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RESEARCH

The Accelerated Aging Effect of Salt Water on Lignocellulosic Fibre Reinforced Composites

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A B S T R A C T

In recent years natural fibre reinforced composite materials have received an increasing attention in consideration of their biodegradability and admirable mechanical properties. The present paper reveals the experimental observations and results of accelerated aging in the cases of ecological composite materials made by lignocellulosic fibres and an eco-friendly resin, when exposed to salt water and temperature. In particular, this research aims at verifying the potential of flax, as a natural fibre reinforcement, coupled with a vinylester with low content of styrene as matrix. Two types of specimens, dried and conditioned, were tested and results compared in terms of flexural strength. Fluid absorption was also monitored. In addition, surface characterization by 3D digital microscope was implemented. Results show an effectiveness of flax as reinforcement, but also a significant drop in flexural properties due to the water absorption which induced the degradation of the fibre/matrix interface.

1. INTRODUCTION

Nowadays, glass fibres surely represent the most preferred reinforcement for composites in the largest gamma applications, as of marine, thanks to a favourable combination of low-cost draft materials, efficient productive technologies [1-3] and high resistance to the effects of degradation. Whenever better properties in materials are necessary and extra costs can be accepted, then, carbon fibres are used to replace glass ones and autoclaves appear in processes [4]. But, unfortunately, neither glass, nor carbon fibres offer the ecosustainable option that meets the modern customers' expectations and desires.

Meanwhile, the use of lignocellulosic fibres (such as wood, flax, hemp, etc.) probably represents the most prominent eco-strategy for reinforcing composite materials by natural fibres [5,6]. In particular, in several investigations (as [7,8]), it is highlighted that, although the mechanical properties of these eco-composites are usually lower than fiberglass [9] and material costs are often higher, they can even be appreciated in practical applications [10]. In the marine sector, this is the case, e.g., of applications for non-structural parts (such as coverings, panels, parts of deck, hatches [11,12]), where a slight loss in strength and higher costs can be offset by the advantages of an environmental awareness.

Nevertheless, the hydrophilic character of the lignocellulosic fibres, together with a consequent reduction in mechanical properties [13-15], can represent a relevant obstacle for the application of natural reinforcements in marine industry or other outdoor constructions. Many researches tried to investigate and solve this criticality [16-19], without providing a definite response.

This research aims at enlarging the current knowledge on eco-composites focusing the attention on flax as natural reinforcement and on a specific vinylester with low content and emission of styrene, as eco-matrix.

Referring to the selection of reinforcement, in comparison with other lignocellulosic fibres, flax fibres present significantly better mechanical properties [20-22], but several precautions have to be taken in account, both in terms of production and use. For instance, previous researches [24] demonstrated that flax fibres start to slowly degrade between 200 °C and 220 °C. Above this temperature, the degradation of fibres is irreversible which sets a limit excluding the possibility of using thermoplastic polymers with a melting point higher than this value [23].

Referring to the selection of matrix, among all resins respecting this thermal limit, vinylester represents a very popular choice in marine industry [25,26]. Anyway, considering the use of a reinforcement fibre (flax) quite uncommon for marine applications, a special attention has to be reserved during the experiment in investigating the correct interaction between matrix and fibres.

This aspect could be particularly critical in marine application considering the prolonged contact between composites and salt water. In fact, moisture absorption strongly influences interface adhesion between lignocellulosic fibre and polymer matrix, creating in turn poor stress transfer efficiency while causing a decline in the mechanical properties. In polymer matrix composites, diffusion of moisture occurs through three different mechanisms: diffusion between polymer chains; capillary transport into the flaws at the interface between reinforcement and matrix; and moisture transport into the fibres causing swelling of lignocellulosic composition [27-30].

In comparison with other resins, vinylester shows low moisture absorption and a good resistance to ultraviolet rays whose nature plays a significant role in the aging behaviour of composites for marine purposes [31]. In particular, according to [32] eco-composites with vinylester matrix seem to show a limited surface damage even with long-term influence of moisture, but this damage can decrease flexural strength and impact resistance [33] of composites structures, as demonstrated for other fibres.

2. MATERIALS AND METHODS

This study aims at investigating the potential influence of a marine environment on the flexural properties of flax fibre reinforced vinylester ecomatrix composites. An accelerated aging was realized by submerging specimens in hot and salt water for a long period. Liquid absorption was monitored by measures of weight. Surface effects and other material damages were observed by 3D digital microscopy, comparing dry and conditioned specimens.

