (1999). "Water absorption and diffusion studies in an epoxy resin system," *J. Polym Sci*. 37(11), 1165-1182. DOI: 10.1002/(SICI)1099-0488(19990601)37:11<1165::AID-POLB11>3.0.CO;2-E

Müssig, J., and Haag, K. (2015). "The use of flax fibres as reinforcements in composites," in: *Biofiber Reinforcements in Composite Materials*, Faruk, O., and

Sain, M. (eds.), Woodhead Publishing (Elsevier), Cambridge, UK, p. 35-85. DOI: 10.1533/9781782421276.1.35.

Naceri A. (2009). "An analysis of moisture diffusion according to Fick's law and the tensile mechanical behavior of a glass-fabric-reinforced composite," *Mechanics of Composite Materials* 45(3), 331-336.

Najafi, A., and Khademi-Eslam, H. (2011). "Lignocellulosic filler/recycled HDPI composites: Effect of filler type of physical and flexural properties," *BioResources* 6(3), 2411-2424. DOI: 10.15376/biores.6.3.2411-2424.

Papanicolaou, G. C., Koutsomitopoulou, A. F., and Sfakianakis, A. (2012). "Effect of thermal fatigue on the mechanical properties of epoxy matrix composites reinforced with olive pits powder," *Journal of Applied Polymer Science* 124(1), 67-76. DOI: 10.1002/app.35092.

Pomiès, F., Carlsson, L. A., and Gillespie, J. W. (1995). "Marine environmental effects on polymer matrix composites," *Composite Materials: Fatique and Fracture*, Vol. 5, ASTM STP 1230, Martin, R. H. (ed.), Philadelphia: American Society for Testing and Materials, 283-303. DOI: 10.1520/STP14020S

Soler, M. (2014). "Textile structures for aeronautics (Part I)," *Annals of the University of Oradea, Fascicle of Textiles, Leatherwork*, No. 2, Vol. XV, ISSN 1843 – 813X, Oradea University, pp. 101-106.

Shen, C.-H., and Springer, G. S. (1976). "Moisture absorption and desorption of composite materials," *J. Composite Materials* 10, 2-20.

Springer, G. S. (1988). Chapter: "Environmental effects," in: *Environmental Effects on Composite Materials*, Vol. 3, Edited by Springer, G. S., Technomic Publishing Company, Lancaster, PA.

Thompson, D. W., Hansen, E. N., Knowles, C., and Muszynski, L. (2010). "Opportunities for wood plastic composite products in the U.S. highway construction sector," *BioResources* 5(3), 1336-1352. DOI: 10.15376/biores.5.3.1336-1552

Wang, H., Zhou, H., Gui, L., and Zhang, X. (2014). "Analysis of effect of fiber orientation on Young's modulus for unidirectional fiber reinforced composites," *Composites Part B: Engineering* 56, 733-739. DOI:10.1016/j.compositesb.2013.09.020.

Zhou, H. W., Yi, H. Y., Gui, L. L., Dai, G. M., Peng, R. D., Wang, H. W, and Mishnaevsky, L. (2013). "Compressive damage mechanism of GFRP composites under off-axis loading: Experimental and numerical investigations," *Composites Part B: Engineering* 55, 119-127. DOI: 10.1016/j.compositesb.2013.06.007.

Article submitted: 16th of March 2015; Peer review completed: June 20, 2015; Revised version received and accepted: July 31, 2016; Published: August 12, 2016.
DOI: 10.15376/biores.11.4.8364-8385

