Manufacturing and mechanical response optimization of epoxy resin/Luffa Cylindrica composite

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ABSTRACT: The present investigation pertains to the existent possibilities of the fibrous natural material Luffa Cylindrica (LC) as reinforcement to thermoset resins. The main purpose was the manufacturing of an engineering material that would, simultaneously, lead to a more sustainable world. In an effort to optimize the final mechanical properties, semi- green Epoxy Resin/Luffa Cylindrica (ER/LC) composites were manufactured, applying a number of different manufacturing parameters combinations. The manufacturing parameters taken into account were: (a) fiber chemical treatments; (b) the external applied pressure during curing; (c) number of plies; (d) stacking sequence effect; (e) LC's structural characteristics; and (f) the influence of fiber weight fraction on composite's behavior. The elastic flexural response of the composite polymer was found improved with respect to neat polymer's response due to fibers' nature and the applied manufacturing optimization process. This improvement was reflected to material's stiffness which optimally increased by 48% for a mechanically applied pressure of 4.6 kPa during curing. Additionally, LC fibers chemically treated with Acetone/ CH_3COOH 1 wt % led to stiffness' improvement up to 30%. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41992.

INTRODUCTION

Natural fibers are worldwide spread as a renewable source of material, abundant in nature. Their light weight and low cost—combined with superior environmental performance in relation to conventional engineering fibers[1,2]—establish them as a strong alternative for various industries, particularly those who are interested in composites.[3–11] Their biodegradability and combustion without producing harmful gases or solid residues, the energy recovery and recyclability of their end-of-life products contribute to a healthier ecosystem[12–16] while their engineering performance fulfill the needs of structural applications.[17–20] Although scientific interest seems to grow, investigation on natural reinforcements has to deepen since transition from research to industrial mass production is in its infancy. In particular, European automotive industry is claimed to use some thousand tons of natural fibers as reinforcements in no critical automotive parts.[21–23] However, the range of selected materials remains small while a multitude of other less known fibers is waiting to emerge. In any case, the manufacturing of (semi-)green composites able to satisfy the required mechanical, thermal, and chemical standards for their practical application and also able to provide recyclability, is regarded with great optimism.

A kind of natural reinforcement merely explored is *Luffa Cylindrica*. LC is the fruit of a sponge-type plant belonging to Curcubitacea family. Common sponges vary in length from 15 cm to 1.5 m[24] while their basic ingredients are the organic substances cellulose (60%), semi-cellulose (30%), and lignin (10%).[25] Plant's composition depends on its type, variety, age as well as its surrounding environmental conditions.[26] Regarding LC's morphology and structure, a feature that has already been illustrated and reveals significant value is its fibrous network nature. The geometry of a LC sponge is cylindrical and it entirely consists of continuous fibers (Figure 1). These fibers are joined together into the cylinder, forming an interlaced structure of micro-trusses. In fact, the whole structure is a fibrous vascular system of networks, each one consisting of micro-trusses. However, fibers within a LC cylinder may grow in different directions but macroscopically they exhibit specific patterns (dominant fiber directions). On the inner surface, fibers grow along longitudinal direction while on the outer surface fibers grow along circumferential direction. In the core region, fibers follow the radial direction.[27]

In general, LC sponge's features can be gathered in such: abundance in nature, low cost, non- toxicity,[28] physical and chemical stability during life expectancy, biodegradability after disposal in
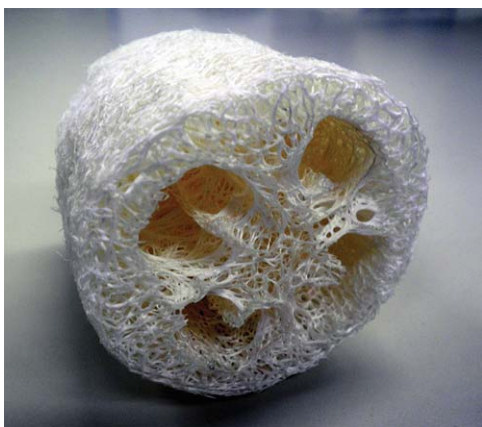
Figure 1. LC fibers network morphology and structure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

composting conditions.[27] These features guarantee LC sponge's commercial viability and easy supply, promoting it as a sustainable environmental product. Albeit biological, LC has revealed significant mechanical properties.[27–33] According to previous studies, a LC fiber has 11.1 ($\pm$85%) MPa tensile strength, while its Young's modulus is 1.3 ($\pm$35%) GPa.[34] Additionally, it is found that LC's energy absorption capabilities are comparable to those of some metallic cellular materials such as aluminum foams and Ni–P microlattices.[27] As seen in Table I, the mechanical properties of various natural fibers are illustrated while compared to LC fibers. From the table, it is noticed that LC tensile strength is relatively mere in respect to these of the other natural fibers. However, considering the specific modulus, LC fibers display a comparable to coir fibers performance.

LC sponges are spread worldwide mainly as cosmetics products and bath sponges. Research has also indicated LC as a potential alternative material for packaging,[36] a removal adsorbent of toxic products from aqueous solutions/ heavy metals from industrial waters,[37–42] a biofuel with low CO_2 emissions,[43] a filter for diesel and steam engines[39] as well as a biomaterial.[44–46] Indicatively, LC is used for medical purposes in sinus conditions,[26] in biotechnology as carrier for plant cell immobilization,[47–51] as a drug controlled release system in wound dressing and wound healing,[52] as a natural medicinal drug[53] etc. However, one of the most restrictive parameters in finding new applications—or widen the already known—is the lack of scientific data concerning materials' structures and properties. In fact, LC fibers do not find engineering acceptance due to a limited field of knowledge. Therefore, it was claimed that a static characterization of LC as a reinforcing material was needed.

Motivated by low density, light weight structures with less environmental impact and targeted to automotive and construction industries, the semi- green Epoxy Resin/Luffa Cylindrica (ER/ LC) composite was designed. Non-structural components like door upholstery or rear shelves and other interior paneling for track vehicles, as well as exterior decks, door paneling elements and other structural elements can be some of the potential applications. Nonetheless, the use of natural fibers in automobiles is partially restricted to non-critical component applications due to poor bond strength between the phases and thus fiber chemical pre-treatment is often required.