In particular, a commercial flax reinforcement (*LINEO® FLAXPLY BL*), consisting of 70 % cellulose and characterized by 300 gr/m^2 (flax weight per square meter), balanced fabrics (0°/90°) was used [34]. This bio-based eco-friendly reinforcement can be used with all conventional processes (RTM, infusion, hand lay-up…), In addition, it offers acceptable mechanical properties that, coupled with low density, enables a general weight reduction.

Referring to the matrix, a commercial vinylester *(DISTITRON ® VEef 220 STZ),* characterized by Low Styrene Emission (LSE) properties was used [35]. It is a thixotropic pre accelerated vinylester resin with interesting mechanical and thermal characteristics providing both excellent chemical resistance to prevent blistering formation and low shrinkage to guarantee a good finishing. In order to comply with environmental requirements for VOC, the resin contains less than 35 % of styrene, without including any other monomer in its formulation, to minimize emissions during application and a LSE system to block the during curing.

Properties of fibres and vinylester matrix declared by material manufacturers and vendors are shown, respectively, in Table 1 and Table 2. In the case of resin (Table 2), the values of strength, elongation and modulus represent the properties a cured (24 h at 23 °C + 3 h at 100 °C) unreinforced condition.

Table 1. Main properties of flax fibres [30].

Property	Unit	Value
Density	g/cm³	1.40
Tensile strength	MPa	1034
Tensile modulus	GPa	51.0
Elongation at break	%	1.5

Table 2 - Main properties of vinylester matrix [31].

Property	Unit	Value
Density at 25 °C	g/cm³	1.03 – 1.16
Viscosity at 25 °C	mPa.s	1900 – 2550
Volatile content	%	<35
Gel time	Min	36 – 49
Curing time	Min	39 – 70
Glass transition T.	°C	115
Tensile strength	MPa	65
Tensile modulus	MPa	3500
Elongation at break	%	2.0
Flexural strength	MPa	105
Flexural modulus	MPa	3600

3. SPECIMENS PREPARATION

Laminates manufacturing was conducted by a wet lay-up hand laminating process overlapping 8 layers of flax balanced fabric and vinylester matrix, with a 24 h long cure at room temperature followed by a 3 h long post-cure at 100 ˚C. After curing, composites were characterized by a total ratio of lignocellulosic reinforcement of 57.3 % (in weight). After post-curing and cooling, the specimens were extracted out from the original laminate by diamond saw and tool machining. Half of the samples (dry) were prepared for flexural testing in dry conditions and the other half (conditioned) was subjected to the accelerated aging immerging them for 1000 h in 35 ppt salt water at 80 °C. This solution, prepared with 35 % g/L of NaCl, intends to represent the overall proportion of inorganic salts representative of ocean water (in accordance with ASTM D1141 [36]), but, for the sake of simplicity, without introducing each salt (as $MgCl_2$, Na_2SO_4, ...).

Immersed specimens in their bath are shown in Fig. 1. The presence of plastic spacers and a frequent manipulation of specimens (for their reallocation) were used to guarantee a homogenous condition of immersion, even in the case of a little container, in accordance with the appropriate dimensions for the T-controlled oven at disposal.

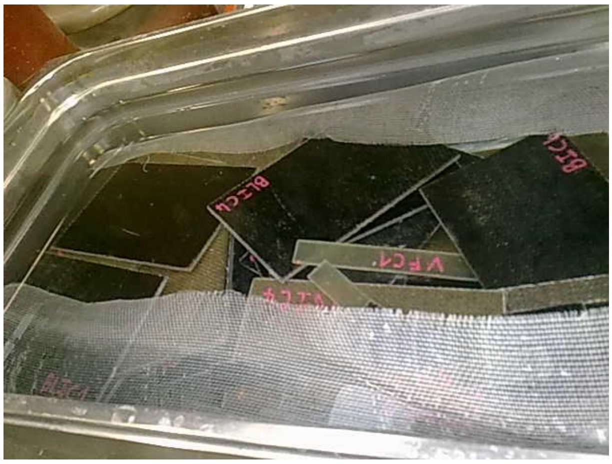

Fig. 1. Specimens in immersion in salt water.

