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IMPROVING PERFORMANCE AND APPLICABILITY OF GREEN COMPOSITE MATERIALS BY HYBRIDIZATION

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Abstract: A growing concern over environmental issues and the common interest to find a viable alternative to the use of glass or carbon composite reinforcements has led to an increased attention in ecologically sustainable polymer composites. These „green" materials are made by natural fibers, as reinforcement, filled with natural-organic fillers, i.e. derived from renewable or biodegradable sources. At the same time, this relatively new class of materials faces several limits in comparison to traditional composites especially regarding the properties of resistance. This paper investigates the advantages of use of combination of natural fibers for improving mechanical proprieties of „green" composite materials. At the moment, the prevailing opinion is that green composites are not usable in structural applications, and, as a consequence, have to be relegated to unworthy applications (as fillers). On the contrary, there are several evidences that mixing different natural fibers (in practice usually called „hybridization") leads to an improvement of these material properties. Although usually quite limited in terms of percentage, these improvements from time to time allow a new enlargement in the fields of applications for green composites. Following a large state-of-the-art on green composites, including potential benefits and limits of these materials, the paper proposes several examples of hybridization showing its effect on mechanical proprieties.

Keywords: ecosustainability, mechanical proprieties, polymer-matrix composites, flax, basalt, vinylester.

1. INTRODUCTION

Hybrid composite materials are obtained by combining two or more different types of fibers in a common matrix. They offer a wider range of properties compared to conventional composite materials, where a single kind of reinforcement is present [1−2]. Hybridization would ideally allow designers to tailor the composite properties to the exact needs of the structure under consideration. This can be achieved provided the properties of the hybrid composite are predictable within a reasonable range of incertitude from those of the originating composites. This is often not the case, especially when one of the reinforcement vegetable fibres is used, such as e.g ., hemp or flax [3−4]. A number of reasons can be accounted for this difficulty, including the presence of internal voids, or lumens, and limiting the homogeneity of vegetable fibres, and the irregular diameter of these fibres, and leading to possible problems in terms e. g., of water absorption [5]. It is also worth reminding that vegetable fibres are composed of sections of variable geometry with an alternation of stronger and weaker parts, as a consequence of the increasing number of defects with length, which tends to discourage the adoption of very long stretches of aligned fibres, whose entanglement can even be detrimental in case a serious damage is applied to the material [6]. This can be partially compensated by the use of woven structures, such as tissues, mats, etc., although it needs to be clarified in this case that technical fibres obtained from plants

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are in reality threads composed via the application of a torque by filaments often only loosely kept together [7]. All these difficulties have resulted in a limited adoption of modelling features for composites and hybrids including vegetable fibres, because the principal laws for predicting the behaviour of composite materials, such as the rule-of-mixtures, need to be adapted to the particular conditions, explained above, due to the presence of vegetable fibres, as was the case of recent studies [8].

In practical terms, the production of hybrid composites has been adopted as an intermediate step in reducing the environmental impact of fiberglass through the partial replacement of glass fibres with vegetable fibres, such as jute, hemp, flax, sisal, kenaf, etc. [9−11]. The limits of this substitution especially arise whenever the service performance is simulated, through dynamical testing, such as impact and fatigue [12−13]. In this case, the residual performance obtained from these materials is also important, as the presence of vegetable fibres can lead to ineffective damage absorption and especially to complex degradation modes as far as significant energy is applied to the material [14].

In recent years, basalt fibres have been considered as an alternative to glass, with some significant advantages: these include, in environmental terms, the absence of a requirement for fibre sizing, since basalt is extracted directly from the molten rock, and the improved resistance of basalt to acid environments, which is particularly desirable e.g., in the automotive sector [15−16]. As a result, basalt has also been applied in hybrid composites with vegetable fibres and with glass [17−18]. These are far from being optimised though, especially with respect to the possible effect of different stacking sequences on their properties [19]. This is of crucial importance whenever the introduction in other application sectors is proposed, such as e.g., the nautical field, where it is going to be coupled with the use of more sustainable thermosetting matrices, not exclusively oil-based.

All these considerations indicate the interest of the present work on hybrid composite materials, as a promising approach to extend the use of natural fibres (Figure 1, 2) to modern applications.