In the present investigation, the semi- green Epoxy Resin/Luffa Cylindrica (ER/LC) composite was manufactured using various different manufacturing parameters such as: various fiber chemical treatments, application of external pressure during composite curing, number of plies and fiber orientation, position of

Table I. Mechanical Properties of Various Natural Fibers

Type of fibre	Density g/cm^3)	Elongation (%)	Tensile strength (MPa)	Young's modulus (GPa)	Specific modulus (GPa·cm^3/g)	Ref.
Cotton	1.5-1.6	2.1-12.0	200-600	5.0-15.1	3.3-10.1	[35]
Jute	1.3-1.5	1.4- 2.1	385-850	9-31	6.9-20.7	[35]
Flax	1.3-1.5	1.1-3.3	340-1600	25-81	16.7-54	[35]
Ramie	1.4-1.5	1.5-4.0	200-1000	41-130	27.3-81	[35]
Sisal	1.3-1.6	1.9-15	400-700	8.5-40	6.5-30.8	[35]
Bamboo	1.2-1.5	1.9-3.2	500-575	27.0-40.0	67.9-50	[35]
Hemp	1.1-1.6	0.8-3.0	285-1735	14.4-44.0	9.6-29.3	[35]
Kenaf	0.6-1.5	1.6-4.3	223-1191	11-60	10-42.9	[35]
Abaca	1.5	1.2-1.5	430-815	31.1-33.6	N/A	[35]
Oil Palm	0.7-1.6	4-18	50-400	0.6-9.0	0.5-7.5	[35]
Betelnut	0.2-0.4	22.0-24.0	120-166	1.3-2.6	1.0-1.9	[35]
Sugarcane Bagasse	1.1-1.6	6.3-7.9	170-350	5.1-6.2	3.6-4.1	[35]
Coir	1.2-1.6	14.0-30.0	170-230	3.0-7.0	2.5-5.0	[35]
Banana	0.5-1.5	2.4-3.5	711-789	4.0-32.7	3.6-27.3	[35]
Pineapple	1.56	2.4	150-1627	11-82	7.8-57.0	[35]
Luffa Cylindrica	0.35-0.65	N/A	1.7-20.5	0.9-1.8	2.55-5.1	[27,34]
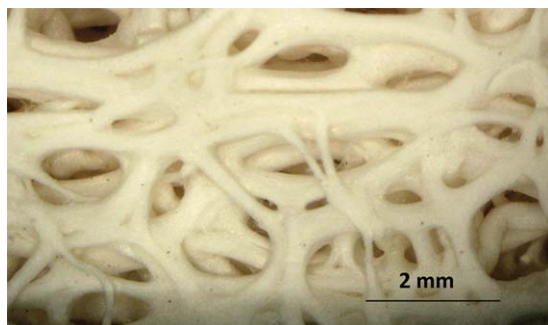
Figure 2. Interfiber pores observed on the supplied LC samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

plies by taking into account LC's structural characteristics, as well as a variable fiber weight fraction into composite. The aim of this parametrical study was the achievement of the optimum composite's mechanical behavior. Specimens were thereafter mechanically characterized by executing three-point bending (3pb) tests along with SEM observations, in order to mainly focus our attention on the structural integrity characteristics of the materials manufactured. The applied manufacturing optimization process led to a considerable improvement of the elastic response of the polymer composites as compared to the neat resin. More precisely, material's stiffness was increased by 48% by applying a mechanical external pressure of 4.6 kPa during composite curing. Additionally, LC chemically treated with Acetone/ CH_3COOH 1 wt % led to stiffness' improvement on the order of 30%.

EXPERIMENTAL

Supplied Fibers Condition

The LC sponges, supplied by Ningbo Kanger Greenees Consumer CO, LTD., were received in form of dry compact layers composed of long continuous fibers parallel oriented to the longitudinal direction of each layer. The plies had dimensions 150 mm in length, 120–140 mm in width and 2–2.5 mm in thickness.

A LC reinforcing ply constitutes a discontinuous body, consisted of pores throughout its extent in the range of millimeter scale (1–4 mm) (Figure 2). Within each layer, fibrils coexist with each other forming micro-trusses, retaining the main orientation fibers together and parallel. Thus, material's structure is quite complicated, especially if it is taken into account laminas' regions where fibers grow in orientations different from the main one.

A layer surface represents the inner surface of a LC column and it is characterized by two regions [Figure 3(a)]. A region defined by a total order of fibers, parallel oriented to lamina's longitudinal direction and a region defined by a random order of fibers interconnected with each other in various directions (nevertheless, two dominant directions: [±45] can be observed). These morphological characteristics are justified by material's processing method during the change of its global geometry from cylinder to lamina. This transformation requires a longitudinal section at any point of cylinder's circumference throughout its wall thickness. Subsequently, the new lamina is subjected to compression throughout layer's thickness leading to the inte-

gration of the damaged core fibers to material's new main body, forming these randomly oriented regions.

Pure Resin Specimens Manufacturing

The matrix material was in all cases a resin, with the commercial designation RENLAM© CY 219, HUNTSMAN, cured with the Ren© HY 5161, HUNTSMAN hardener at a weight ratio 2 : 1. The pre-polymer was heated up to 50°C in order to have its viscosity decreased. Proper amounts of curing agent were, subsequently, added and the mixture—after being stirred thoroughly—was put in a vacuum chamber for 7 min in order to be degassed. Subsequently, it was cast into a rectangular glass mould 160 × 140 × 4 mm, previously cleaned and polished. The material was subjected to a 24 h thermal processing, consisting of a temperature rise at 5°C/h, maintained constant at 50°C and finally dropped to ambient at 1°C/h. In this way, complete polymerization of the matrix material was obtained and, consequently, the properties of the final product were not exhibiting any storage-dependence. The 3pb test specimens were machined from each casting, i.e., three beam specimens with dimensions of 100 × 12.8 × 2.2 (±0.2) mm.

Composite Manufacturing

The manufacturing process was carried out in a female mould—a glass mould with a polished surface on the inside. The following procedure was adopted:

1. The mould was washed carefully with acetone solution to remove any old release agent, dust, grease, finger marks, etc and, subsequently, dried thoroughly.
2. A mould release wax was applied with a circular motion, using a small piece of cloth. Care was taken to remove all streaks of wax.
3. Each LC layer had previously been cut to the shape of the mould by approximate measurements taken directly from the mould.