4. ABSORPTION MONITORING

In order to determine the stability of the composites, gravimetric water absorption analysis was done. The specimens were dried for 24 h at 60 ˚C and cooled to room temperature in a desiccator and the initial weight (w_0) was taken to the nearest 0.001 g. The specimens were then immersed in the solution and weekly extracted for weight recording. In these monitoring events, the water on the surface was wiped away and the weight of each specimen was taken again (w). All specimens were analysed and the average weight was taken. The percentage of water absorption (WA in %) was calculated using the Equation (1):

$$WA = \left(\frac{w - w_0}{w_0}\right) \times 100 \qquad (1)$$

where, wo represents the initial weight after drying and w the weight after water immersion.
In Table 3, the change in weight of specimens is reported along with a absorption rate estimative.

Table 3. Measure of weight and absorption estimation.

Specimen	Weight [10^{-3} kg]		Absorption
	dry	**aged**	**[%]**
LVFC1	13.354	14.308	7.14
LVFC2	13.766	14.631	6.28
LVFC3	14.400	15.362	6.68
LVFC4	14.764	15.709	6.40
LVFC5	14.763	15.622	5.82
Mean	*14.209*	*15.126*	*6.46*
St. Dev..	*0.62*	*0.62*	*0.48*

Furthermore, with the aim at providing useful references for a better comprehension of the absorption phenomena in composites, laminates from other materials were also manufactured and their samples conditioned at the same environmental conditions (salt water at 15 %, 80 °C, 1000 hr). Specific resins and fibres were selected with the scope to be highly representative in respect to the main material under investigation (low-styrene vinylester, reinforced by flax). In particular, the same "green" vinylester was used as matrix, but reinforced by basalt or by a mix of basalt and flax fibres (as also reported in [37,38]). In this way, the specific effect of flax on water absorption rate could be easily analysed thanks to the constancy of matrix. In addition, as inevitable reference, a fibreglass laminate was also realized, but selecting a standard vinylester. A comparison among the different absorption tendencies is available in Table 4. Values are reported in terms of weight improvement (in %) in respect to the dry materials. 7 specimens for each materials were used. Weight was initially evaluated in wet conditions, after 6 hours from the first immersion, and, then, weekly till the end of the aging period (1000 hrs).

Table 4. Weight improvement (regarding dry specimens) for different fibres and vinylesters.

Matrix	Fibres	Wet	Aged
Vinylester^{stand}	Glass	0.40 %	0.67 %
Vinylester^{eco}	Basalt	0.31 %	0.67 %
Vinylester^{eco}	Basalt & Flax	2.01 %	5.01 %
Vinylester^{eco}	Flax	2.81 %	6.18 %

Table 4 shows that:

- vinylesters are not particularly sensitive to the aging effect of salt water, neither standard nor "green", confirming a behaviour quite different from Fick's theory of diffusion and a gain in weight much lower than other common commercial resins [39].
- fiberglass is extremely stable and inert confirming its properness for marine applications;
- basalt, an emerging and sustainable material, especially interesting for its extreme mechanical properties, offer a similar stability when compared with carbon [9, 37];
- flax seems to significantly accelerate the water absorption.

As a probable consequence of this last feature, it is expected that several material properties of flax fibre reinforced composites change in consideration of immersion in water.

5. EXPERIMENTAL TEST

The flexural strength in the case of *dry* and *conditioned* composites (before and after water immersion) was determined by an Instron 8033 servo-hydraulic testing machine, using a three-point bending test method. Tests were performed according to ASTM D7264 [40], an experimental standard for flexural properties determination of polymer matrix composite materials. Specimens were placed over two supports. Loads were applied midway by a bar with rectangular cross section and a crosshead speed of 2 mm/min. A span of 80 mm was used in a 25 kN load cell.

Fig. 2. Sequential images from the flexural test.

a) b)

Fig. 3. Specimens after three-point flexural testing: a) dry and b) conditioned.

Test stages are shown in Fig. 2. Photographs of dry and conditioned specimens after flexural testing are shown on the Fig. 3.

6. RESULTS AND DISCUSSION

Experimental results obtained during flexural testing are summarized in Table 5 while stress-strain diagrams are shown in Figs. 4 and 5 for, respectively, dry and conditioned specimens.

Table 5. Flexural strength and strain at break for dry and conditioned specimens.