APPENDIX – SUPPLEMENTARY IMAGES OF THE ANALYSED SPECIMENS

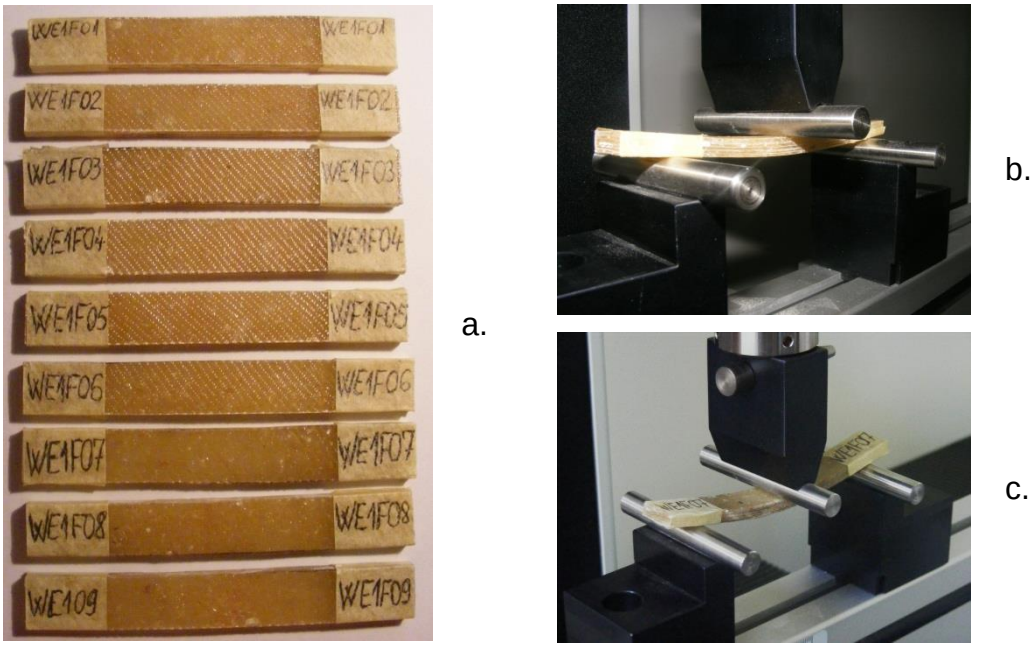


Fig. S.1. Flexural specimens made of E200-glass, 7 layers (14.73 wt.%) / fir wood flour (9.42 wt.%) / epoxy Epolam 2015: a. Dried specimens before bending test; b. Dried specimens during the bending test

Fig. S.2. Flexural specimens made of E200-glass, 7 layers (14.73 wt.%) / fir wood flour (9.42 wt.%) / epoxy after bending test:
a. Dried specimens; b. Wet specimens after 1177 h of immersion in water;
c. Wet specimens after 3048 h of immersion; d. Wet specimens after 6572 h of immersion

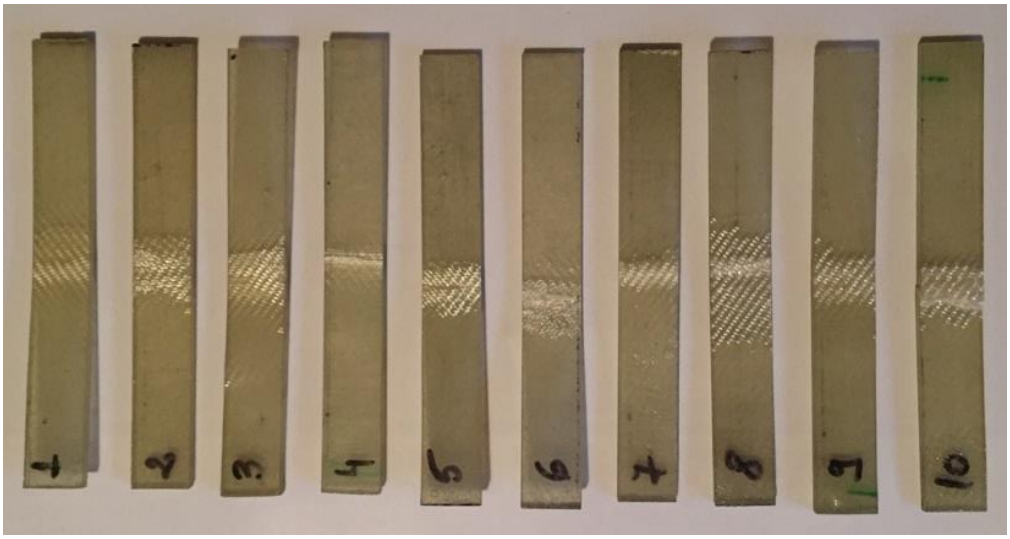


Fig. S.3. Flexural specimens made of E200-glass, 7 layers / epoxy Epolam 2015 after bending test (blank specimens)