A lay-up process took place in the following stages:

1. The laminating resin was weighed out and then catalyzed.
2. A brush or roller was used to apply a liberal coating of resin to the mould surface.
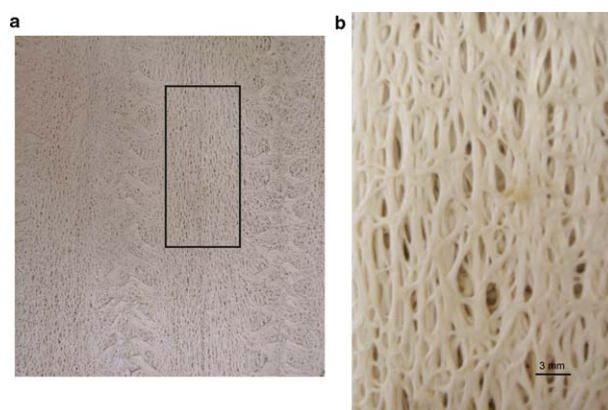
Figure 3. (a) Macroscopic view of a LC layer as received. (b) Region of ply experimentally exploited. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. A single ply and a double ply ER/LC specimen after 3pb. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

3. A shaped LC layer was placed carefully in the mould and the previously applied resin passed through it. Additionally, resin was applied to the other surface of the ply and all fibers were stippled or rolled until thoroughly and evenly wetted out with resin.

4. In the case of a double-ply laminate, a second LC layer was applied as soon as the first was thoroughly wetted out.

5. Immediately after the second layer had been applied, a compression roller was used to compress the laminate, squeeze the air bubbles and impose the excess quantity of resin to flow out from the laminate. This technique appreciably improves the strength of the composite by increasing its density and reducing its porosity on the inside surface and therefore, it was important that the roller be used firmly and evenly across the entire surface.

6. The system was cured into an oven at 50°C for 24 h. In some cases, additional external mechanical pressure was applied to the laminate system during curing.

Since the laminate would generate heat during the polymerization of the resin, it was important to limit the thickness of the lay-up. Otherwise, there would be a risk of over-heating the molding which could result in warping and weakening of the finished product.

Simultaneously with ER/LC, neat resin plates were also manufactured. That was claimed crucial due to the need of distinguishing between the reinforced and the unreinforced thermoset (reference material) and getting the prospective reinforcing value revealed.

From the manufactured composite plates, specimens were cut in dimensions 100 × 12.8 × 2.2 (±0.2) mm in order to determine composite's bending behavior (Figure 4). Specimens were strictly taken from the areas of the plate where the reinforcing fibers had common orientation [Figure 3(b)]. Where necessary, a slight smoothing of the transverse surfaces was applied in order to avoid the development of edge stresses. Six specimens—per each specific combination of parameters studied— were manufactured and subsequently tested.

Table II. Matrix RENLAM© CY 219, HUNTSMAN Physical Properties

Property	Unit	RENLAM CY 219
Appearance Color	Visual	Clear liquid Amber
Viscosity at 25°C	mPa/s	10,000–12,000
Density	g/cm^3	1.1

Table III. Hardener Ren© HY 5161, HUNTSMAN Physical Properties

Property	Unit	Ren© HY 5161
Appearance Color	Visual	Clear liquid Amber
Viscosity at 25°C	mPa/s	30–70
Density	g/cm^3	1.0

Table IV. Resin/Hardener Mixture Physical Properties

Property	Unit	RENLAM CY 219
Appearance	Visual	Yellowish
Viscosity at 25°C	mPa/s	1,000–1,200
Density	g/cm^3	1.1

Reinforcement weight fraction was calculated as:

$$W_f(\%) = \frac{\text{LC layer(s) mass x 100}}{\text{composite mass}}$$

The physical properties of the neat resin, the hardener and the mixture are tabulated in Tables (II–IV).

Manufacturing Optimization—Parametrical Study
There is an abundance of options concerning the possible combinations of manufacturing parameters, as each one of them leads to a different material structure and finally to a different macroscopic behavior of the material. On the grounds of behavior optimization, we altered one manufacturing parameter at the time, keeping all the rest constant. Subsequently, 3pb tests were conducted in order to determine the static properties of each structure and to reveal the optimal ones.

Fiber Chemical Treatments. A range of coatings was imposed to natural LC before manufacturing procedure, in order to enhance compatibility between fibers and matrix.[54–56] The adhesion between fibers and matrix is known to be crucial.[25,26,29] Therefore, six different chemical coatings were applied to the surface of LC fiber to increase fiber-matrix adhesion (Table V). Given the origin of the raw material and its highly hygroscopic behavior, acetone and acidic solutions in acetone were used to clean up the fibers.

1. Acetone clean-up, 6 h/ 37°C/ supersonic assistance.
2. 1 wt % Formic Acid in acetone, 6 h/ 37°C/ supersonic assistance.
3. 1 wt % Acetic Acid in acetone, 6 h/ 37°C/ supersonic assistance.

Table V. Types of Fiber Chemical Treatments Applied

I	Acetone
II	Acetone/ 1% HCOOH
III	Acetone/ CH_3COOH 1%
IV	CH_3CN: $(CH_3CO)_2CO$/ 3 : 1/ $HClO_4$ (catalyt.)
V	1M NaOH (aq)/ H_2O_2
VI	1M NaOH (aq)/ H_2O_2/ CH_3CN/ $(CH_3CO)_2CO$/ 3 : 1

Chemical surface treatment has also been applied:

4. A modification of the acetylation technique was applied, by soaking (6 h/ 37°C/ supersonic assistance) the fibers in Acetonitrile/ Acetic Anhydrid 3 : 1 mix, at the presence of HClO4.
5. Alkali treatment (NaOH) in aqueous solution (mercerization) followed by peroxidation.

Finally, a combination of acetylation and mercerization was used.

The chemically treated LC layers were, afterwards, used as reinforcements to single-ply epoxy matrix composites. All composites manufactured were unidirectional ([0]). A 2 : 1 matrix to hardener mass ratio was in all cases used and the external applied pressure—during the whole period of curing—was kept at 4 kPa.

Influence of the Mechanically Applied Pressure During Curing on ER/LC Static Properties. A range of different mechanically applied pressures was imposed to the—under construction—material during curing, in order to find the pressure effect that leads to the optimum static properties.

The values of the mechanically applied pressures were 2.9 kPa, 3.6 kPa, 4.2 kPa, 4.6 kPa, and 4.9 kPa. One LC ply without any coating was in all cases used. Fibers' orientation was axial [0] and the matrix to hardener mass ratio was in all cases 2 : 1.