	Dry		Conditioned	
	Strength MPa	**Strain %**	**Strength MPa**	**Strain %**
	140.9	5.77	74.8	6.51
	122.9	5.25	76.3	6.48
	130.9	6.28	77.2	6.48
	120.6	5.23	79.8	7.14
	131.7	5.34	72.9	6.25
Mean	129.4	5.57	76.2	6.57
Dev. St.	8.1	0.45	2.6	0.33

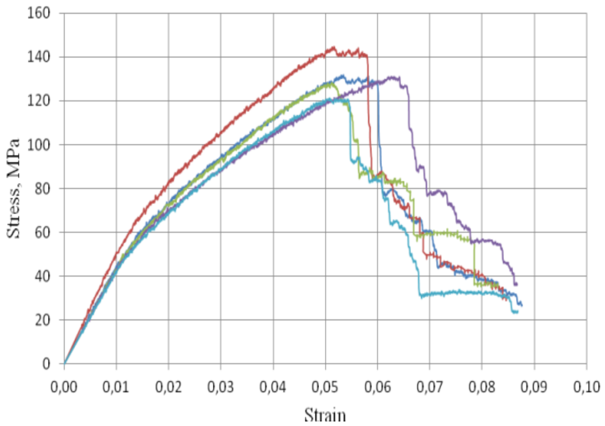

Fig. 4. Flexural stress-strain diagrams for dry flax/vinylester composites.

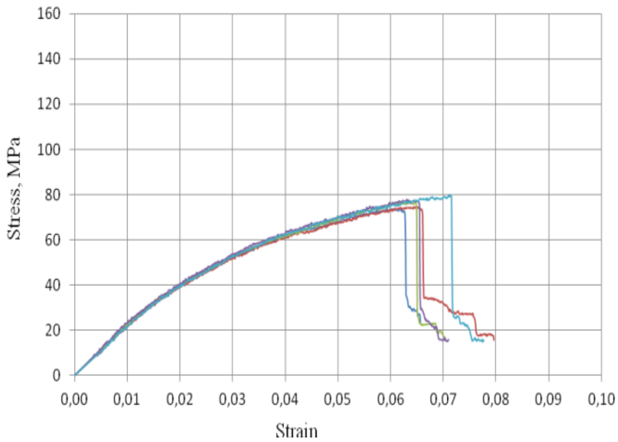

Fig. 5. Flexural stress-strain diagrams for conditioned flax/vinylester composites.

Improvements in the flexural strength offered by the flax reinforcement can be immediately noticed. Comparing the values of flexural strength of cured, but unreinforced resin, as declared by vendor and reported in Table 2, with the experimental data, it is possible to estimate, on average, an increasing of 22.8 % (from 105 MPa to 129±8 MPa) in this property and a peak of 33 % in the case of the specimen that, with 140 MPa, showed the best performance during tests.

These results are in line with similar researches, as reported in [41], where the influence of direction of fibres on the flexural properties in a flax fibre-reinforced composite (with acrylated epoxidized soybean matrix) was analysed. In particular, it is demonstrated that significantly better improvements could be obtained when a unidirectional fabric is preferred to the balanced one. Material technical datasheet for this specific reinforcement highlights, for instance, an ultimate stress strength in flexion up to 300 MPa in the case of 12 layers of unidirectional fabrics [32]. But, with only 180 gr of flax/m^2 (instead of 300 gr) and 4 additional layers, this solution appeared less interesting in terms of productivity, costs and eco sustainability.

Meanwhile, a decrease in mechanical resistance of the conditioned specimens compared to the dry specimens can be also immediately noticed. In particular, referring to the mean values, the flexural strength fall from 129.4 MPa to 76.2 MPa, losing more than 40 %. On the contrary, the strain at break highlights a light increase, about +14 %, from 5.57 % to 6.57 %. In other terms, accelerated aging by salt water and temperature improves the material ductility and reduces its mechanical resistance.

This phenomenon of brittle rupture is also suggested by the stress-strain diagram where the effect of first break, in the case of conditioned specimens, consists of a sudden and steeper fall.

Another noteworthy aspect, emerged from experiments, less evident at first sight, is related to the change in variability of the experimental values and its physical sense. In particular, Fig. 4 shows a larger variability in the elastoplastic behaviour in the case of dry composites. Even if the strain at break is almost the same for all samples (6.57±0.33 %) while the maximum stress shows relatively slight variances (129±8 MPa), their stress-strain diagrams look quite different between specimens. In contrast, the stress-strain diagrams for conditioned composites are identical to the ultimate stress, as shown in Fig. 5. In other terms, water absorption and accelerated aging tend to level the difference in material structures and, as a consequence, in their mechanical properties.