Figure 1. Field of flax

Figure 2. Bamboo plantation

2. STATE OF ART ON GREEN COMPOSITES

Currently, as already stated, numerous research groups are dedicated to minimising the environmental impact of polymer composite production, where the polymer matrices are derived from renewable resources such as polylactide (PLA), thermoplastic starch (TPS) or thermoset matrices. Their high renewable content derives from vegetable oils and, combined with natural reinforced fibers (NF) to form environment-friendly and fully degradable composite laminates, they represent a potential substitute for petroleum-based resins.

Natural matrices

„Green" matrices are partially or totally obtained by renewable sources and/or made by biodegradable polymers. The availability of bio-based polymer matrices is nowadays relatively poor (Figure 3), but it rapidly grows as more studies are done and more information is available.

Three different bio-based polymer matrices commonly used:

− Thermoset matrices: polyols are compounds with multiple hydroxyl functional groups available for organic reactions, and they react with a large number of chemical species, called curatives or hardeners, to produce cross-linked thermoset matrices. The most important oil used in polyols production is soy bean oil, but cashew nut oil can give the same results too. In order to decrease the impact of its activity on global warming, polyols can also be combined with petroleum-based chemicals.

− Thermoplastic matrices: the plastic matrix most commercially available is the cellulose one, properly toughened; therefore, it is considered a 100% bio- based matrix. Starch-based polymers and Poly lactic acid (PLA) are both available: the employment of the former depends on the ability to reduce their moisture absorption, while the latter has similar properties to polystyrene. In summary, the employment of these bio-based polymers depends on the possibility to modify their properties in order to have easier processing and improve toughness in the final biocomposite.

Figure 3. An example of bio-based resin

Green resins offer several advantages, such as:

− Low VOCs (Volatile Organic Compounds)
− Low emission of styrene
− No bisphenol or epichlorohydrin (toxic)
− Based on vegetable oil (by around 30−40%)
− No toxic exhalation
− No formaldehydes
− Hypoallergenic

But even relevant disadvantages, such as:

− Low processability
− Higher costs.

Natural Fibers

Natural fibers (Figure 4) are compounds derived by combining cellulose, hemicellulose and lignin; they can be derived from leaf (e. g. sisal), bast (e. g. flax, hemp), seed (e.g. cotton) and fruit (e. g. coir). Cellulose is a linear polymer obtained by polycondensation glucose monomer (C6H12O6).

The most important advantages of use of natural fibers are, of course, related to the environmental issues: they are biodegradable and carbon-positive since they absorb more carbon dioxide than they produce. In addition, they are non-irritating and tend to be non-abrasive, with the latter property resulting in reduced wear on tooling and manufacturing equipment. Other important advantages are shown in terms of specific material properties: by using natural fibers in substitution of synthetic ones, it is possible to reduce the weight of an artifact by up to 40% as well as to improve flexural strength, stiffness and ductility. To sum up, natural fibers as reinforcement in composites allow:

− low density, typically 1.2−1.5 g/cm^3 against 2.5 for glass and 1.7 for carbon
− good thermal and acoustic isolation
− low level of abrasion for process equipment
− low cost of materials
− easy to find and abundance of material with yearly renewable resources
− sustainable cultivation compared to other chemical processes
− biodegradability
− low toxicity for workers.

Figure 4. The most common natural fibers used as reinforcement

On the contrary, several disadvantages characterize the use of natural fibers, such as:

− variability in mechanical proprieties, related to physiological variability (e.g. age, harvest, techniques for harvest and processing, environmental and climate factors);

− not excellent mechanical proprieties, in particular, related to fatigue and creep resistance;

− low detectability in morphology, with high difficulty in controlling aspects as fibre porosity and thickness.

− biodegradability.

Natural fibers have lower density values and perfectly fit for non structural uses. In these terms, natural fibers can replace synthetic ones obtaining even more efficient results. In terms of overall strengths, for instance, even if mechanical proprieties are sometimes comparable, as in the case of fiberglass, synthetic fibres usually perform better than natural ones (Table 1).