Manufacture of Double Ply Composites. *Influence of number of plies (on-axis structures).* Number of plies was increased from 1 to 2 so that ER/LC [0_2] structure could be compared to untreated ER/LC [0] as well as to neat resin. None coating was applied, while fibers' orientation was axial in both plies ([0_2]). In all cases a 2 : 1 matrix to hardener mass ratio was used and the externally applied mechanical pressure was kept constant at 3.6 kPa during the whole period of curing.

Position of ER/LC [0_2] plies depending on LC's structural characteristics. As already mentioned, LC cylinder can be divided into four regions, namely, the inner surface, the outer surface, interlayer and core. Each one of them is characterized by different structure, fiber orientation and interconnection. Since LC sheets supplied were derived by cutting and flattening the original LC cylinder fruit, the two faces of the supplied sheets presented differences in structure and roughness. The so-called external surface of a LC sheet is much more matt and rough, in comparison to the so-called internal surface. Thus, there was a question about how the successive layers had to be placed (the one on top of the other) and if the specific placement would affect the final mechanical properties of the double layered laminate. Then, it was decided two alternatives to be checked and studied, namely: (a) the two matt (external) surfaces of the two plies to face each other and (b) the external surface of the first ply to be in contact with the internal surface of the second ply.

None coating was applied to the fibers. Fibers' orientation was axial in both successive plies ([0_2]) while the matrix to hardener
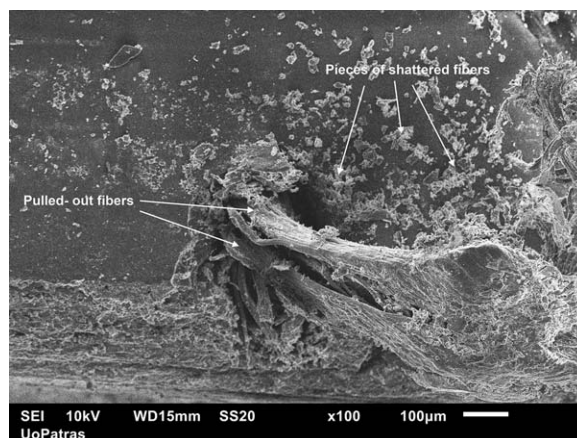
Figure 5. Scanning electron photomicrograph of a single ply ER/LC coated with CH_3CN: $(CH_3CO)_2CO$/ 3 : 1/ $HClO_4$ (solution IV). Transverse fracture section, pulled-out fibers (x100).

mass ratio was 2 : 1 and a uniform surface pressure equal to 3.6 kPa was applied during the whole period of curing.

Influence of fiber weight fraction on ER/LC's static properties. Preserving all the rest parameters constant, resin mass content was increased from 50 wt % to 70 wt % in order the ideal matrix quantity and its influence on the ER/LC's composite mechanical response to be investigated. Two LC uncoated plies ([0_2]) with axial fibers' orientation were used in all cases. The external applied pressure was kept at 3.6 kPa during the whole period of curing.

Changes in stacking sequence (off-axis structures). Besides [0_2] (on-axis) specimens, off-axis specimens fiber orientation [90_2] and [± 45]$_T$ were also manufactured and characterized. None coating was applied while a 2 : 1 mass ratio of resin and hardener was used and a uniform surface pressure equal to 3.6 kPa was applied during the whole period of curing.

Techniques for Composite's Mechanical and Morphological Characterization. *Morphological characterization.* A GEOL JSM 6610 LV Scanning Electron Microscope (SEM) was used in order to examine fibers' surface topology and morphology. Also, a LEICA MZ 16 Stereomicroscope was used in order to capture LC plies' surface microstructure.

Three-point bending testing (3pb). The static experimental characterization of composite structures was carried out according to ASTM D790-99. The 3 pb flexural tests were conducted at a Universal testing tensile machine INSTRON 4301 with a span at 63 mm and a strain rate at 1 mm/min. Flexural strength and strain at maximum stress were, respectively, evaluated by the following formulas based on the classical bending theory:

$$\sigma_f = \frac{3Pl}{2wt^2}$$

$$\varepsilon_f = \frac{6vt}{l^2}$$

where P is the external applied load, v the mid-span displacement, l is the span length, w is the specimen's width, and t is the specimen's thickness.
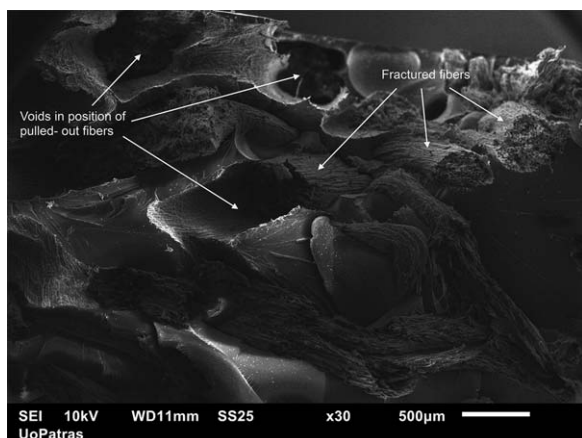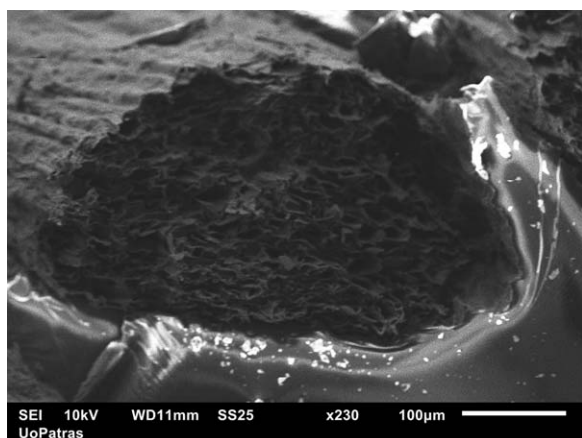
Figure 6. Scanning electron photomicrograph of a single ply ER/LC coated with 1*M* NaOH (aq)/ H_2O_2 (solution V). Transverse fracture section (x30).