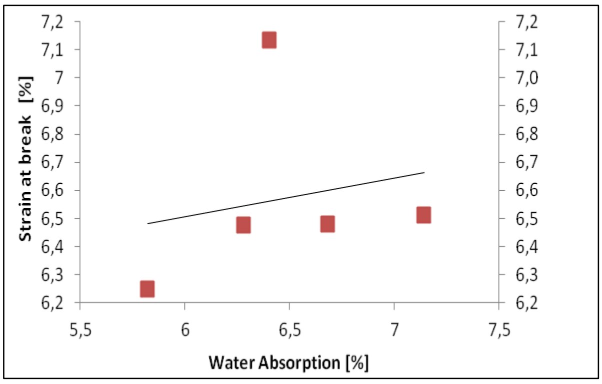

Fig. 6. Relation between strain at break and water absorption.

This supposition was also investigated trying to directly relate the flexural behaviour to the moisture absorption. In Fig. 6, the strain at break is plotted versus the water absorption (expressed in %). Even if the reduced number of specimens and the variability of the phenomena do not permit a definite response, a slight incremental correlation can be initially observed. Further tests are necessary before any confirmation.

7. FURTHER CONSIDERATIONS

The degradation of mechanical properties can be related to the formation of hydrogen bonding between the water molecules and lignocellulosic fibres. Hydrophilic nature of lignocellulosic fibres with a large number of hydroxyl groups in the fibre structure enables formation of a large number of hydrogen bonds between the macromolecules of the cellulose and polymer matrix. This process is described in [40] and demonstrates that natural lignocellulosic fibres, such as flax, due to the intense presence of –OH groups, exhibit a very low resistance in the aquatic environment. In addition, the reduction in the interfacial adhesion between fibre and matrix causes dimensional variation and leads to decrease the mechanical properties these materials (as reported in [30,42, 43]).

The drop in strength seems too intense to be explained only by formation of a large number of hydrogen bonds between the macromolecules of the cellulosic reinforcement and polymer matrix: also polymer matrix degradation has to be present [44].

The hydrophilic flax fibre, attacked by the salt water, starts swelling, causing micro cracking of the brittle polymer matrix. At the same time, flax fibres, due to their high cellulose content, attract the water molecules which penetrate into the interface through these micro cracks activating capillarity transport of water to the interface region of composite material. Thus, the process of water diffusion through the matrix takes place, causing delamination and seriously damage of composite material (as detailed in [45]).

A validation of this hypothesis was investigated at the microscopic scale. Images obtained by *HIROX multifocal* 3D digital microscope are shown in Figs. 7 and 8. These micrographs confirm that the vinylester embrittles with aging, but also highlight the presence of structural defects in materials as delamination and micro cracking.

a)

b)

Fig. 7. Micrographs of composite surfaces, before (a) and after (b) the aging, showing the effect of embrittlement.

The limit introduced by the hydrophilic nature of lignocellulosic fibres could be practically solved in applications with the addition a skin coat on the composite's surfaces.

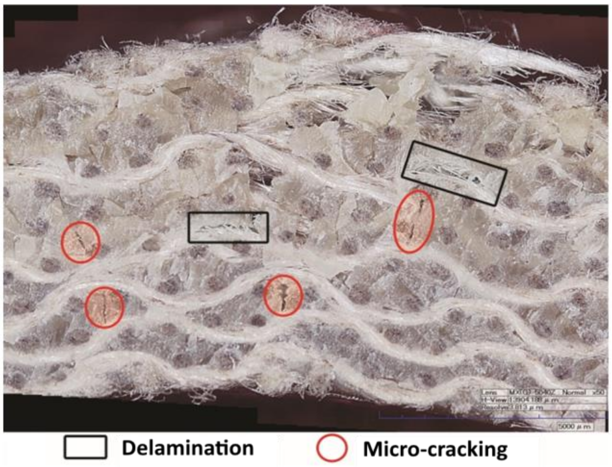

Fig. 8. Micrograph of a specimen after aging, showing structural defects.

The skin coat can be composite laminate with water resistant reinforcement as basalt fibre, which can also improve mechanical properties of composite structure [29, 30].