Table 1. Physical and mechanical properties in natural and synthetic fibers

PROPERTIES FIBERS	DENSITY (g/cm^3)	TENSILE STRENGTH (MPa)	TENSILE MODULUS (GPa)	STRAIN (%)
JUTE	1.3-1.45	393-773	13-26.5	1.16-1.5
FLAX	1.50	345-1100	27.6-80.0	2.7-3.2
HEMP	-	690	-	0.6
BASALT	2.65-2.80	4000-4700	84-87	3.15
SISAL	1.45	468-640	9.4-22.0	3-7
E-GLASS	2.5	2000-3500	70	2.5
ARAMID	1.4	3000-3150	63-67	3.3-3.7
CARBON	1.7	4000	230-240	1.4-1.8

Processing and processability

Regarding processes, literature data on green composites show a clear prevalence of wood and natural fibers in combination with polyolefins: this influences the information available on processing and processability. Typical processing techniques include extrusion followed by injection or compression molding. During processing, temperature must not exceed 200 °C and the retention time of the material exposed to high temperatures should not be too long to avoid fiber degradation. Very common technologies for composite materials include resin transfer molding, vacuum injection molding, structural reacting injection molding, injection molding and compression molding. In specific applications, as prototypes, resin infusion and hand-up molding is also used.

3. MATERIALS AND METHODS

The potential relevance of hybridization in improving the mechanical proprieties of natural composites and, as a consequence, in extending the field of application for this class of material can be investigated by specific experimental sessions as performed by authors in previous studies [17,20−22].

In particular, during an investigation focused on sustainable materials for sailing applications [23], five types of laminates were produced by resin infusion and hand-up molding. Three of them were composed of two natural fibers, flax or basalt (Figure 5) combined with eco-friendly matrices (epoxy or vinylester). The other two were hybrids, obtained by combining fibers (natural or not), mixed with green thermoset resin: the first one is compound with both synthetic and natural fibers (carbon and flax), and the last one is a compound with two different natural fibers (basalt and flax) (Figure 6).

Finally, for the sake of comparison, two „traditional" glass fiber-reinforced composites were manufactured, one obtained combining fibers with polyester resin and the other using glass fiber fabrics with epoxy as impregnant.

Flax fibers are commonly used for natural reinforced composites. They are considered to be complementary to glass ones. In terms of comparison, flax fibers tensile modulus is very close to glass fibers one, while their lower density makes them lighter. They can also be matched to the most important thermoset resins.

Basalt fibers are quite similar to carbon and glass fibers. They are cheaper than the first ones and have better mechanical properties than the second ones. At the same time, basalt fibers are ecologically clean and non-toxic for the end user.

Epoxy is, probably, the most common choice of resin for matrix in the production of composite materials. Its chemical formulation can largely be changed offering radically different properties to the materials. In the case of "green epoxy", a high percentage of carbon biomass is included, in which 56% of the molecule is bio-renewable because of its plant origin.

Vinylester matrices have been patented as a revolutionary resin technology with extremely low content and emission of styrene. This low-VOC and low-HAP resin formulation minimizes emissions thus reducing workplace exposure and environmental impact.

The composition of the laminates used during the tests is shown in Table 2.

Figure 5. Natural and technological fibers used as reinforcement during experiments: flax, basalt, carbon and glass

Table 2. Details of composition for laminates

SPECIMEN	FIBER	MATRIX	ECO
I	FLAX	EPOXY (green)	Green
II	FLAX	VINYLESTER (low styrene)	Green
III	BASALT	VINYLESTER (low styrene)	Green
IV	FLAX-CARBON	EPOXY (green)	Hybrid
V	FLAX-BASALT	VINYLESTER (low styrene)	Hybrid
VI	GLASS	POLYESTER	Synthetic
VII	GLASS	EPOXY	Synthetic

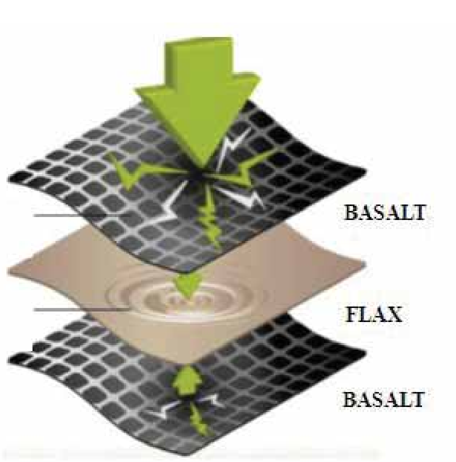

Figure 6. Example of stratification of layers in a hybrid material

In order to determine all mechanical properties of green materials and hybrid laminates, four tests have been carried out according to the relevant standards (Figure 7):