Figure 8. Scanning electron photomicrograph of a single ply ER/LC coated with 1*M* NaOH (aq)/ H_2O_2 (solution V). Cross- section of a LC fiber (x1000).
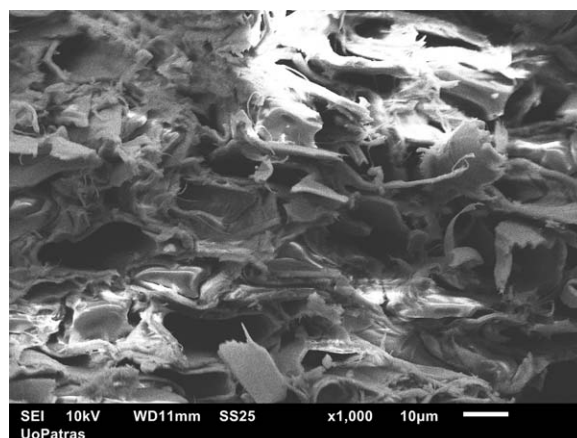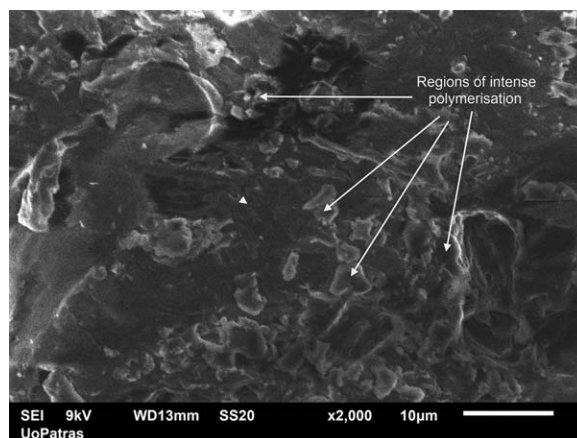
RESULTS AND DISCUSSION

Figure 5 shows the main body of two LC fibers in a transverse fracture section of the composite, as well as fibers' deformation at break. Air voids and pieces of shattered fibers are also observed on the polymer surface. Poor adhesion between fibers and matrix becomes apparent with a large void being formed at the interface. Fractured fibers and formed voids in several locations, where fibers were pulled-out, can also be observed through SEM in Figure 6.

Figure 7 shows the microstructure profile of a LC fiber which is partially covered by resin. As far as wetting is concerned, a problem that can cost adhesion gets revealed. As seen in Figure 8, in a molecular level, there is a complex structure of random molecular orientation where cellulose, semi-cellulose and lignin coexist, forming an interlaced network.

In Figure 9, the amorphous mass of resin is depicted. More and less cured regions can be observed, while the islets of intensive curing actually constitute, in part, some reinforcing regions

embedded into the mass of the thermoset itself, creating in that way a *hybrid composite polymer.*

Mechanical Characterization

Fiber Chemical Treatments. As shown in Table VI, amongst the seven ER/LC [0] different coated structures, the composite structure treated with *Acetone/CH₃COOH 1% (III)* showed the highest bending modulus. In contrary, as shown in the same table, the highest strength and strain at maximum stress were presented by the ER/LC structure whose reinforcement was treated with *1M NaOH(aq)/H₂O₂ (V).* For convenience, the uncoated LC fibers are marked as ULC.

Regarding the majority of the comparative test results, bending modulus was improved when compared to that of the pure resin (Table VII). Chemical coatings contributed to the highest stiffness increase were: (a) *Acetone/ CH₃COOH 1% (III)*; (b) *CH₃CN: (CH₃CO)₂CO/ 3 : 1/ HClO₄ (catal.) (IV);* and (c) *non-chemically treated fibers (ULC).* In contrary, a decrease in strength and strain at maximum stress was observed in almost all cases.

Figure 7. Scanning electron photomicrograph of a single ply ER/LC coated with 1*M* NaOH (aq)/ H_2O_2 (solution V). Transverse fracture section, cross- section profile of a LC fiber (x230).

Figure 9. Scanning electron photomicrograph of a single ply ER/LC coated with CH₃CN: (CH₃CO)₂CO/ 3 : 1/ HClO₄ (solution IV).Amorphous bulk matrix (x2000).

Table VI. Mechanical Properties of ER/LC [0] for the Different Chemical Coatings (W_f = 25 wt %)

Coating	Bending Modulus (GPa)	Strength (MPa)	Strain at σ_u (%)	Bending modulus standard deviation (GPa)	Strength standard deviation (MPa)	Strain at σ_u standard deviation
Acetone (I)	2.89	44.22	2.61	0.025	2.8	0.000
Acetone/ 1% HCOOH (II)	2.692	55.51	3.8	0.193	0.474	0.002
Acetone/ CH$_3$COOH 1% (III)	3.119	55.17	3.64	0.008	1.124	0.006
CH$_3$CN: (CH$_3$CO)$_2$CO/ 3:1/ HClO$_4$ (catal.) (IV)	3.074	65.2	4.19	0.101	0.736	0.007
1M NaOH(aq)/ H$_2$O$_2$ (V)	2.716	67.77	4.93	0.006	1.782	0.009
1M NaOH(aq)/ H$_2$O$_2$/ CH$_3$CN/ (CH$_3$CO)$_2$CO/ 3:1 (VI)	2.31	48.47	3.62	0.005	0.304	0.001
Non- treated (ULC)	2.971	60.41	4.03	0.139	3.861	0.004
pure resin	2.4	72.12	4.48	0.029	0.239	0.002

An explanation of strength's unsuccessful improvement could be the deficient wetting of fibers by the matrix which, subsequently, resulted to reduced load transfer from the matrix to the fibers. In addition, existed fiber pores play the role of stress concentration points from where crack propagation may initiate, leading to a strength reduction.

ER/LC [0] 1M NaOH(aq)/ H$_2$O$_2$ (V) strength—although higher than any other structure—was 6.03% lower than the relevant matrix strength (Table VII). As far as strain at maximum stress is concerned, chemical solution NaOH(aq)/ H$_2$O$_2$ (V) provided not only the maximum but also the only one higher in relation to neat resin's strain. Mercerization followed by peroxidation is known in literature as the "mixed treatment" and it constitutes one of the most effective methods for treating natural fibers.[25] In the present study, 1M NaOH(aq)/ H$_2$O$_2$ (V) coating provided the highest strength and strain at maximum stress among all coatings and relevant structures, while it also achieved to increase (up to 13.17%) composite's stiffness.