8. CONCLUSIONS

The effect of the salt water on the mechanical properties of flax fiber reinforced vinylester matrix composites was investigated by accelerated aging, flexural tests and micrographs. Experimental results confirm that natural flax reinforcements really improve the properties of composites and that, in general, vinylester represents a valid solution as matrix in marine applications because of the good mechanical properties and low absorption rate it presents. Contemporaneously, the same results demonstrate that, in the case of vinylester reinforced by flax, a significant drop in flexural properties is due to the substantial water absorption that induces several phenomena, including the degradation of the fibre/matrix interface. Under the influence of moisture the hydrophilic flax fibre swells and micro cracking of the brittle polymer matrix occurs. Than the molecules of water penetrate into the interface and the process of water diffusion through the matrix causes delamination and seriously damage of the composite material. Microscopic analysis proves micro cracking and delamination damage mechanisms into the accelerated aged composite materials during flexural testing. It should be noted that vinylester resin continues to cure during accelerated aging which makes it more brittle than in dry condition. To overcome the problem of water absorption sensitivity authors recommended the usage of basalt fibre based skin coat on both sides of the lignocellulosic fibre reinforced composite material.

REFERENCES

[1] P. Compston, P.-Y.B. Jar, P. Davies, *Matrix effect on the static and dynamic interlaminar fracture toughness of glass-fibre marine composites*, Composites Part B: Engineering, vol. 29, no. 4, pp. 505-516, 1998, doi: 10.1016/S1359-8368(98)00004-3

[2] A.P. Mouritz, A. Kootsookos, G. Mathys, *Stability of polyester-and vinyl ester-based composites in seawater*, Journal of Materials Science, vol. 39, iss. 19, pp. 6073-6077, 2004, doi: 10.1023/B:JMSC.0000041704.71226.ee

[3] F. Vannucchi de Camargo, C.E.M. Guilherme, C. Fragassa, A. Pavlovic, *Cyclic Stress Analysis of Polyester, Aramid, Polyethylene and Liquid Crystal Polymer Yarns*, Acta Polytechnica, vol. 56, no. 5, pp. 402-408, 2016, doi: 10.14311/AP.2016.56.0402

[4] M.N. Alias, R. Brown, *Corrosion behavior of carbon fiber composites in the marine environment*, Corrosion science, vol. 35, iss. 1-4, pp. 395-402, 1993, doi: 10.1016/0010-938X(93)90172-D

[5] O. Faruk, A.K. Bledzki, H.P. Fink, M. Sain, *Biocomposites reinforced with natural fibers: 2000–2010*, Progress in polymer science, vol. 37, iss. 11, pp. 1552-1596, 2012, doi: 10.1016/j.progpolymsci.2012.04.003

[6] S. De Paola, C. Fragassa, G. Minak, A. Pavlovic, *Green composites: A review of state of art*, in 30th Danubia-Adria Symposium on Advances in Experimental Mechanics, 25-28 September, 2013, DAS 2013, Primošten, Croatia, pp. 77-78.

[7] S. Kalia, A. Dufresne, B.M. Cherian, B.S. Kaith, L. Avérous, J. Njuguna, E. Nassiopoulos, *Cellulose-based Bio-and Nanocomposites: A Review*, International Journal of Polymer Science, vol. 2011, Article ID 837875, pp. 1-35 , 2011, doi: 10.1155/2011/837875

[8] O. Adekomaya, T. Jamiru, R. Sadiku, Z. Huan, *A review on the sustainability of natural fiber in matrix reinforcement–A practical perspective*, Journal of Reinforced Plastics and Composites, vol. 35, no. 1, pp. 3-7, 2016, doi: 10.1177/0731684415611974

[9] A. Hyseni, S. De Paola, G. Minak, C. Fragassa, *Mechanical characterization of ecocomposites*, in 30th Danubia-Adria Symposium on Advances in Experimental Mechanics, 25-28 September, 2013, DAS 2013, Primošten, Croatia, pp. 175-176.

[10] S. Pilla, *Handbook of bioplastics and biocomposites engineering applications*, John Wiley and Sons, 2011.

[11] J.B. Cleveland, *The potential application of Natural Fiber Reinforced Bio-polymer (NFRbP) Composites in Architecture*, ProQuest, 2008.

[12] C. Fragassa, *Marine Applications of Natural Fibre-Reinforced Composites: A Manufacturing Case Study*, *Advances in Application of Industrial Biomaterials*, Springer, Cham, pp. 21-47, 2017, doi: 10.1007/978-3-319-62767-0_2

[13] K.G. Satyanarayana, G.G.C. Arizaga, F. Wypych, *Biodegradable composites based on lignocellulosic fibers - An overview*, Progress in Polymer Science, vol. 34, iss. 9, pp. 982-1021, 2009, doi: 10.1016/j.progpolymsci.2008.12.002