− Tensile test is performed according to ASTM D 3039 standard: a thin flat strip of material having a constant rectangular cross section is mounted in the grips of a mechanical testing machine and monotonically loaded in tension while recording load. The ultimate strength of the material can be determined from the maximum load carried before failure.

− Flexural test is performed according to ASTM D 790 standard: a bar of rectangular cross section rests on two supports and is loaded by means of a loading nose midway between the supports.

− The drop-weight impact test is performed, according to ASTM D 7136.

− Standard, using a balanced, symmetric laminated plate. Damage is imparted through out-of-plane, concentrated impact (perpendicular to the plane of the laminated plate) using a falling weight with a hemispherical striker tip. The damage resistance is quantified in terms of the resulting size and type of the damage in the specimen.

− Accelerated aging test uses aggravated conditions of heat and saline solution to speed up the normal aging processes of materials. It is used to determine the long-term effects of expected levels of stress within a shorter time, usually in a laboratory by controlled standard test methods.

Figure 7. Performing experimental (tensile) tests

A full description regarding the experimental sessions and measures are available in [23−25]. A brief synthesis is here reported.

4. EXPERIMENTAL EVIDENCES

Elastic modulus and yield/ultimate stress from experimental sessions are reported in Table 3. Stress-strain diagrams in the case of synthetic, natural and hybrid fibers for tensional and flexural tests are reported, respectively, in Figures 8−9.

Since these earliest results, it is already evident that green composites (e.g. basalt fiber and vinylester matrix) can perform like other most common materials (e. g. fiberglass), but adding an important property of eco-sustainability.

In particular, basalt is a mineral fibre with several important properties as total reuse, high mechanical characteristics (stress resistance and elastic modulus 15−20% higher than glass fibre). It is evident how basalt represents a valid alternative to fiberglass (with an exception of the price) and can challenge with carbon in a significant range of advanced applications.

The stress-strain diagrams clearly show how changes in the composition (as fibers and matrices), permitted by hybridization, not only effect the mechanical resistances, but also the material behaviour as a whole. For instance, mixing flax fibers with basalt fibers, reduces the mechanical (flexural and tensile) resistance, but, on the other side, transforms a brittle composite in a ductile material.

Table 3. Mechanical proprieties of laminates

N.	FIBERS	MATRIX	Tensile					Flexural		
			σ MPa	ε %	E MPa	G MPa	ν –	σ MPa	ε %	E MPa
I	FLAX	EPOXY	–	–	–	–	–	115.0	1.66	6930
II	FLAX	VINYLESTER	47.5	0.93	4854	2001	0.21	–	–	–
III	BASALT	VINYLESTER	165	1.47	11042	5368	0.03	266.7	1.84	14481
IV	FLAX- CARBON	EPOXY	–	–	–	–	–	–	–	–
V	FLAX- BASALT	VINYLESTER	86.5	1.12	8151	3879	0.13	139.5	1.69	8275
VI	GLASS	POLYESTER	67.05	0.89	8808	3755	0.17	127.5	2.16	5898
VII	GLASS	VINYLESTER	92.4	–	–	–	–	168.8	2.74	6157

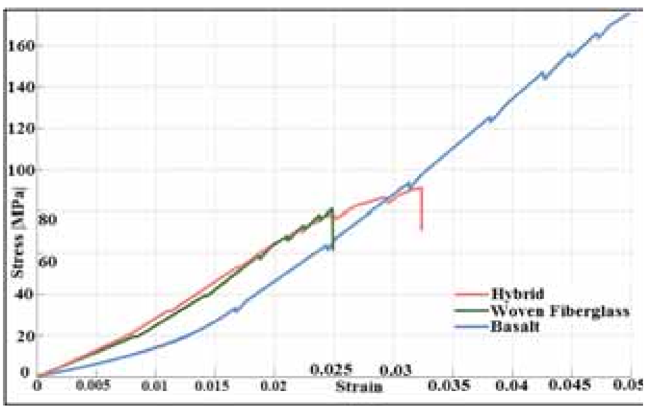

Figure 8. Tensional stress–strain diagram in the case of synthetic, natural and hybrid fibers