Regarding non-treated LC (UCL), it is interesting to note that natural layers can sufficiently reinforce epoxy matrix, providing a 23.79% modulus improvement (Table VII). Also, ER/LC

treated with *Acetone/ CH$_3$COOH 1% (III)* and *1M NaOH(aq)/ H$_2$O$_2$ (V)* provide only a 4.98% higher stiffness and a 12.18% higher strength respectively, in relation to naturally reinforced composite (Table VIII).

Thus, on the basis of stiffness (and not strength for which there was no improvement), it can be claimed that ER/LC non-chemically treated has similar response to ER/LC treated with Acetone/CH$_3$COOH 1 wt %. Therefore, there are strong grounds for avoiding manufacturing by chemical means with the aim of designing a more environmentally friendly composite (chemical solvents are environmentally harmful products).

At this point, we would like to stress our attention to data found in literature. Although such relevant sources can hardly be found in literature, to authors' knowledge, two published articles[57,58] are on an epoxy resin reinforced with LC fibers. More precisely, Saw et al.[57] claimed to have enhanced tensile properties of an epoxy resin system by reinforcing it with (a) untreated LC fibers; (b) alkali-treated fibers and (c) grafted fibers. Specifically, the tensile strength and modulus of pure epoxy were recorded at 6.9 MPa and 166 MPa respectively, while composite's properties were found, in all cases, enhanced in relation to those of neat matrix. Regarding the composite structure with untreated fibers, figures show an improvement of

Table VII. Deviations of Mechanical Property Values of the Different Coated ER/LC [0] Structures from Those of Pure Resin

Reference material: pure resin			
	Bending Modulus (%)	Strength (%)	Strain at σ_u (%)
I	20.42	−38.69	−41.74
II	12.17	−23.03	−15.18
III	29.96	−23.50	−18.75
IV	28.08	−9.60	−6.47
V	13.17	−6.03	10.04
VI	−3.75	−32.79	−19.20
ULC	23.79	−16.24	−10.04

Table VIII. Deviations of Mechanical Property Values of the Different Coated ER/LC [0] Structures from Those of ULC [0]

Reference material : ULC			
	Bending Modulus (%)	Strength (%)	Strain at σ_u (%)
I	−2.73	−26.80	−35.24
II	−9.39	−8.11	−5.71
III	4.98	−8.67	−9.68
IV	3.47	7.93	3.97
V	−8.58	12.18	22.33
VI	−22.25	−19.76	−10.17
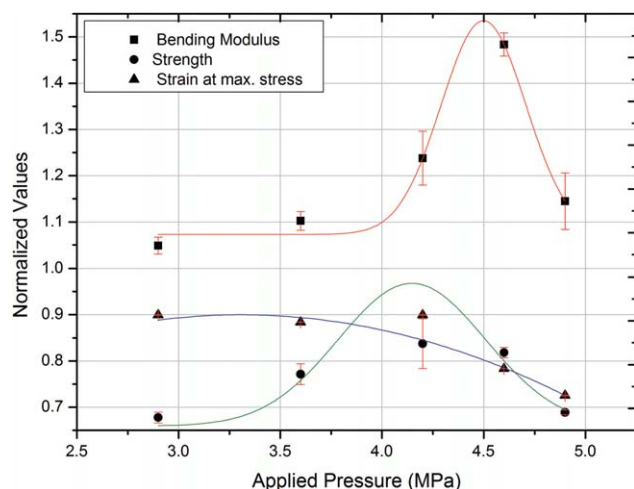
Figure 10. Normalized- with respect to pure matrix- Bending Modulus, Strength and Strain at maximun stress of the uncoated ER/LC [0], as a function of the mechanically applied pressure during curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

approximately 103% and 75% for strength and modulus respectively. Regarding the composite structure with alkali fibers, figures show an improvement of approximately 240% and 200% for strength and modulus respectively. Finally, regarding the composite structure with grafted fibers, figures show an improvement of approximately 306% and 280% for strength and modulus respectively. However, according to manufacturers' data[59] *(commercial designation for epoxy is Araldite and for hardener is HV 153 IN)*, strength and modulus for the resin used, are at 60 MPa and 1.9 GPa respectively (cure 16 h/ 40°C) and not at 6.9 MPa and 166 MPa as reported in the article. Such a great difference cannot be attributed to the manufacturing procedure followed by the authors. So with great respect to them, we have to question these improvements of strength and modulus.

Influence of the Mechanically Applied Pressure During Curing on the Uncoated ER/LC [0] Static Properties. ER/LC's bending modulus was found improved as compared to the neat polymer modulus—regardless the value of the applied pressure—just due to the addition of the natural fibers. This finding is better shown in Figure 10, where the normalized composite modulus (E_c/E_m) is plotted as a function of the applied external pressure during the whole period of curing. This fact can be

explained by the nature of the reinforcing material and its contribution to the total behavior of the composite.

The explanation for the observed strength reduction, shown in Figure 10, lies on the deficient wetting of the fibers by the matrix which, subsequently, affects load transfer from the matrix to the fibers. However, an interesting observation is that pressure's increase leads to strength increase due to the compression of the laminate, squeezing the air bubbles and imposing the excess quantity of resin to flow out from the laminate. This technique appreciably improves the strength of the composite by increasing its density and reducing its porosity. Consequently, discontinuities of matter get minimized, composite structure becomes more and more continuous and load can be transferred more regularly from the matrix to the fibers.

Regarding strain at maximum stress, an overall decrease is observed as pressure increases (Figure 10). The successive increase in pressure leads to a continuous increase in bending modulus up to an upper limit (Table IX). Any further pressure increase above a specific threshold leads to stiffness as well as strength decrease. This threshold refers to 4.6 kPa applied pressure and it corresponds to the minimum quantity of resin needed in order to have all the fibers covered. In fact, it is a minimum resin film playing the role of "glue", keeping the fibers parallel restrained. Therefore, at 4.9 kPa external pressure, modulus decreased by 22.84% when compared to the relevant modulus of 4.6 kPa applied pressure. This behavior is due to an extensive resin's flow out of the structure during curing.

From Table X, we can observe that the optimum ER/LC bending modulus is by 48.33% higher than the neat matrix respective modulus and it corresponds to the 4.6 kPa external pressure applied.