[14] A.K. Bledzki, J. Gassan, *Composites reinforced with cellulose based fibres*, Progress in Polymer Science, vol. 24, no. 2, pp. 221-274, 1999, doi: 10.1016/S0079-6700(98)00018-5

[15] H.M. Akil, C. Santulli, F. Sarasini, J. Tirillò, T. Valente, *Environmental effects on the mechanical behaviour of pultruded jute/glass fibre-reinforced polyester hybrid composites*, Composites Science and Technology, vol. 94, pp. 62-70, 2014, doi: 10.1016/j.compscitech.2014.01.017

[16] I. Zivkovic, A. Pavlovic, C. Fragassa, *Improvements in wood thermoplastic matrix composite materials properties by physical and chemical treatments*, International Journal of Quality Research, vol. 10, no. 1, pp. 205-2018, 2016.

[17] M.D.H. Beg, K.L. Pickering, *Reprocessing of wood fibre reinforced polypropylene composites. Part I: Effects on physical and mechanical properties*, Composites Part A: Applied Science and Manufacturing, vol. 39, iss. 7, pp. 1091-1100, 2008, doi: 10.1016/j.compositesa.2008.04.013

[18] M. Bengtsson, K. Oksman, *The use of silane technology in crosslinking polyethylene/wood flour composites*, Composites Part A: Applied Science and Manufacturing, vol. 37, iss. 5, pp. 752-765, 2006, doi: 10.1016/j.compositesa.2005.06.014

[19] A. K. Bledzki, O. Faruk, M. Huque, *Physico-mechanical studies of wood fiber reinforced composites*, Polymer-Plastics Technology and Engineering, vol. 41, iss. 3, pp. 435-451, 2002, doi: 10.1081/PPT-120004361

[20] G. Romhány, J. Karger-Kocsis, T. Czigány, *Tensile Fracture and Failure Behavior of Thermoplastic Starch with Unidirectional and Cross-Ply Flax Fiber Reinforcements*, Macromolecular Materials and Engineering, vol. 288, iss. 9, pp. 699-707, 2003, doi: 10.1002/mame.200300040

[21] P. Wambua, J. Ivens, I. Verpoest, *Natural fibres: can they replace glass in fibre reinforced plastics?*, Composites Science and Technology, vol. 63, iss. 9, pp. 1259-1264, 2003, doi: 10.1016/S0266-3538(03)00096-4

[22] J. Meredith, S.R. Coles, R. Powe, E. Collings, S. Cozien-Cazuc, B. Weager, K. Kirwan, *On the static and dynamic properties of flax and Cordenka epoxy composites*, Composites Science and Technology, vol. 80, pp. 31-38, 2013, doi: 10.1016/j.compscitech.2013.03.003

[23] S. Alimuzzaman, R.H. Gong, M. Akonda, *Nonwoven polylactic acid and flax biocomposites*, Polymer Composites, vol. 34, iss. 10, pp. 1611-1619, 2013, doi: 10.1002/pc.22561

[24] B. Wielage, T. Lampke, G. Marx, K. Nestler, D. Starke, *Thermogravimetric and differential scanning calorimetric analysis of natural fibres and polypropylene*, Thermochimica Acta, vol. 337, iss. 1, pp. 169-177, 1999, doi: 10.1016/S0040-6031(99)00161-6

[25] A.M. Figliolini, L.A. Carlsson, *Seawater Aging of Vinylester and Carbon Reinforced Vinylester*, Durability of Composites in a Marine Environment, vol. 208, pp. 143-153, 2014, doi: 10.1007/978-94-007-7417-9_6

[26] F.A. Almansour, H.N. Dhakal, Z.Y. Zhang, H. Ghasemnejad, *Effect of hybridization on the mode II fracture toughness properties of flax/vinyl ester composites*, Polymer Composites, 2015, doi: 10.1002/pc.23743

[27] B. Dan-asabe, A.S. Yaro, D.S. Yawas, S.Y. Aku, I.A. Samotu, U. Abubakar, D.O. Obada, *Mechanical, Spectroscopic and Micro - structural Characterization of Banana Particulate Reinforced PVC Composite as Piping Material*, Tribology in Industry, vol. 38, no. 2, pp. 255-266, 2016.