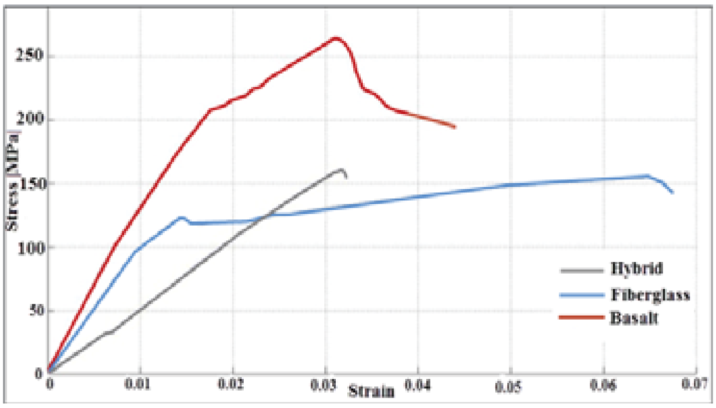

Figure 9. Flexural stress–strain diagram in the case of synthetic, natural and hybrid fibers

5. CONCLUSION

New environmental regulations and changing governmental attitudes encourage the research of new products and processes in an environmental-friendly manner. Green composites seem to represent an emerging eco-sustainable alternative to composites produced by traditional synthetic fibres and matrixes. The use of natural fibres within composite materials is predicted to become a growing market. Natural fiber-reinforced biodegradable polymer composites appear to have a bright future for a wide range of applications. These biocomposites, characterised by various interesting technical properties, may soon be competitive with the existing fossil plastic materials. However, the present low level of production of natural fibers and resins, and, as a consequence, their higher cost in the market, reduces their applicability in industrial uses. Using hybrid systems for improving materials or structural performances of composites is a well-known concept in engineering design. All investigations have shown that the properties of hybrid natural/glass composites have proved to be an effective way to improve composite's mechanical properties and dimensional stability (moisture, temperature, etc.). The stiffness of biocomposites can thus be overcome by structural configurations that place material in specific locations for higher structural performances.

6. ACKNOWLEDGMENT

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ПОБОЉШАЊЕ ПЕРФОРМАНСИ И ПРИМЕНЉИВОСТИ ЗЕЛЕНИХ КОМПОЗИТНИХ МАТЕРИЈАЛА ХИБРИДИЗАЦИЈОМ

Сажетак: Раст забринутости због еколошких питања и заједнички интерес да се пронађе одржива алтернатива употреби стакла или угљеничним ојачањима композита довело је до повећаног истраживања еколошки одрживих композитних полимера. Ови „зелени” материјали су направљени од природних влакана, а да би се ојачали напуњени су природним органским смолама, дакле биодеградабилним, или изведени из обновљивих извора. Истовремено, ова нова класа материјала релативно се суочава са неколико ограничења у односу на традиционалне композите, посебно у погледу својстава саме отпорности. Овај рад истражује предности коришћења комбинације природних влакана за побољшање механичких особина „зелених” композитних материјала. У овом тренутку, опште мишљење је да зелени композити нису употребљиви у структурним апликацијама, и као последица тога, потиснути су ка неприкладним апликацијама (као пунила). Напротив, постоји неколико доказа да мешање различитих природних влакана (у пракси обично познато као

„хибридизација”) доводи до побољшања механичких особина. Чак и ако обично ограничена у процентима, с времена на време ова побољшања дозвољавају проширење у области апликација за зелене композите. Након праћења светских трендова и знања о зеленим композитима, укључујући и потенцијалне користи и ограничења ових материјала, овај рад предлаже неколико примера укрштања влакана показујући њихов утицај на механичке особине.

Кључне ријечи: еко-одрживост, механичка својства, полимер-матрица композита, лан, базалт, винил-естар.

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