Coming back to the relevant information found in literature, there is another paper written by Mohanta and Acharya[58] claimed to have enhanced epoxy's LY 556 (Ciba Geigy Ltd.) mechanical response by reinforcing it with LC uncoated fibers. According to that work, three composite structures were manufactured: a single layer, a double layer and a triple layer composite. Neat resin's tensile strength was found at 13.5 MPa, while its flexural strength was found at 17.16 MPa. Consequently, based on these findings, a 20.7% and 32.2% improvement for tensile and flexural strength was found respectively for single ply structure; a 24.1% and 44.7% improvement for the tensile and flexural strength was found respectively for the double ply

Table IX. Uncoated ER/LC's [0] Static Properties as a Function of Pressure During Curing

Applied Pressure (kPa)	W_f (wt %)	Bending Modulus (GPa)	Strength (MPa)	Strain at σ_u (%)	Bending modulus standard deviation (GPa)	Strength standard deviation (MPa)	Strain at σ_u standard deviation
4.9	56.51	2.747	49.68	3.25	0.147	0.358	0.003
4.6	48.92	3.560	59.01	3.51	0.060	0.820	0.001
4.2	48.43	2.971	60.41	4.03	0.140	3.860	0.004
3.6	40.31	2.645	55.64	3.96	0.048	1.615	0.002
2.9	39.27	2.517	48.87	4.03	0.044	0.858	0.004
Pure resin	0	2.4	72.12	4.48	0.029	0.239	0.002

Table X. Deviations of Mechanical Property Values of the Uncoated ER/LC [0] Subjected to Different Pressures, as Compared to the Respective Mechanical Properties of Neat Resin

Applied pressure (kPa)	Bending modulus (%)	Strength (%)	Strain at σ_u (%)
4.9	14.46	−31.11	−27.46
4.6	48.33	−18.18	−21.65
4.2	23.79	−16.24	−10.04
3.6	10.21	−22.85	−11.61
2.9	4.88	−32.24	−10.04
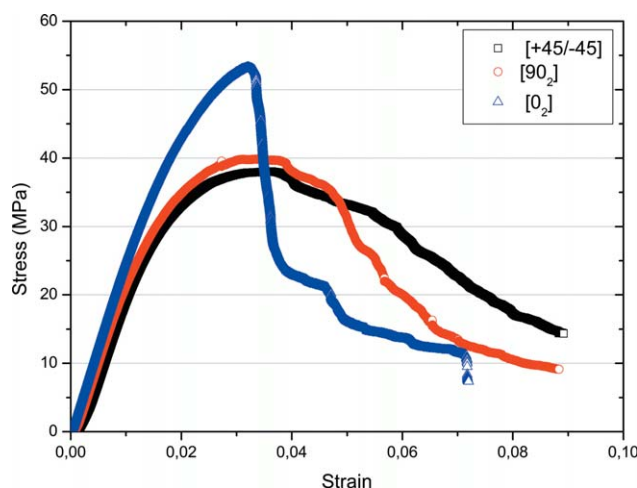
Figure 11. Stress–strain curves of the uncoated ER/LC [0_2], [±45], and [90_2] ER/LC structures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structure and, finally, a 16.9% and 30.6% improvement for tensile and flexural strength was found respectively for the triple-ply structure. However, according to the manufacturer,[60] neat resin tensile strength is at 83–93 MPa, while the flexural strength is at 125–135 MPa. Thus, once more with great respect to the authors, we have to question the reported enhancement of strength.

Uncoated Double Ply Composites. In relation to reference material, double ply ER/LC (regardless stacking sequence) provides not only a negligible stiffness improvement but also a

Table XII. Deviations of Mechanical Property Values of Double Ply ER/LC with Different Stacking Sequences from Those of Neat Matrix

Ply lay-up	Bending modulus (%)	Strength (%)	Strain at σ_u (%)
[90_2]	4.21	−44.40	−26.79
[±45]	4.21	−47.06	−24.55
[0_2]	9.13	−26.36	−26.79

Table XIII. Static Properties of the Uncoated ER/LC [0] and [0_2] and Their Relative Deviations with Respect to the Uncoated [0] Composite

Ply lay-up	Bending modulus (GPa)	Strength (MPa)	Strain at σ_u (%)
[0]	2.645	55.64	3.96
[0_2]	2.619	53.11	3.28
	−0.98%	−4.55%	−17.17%

Table XIV. Static Properties of the Uncoated ER/LC [0_2] and [0_2] Rev and Their In-Between Deviations (Reference structure: [0_2], W_f =50 wt %)

| Ply lay-up	Bending modulus (GPa)	Strength (MPa)	Strain at σ_u (%)
[0_2]	2.619	53.11	3.28
[0_2]rev	2.502	47.46	3.55
	−4.47%	−10.64%	8.23%

degraded strength and strain at maximum stress (Figure 11 and Tables XI, XII).

Single and double ply composite comparison. Both ER/LC structures were manufactured under common conditions (3.6 kPa applied pressure during curing), preserving all manufacturing parameters stable except the ply number.

As far as bending modulus and strength are concerned, deviations between ER/LC [0] and ER/LC [0_2] are negligible (Table XIII). The only significant difference between these two structures refers to strain at failure. As seen in the relevant graph, ER/LC [0_2] structure endures higher deformations while ER/LC [0] is more brittle (Figure 12).

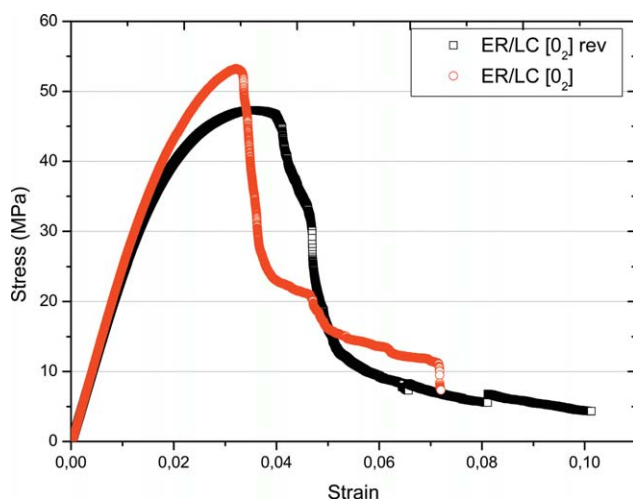**Table XI.** Effect of Stacking Sequence on the Mechanical Propertiesof the Uncoated Double Ply ER/LC