[28] A. Espert, F. Vilaplana, S. Karlsson, *Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties*, Composites Part A: Applied Science and Manufacturing, vol. 35, iss. 11, pp.1267-1276, 2004, doi: 10.1016/j.compositesa.2004.04.004

[29] H.N. Dhakal, Z.Y. Zhang, M.O.W. Richardson, *Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites*, Composites Science and Technology, vol. 67, iss. 7, pp. 1674-1683, 2007, doi: 10.1016/j.compscitech.2006.06.019

[30] F. Živić, N. Grujović, S. Mitrović, D. Adamović, V. Petrović, A. Radovanović, S. Đurić, N. Palić, *Friction and Adhesion in Porous Biomaterial Structure*, Tribology in Industry, vol. 38, no. 3, pp. 361-370, 2016.

[31] K.N. Shivakumar, G. Swaminathan, M. Sharpe, *Carbon/Vinyl Ester Composites for Enhanced Performance in Marine Applications*, Reinforced Plastics and Composites, vol. 25, iss. 10, pp. 1101-1116, 2006, doi:10.1177/0731684406065194

[32] A. Afshar, M. Alkhader, C.S. Korach, F.P. Chiang, *Effect of long-term exposure to marine environments on the flexural properties of carbon fiber vinylester composites*, Composite Structures, vol. 126, pp. 72-77, 2015, doi: 10.1016/j.compstruct.2015.02.008

[33] I. Živković, C. Fragassa, A. Pavlovic, T.M. Brugo, *Influence of moisture absorption on the impact properties of flax, basalt and hybrid flax/basalt fiber reinforced green composites*, Composites Part B: Engineering, vol. 111, pp. 148-164, 2017, doi: 10.1016/j.compositesb.2016.12.018

[34] Lineo, Flaxply Technical Data Sheet, 2013.

[35] Polynt, DISTITRON ® VEef 220 STZ Technical Data Sheet, 2013.

[36] ASTM D 1141, *An American National Standard Practice for the Preparation of Substitute Ocean Water*, 2003.

[37] C. Fragassa, *Effect of natural fibers and bio-resins on mechanical properties in hybrid and non-hybrid composites*, in VIII International Conference on Times of Polymers And Composites: From Aerospace to Nanotechnology, 19-23th June, 2016, AIP Conference Proceedings, vol. 1736, iss. 1, Ischia, Italy, article no. 4949693, doi: 10.1063/1.4949693

[38] S. Boria, A. Pavlovic, C. Fragassa, C. Santulli, *Modeling of Falling Weight Impact Behavior of Hybrid Basalt/Flax Vinylester Composites*, Procedia Engineering, vol. 167, pp. 223-230, 2016, doi: 10.1016/j.proeng.2016.11.691

[39] C. Baley, Y. Perrot, F. Busnel, H. Guezenoc, P. Davies, *Transverse tensile behaviour of unidirectional plies reinforced with flax fibres*, Materials Letters, vol. 60, iss. 24, pp. 2984-2987, 2006, doi: 10.1016/j.matlet.2006.02.028

[40] ASTM D7264/D7264M, *Standard Test Method for Flexural Properties of Polymer Matrix Composite Materials*, 2015.

[41] K. Adekunle, S.W. Cho, C. Patzelt, T. Blomfeldt, M. Skrifvars, *Impact and flexural properties of flax fabrics and Lyocell fiber-reinforced bio-based thermoset*, Journal of Reinforced Plastics and Composites, 2011, doi: 10.1177/0731684411405874

[42] N. Sombatsompop, K. Chaochanchaikul, *Effect of moisture content on mechanical properties, thermal and structural stability and extrudate texture of poly (vinyl chloride)/wood sawdust composites*, Polymer International, vol. 53, iss. 9, pp. 1210-1218, 2004, doi: 10.1002/pi.1535

[43] Y. Diamant, G. Marom, L.J. Broutman, *The effect of network structure on moisture absorption of epoxy resins*, Journal of Applied Polymer Science, vol. 26, iss. 9, pp. 3015-3025, 1981, doi: 10.1002/app.1981.070260917

[44] Y. Perrot, C. Baley, Y. Grohens, P. Davies, *Damage resistance of composites based on glass fibre reinforced low styrene emission resins for marine applications*, Applied Composite Materials, vol. 14, iss. 1, pp. 67-87, 2007, doi: 10.1007/s10443-006-9033-8

[45] A. Bismarck, I. Aranberri-Askargorta, J. Springer, T. Lampke, B. Wielage, A. Stamboulis, I. Shenderovich, H.-H. Limbach, *Surface characterization of flax, hemp and cellulose fibers; surface properties and the water uptake behavior*, Polymer Composites, vol. 23, no. 5, iss. 872-894, 2002, doi: 10.1002/pc.10485