ply lay-up	W_f (wt %)	Bending modulus (GPa)	Strength (MPa)	Strain at σ_u (%)	Bending modulus standard deviation (GPa)	Strength standard deviation (MPa)	Strain at σ_u standard deviation
[90_2]	50	2.501	40.1	3.28	0.363	9.785	0.002
[±45]	50	2.501	38.18	3.38	0.034	2.099	0.003
[0_2]	50	2.619	53.92	3.28	0.269	6.015	0.003
[0_2] rev	50	2.502	47.46	3.55	0.100	2.100	0.002
[0_2]	30	2.37	43.32	4.09	0.066	0.900	0.002
Pure resin	0	2.4	72.12	4.48	0.029	0.239	0.002
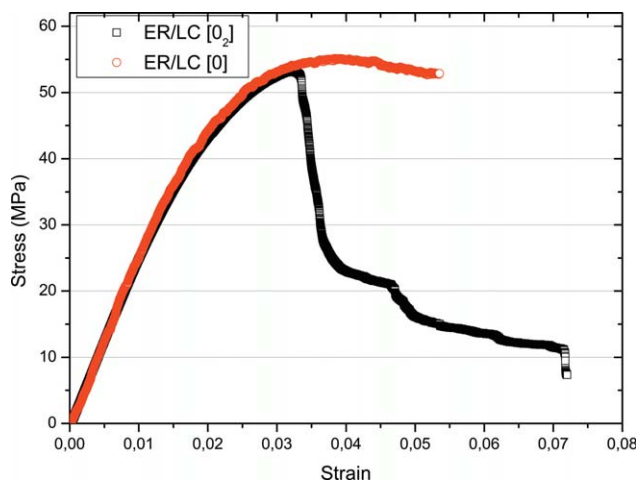
Figure 12. Stress–strain curves of the uncoated ER/LC [0] and [0_2] manufactured under applied pressure of 3.6 kPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
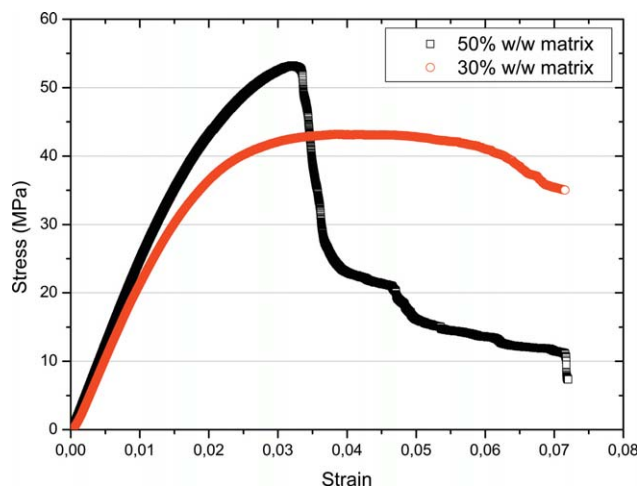
Figure 14. Stress–strain curves of 30% and 50% fiber weight fraction in the uncoated ER/LC [0_2] composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Position of ER/LC [0_2] plies by taking into account LC's structural and morphological characteristics. Structure marked as "rev" (reversed) refers to plies' position in such a way that the two matt surfaces (external) are in contact (*see Manufacturing Optimization-Parametrical Study*).

As observed from the data shown in Table XIV and Figure 13, the position of ER/LC [0_2] plays a non-important role to the final mechanical properties of the composite manufactured.

Influence of fiber weight fraction on the uncoated ER/LC static properties. Data shown in Table XV refer to ER/LC [0_2] specimens manufactured under the same conditions having different fiber weight fractions. As observed, ER/LC structure with higher fiber weight fraction shows superior properties, as expected.

The above-mentioned difference in mechanical behavior can also be observed from the stress–strain curves comparison, shown in Figure 14. It can be easily observed that the 30 wt % fiber weight fraction ER/LC [0] stress–strain curve has a similar trend to the respective one of a pure polymer.

Figure 13. Stress–strain curves of the uncoated ER/LC [0_2] with two layers placed in such a way where having contact: (a) the two mat surfaces (rev) (b) the external (in a LC column) surface of the first layer with the internal surface of the second layer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In double ply composite, a delamination effect was observed during loading. The two LC plies were delaminated as the load reached its maximum value.

Table XV. Static Properties of the Uncoated ER/LC [0_2] for 30% and 50% Fiber Weight Fraction and their In-Between Deviations (Reference Structure: ER/LC W_f=50 wt %)

Ply lay-up	W_f (wt %)	Bending modulus (GPa)	Strength (MPa)	Strain at σ_u (%)
[0_2]	50	2.619	53.11	3.28
[0_2]	30	2.37	43.32	4.09
		−9.51%	−18.43%	24.70%

CONCLUSIONS

The aim of the present study was the manufacturing of a polymeric matrix reinforced by LC natural fibers in order to investigate natural material's reinforcing value. That aim achieved by ER/LC manufacturing (Epoxy Resin/ Luffa Cylindrica), a semi-green material whose behavior mechanically studied. The composite was subjected to mechanical experimental characterization (3 pb) accompanied by its static properties' optimization process. Based on the study, the following conclusions can be drawn:

1. The mechanical response of the composite was found improved in relation to neat polymer, due to the insert of natural fibers. This fact can be explained by the nature of the reinforcing material and its contribution to the total behavior of the composite. This improvement concerns material's stiffness which optimally increased by 48% for a

mechanically applied pressure of 4.6 kPa during curing. Additionally, LC chemical treatment leaded to stiffness' improvement up to 30% (coating: Acetone/ CH3COOH 1%).

2. No strength increase was achieved due to LC structure which was not supported by the hand lay-up process. The main problem was fibers' bad wetting and the deficient load transfer due to the unsuccessful cover of all the layer's micropores by resin. A more sophisticated manufacturing method (i.e. infusion) could guarantee a proper wetting of reinforcement and subsequently composite's strength different behavior.

3. The successive increase of pressure leads to a continuous increase of bending modulus up to an upper (optimum) limit. This limit (4.6 kPa) corresponds to the minimum quantity of resin needed in order to have all the fibers covered. Any further increase of the applied pressure leads to the decrease of static properties due to the flow of the resin out of the structure during curing.

4. External pressure's influence—during curing—on ER/LC's static properties leads both to stiffness and strength increase.

5. Regarding the parametric study and the number of the ER/LC structures, we can conclude that the selection of the optimum structure is not an "absolute issue" but it occurs on the basis of the desirable application and its needs.

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