

Dynamic Mechanical Behavior of Vinylester Matrix Composites Reinforced by *Luffa cylindrica* Modified Fibers

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ABSTRACT: Currently, there is a demand for new engineering materials presenting a combination of strength, low density, processing easiness, and reduced costs. In this context, polymer matrix composites reinforced by natural fibers have been studied in recent years due to their ecological and economic advantages. Some fibers are still little explored in literature despite presenting a great potential as reinforcement like *Luffa cylindrica*. The present work aims at the preparation and characterization of a vinylester thermoset matrix composite material reinforced by fibers of the natural *L. cylindrica* fruit after modification treatments. In this study, extraction treatments in organic solvents, mercerization, and

a quite new esterification with BTDA dianhydrides were used and the results showed that in all cases, the composite materials reinforced by *Luffa* fibers have showed improvements in mechanical and thermal properties compared to the vinylester matrix. As an example, 50% tensile increase was obtained for the composite reinforced by fibers esterified with benzophenone tetracarboxylic dianhydride when compared with thermoset matrix. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1967–1975, 2012

Key words: composites; fibers; mechanical properties; surface modification

INTRODUCTION

To replace synthetic fibers by ecological and economic interest materials, natural fibers have been extensively studied in recent years as reinforcements for thermoplastic and thermoset polymeric matrices. The number of researches involving the use of reinforcement natural fibers such as sisal, curaua, hemp, coconut, palm, and banana among others has grown considerably.^{1–4}

Natural fibers are lignocellulosic structures cultivated worldwide as a nontoxic, renewable, and biodegradable material resource which may contribute to a healthy ecosystem.¹ Nowadays, the low cost and reasonable performance of these fibers, under varied environmental conditions, meet the economic interest of several industrial sectors.

On the other hand, polymeric composites reinforced by natural fibers present advantages such as low weight, reasonable strength and hardness, renewability, and biodegradability, in addition to

important ecological and economic character properties.^{5–7} Works relating to the preparation and characterization of polymeric matrix composites reinforced by natural fibers have been reported in current literature such as polypropylene matrix reinforced by cellulose fibers,⁸ palm fibers,⁹ and jute fibers^{4,10,11}; hemp fibers in unsaturated polyester matrix¹²; sisal fibers reinforcing epoxy and polyester resin matrix¹³ and polyethylene rubber.^{14,15} However, the greatest limitation in the potential use of these natural fibers in polymer matrix composites is related to the low compatibility of the fibers with a great number of polymeric matrices due to their high hydrophilicity.¹

Therefore, physical and chemical surface treatments have been absolutely proposed to improve the wettability and adhesion of these natural fibers by polymeric matrices of considerable hydrophobic character.^{1,3,4,5,14,16–18}

Some fibers are still little explored in literature despite presenting a great potential as a reinforcement element in typically polymeric composites. *Luffa cylindrica* (Brazilian sponge gourds) is a species of a subtropical plant commonly found in China, Japan, and other countries in Asia, Central America, and South America.^{19,20} Some researchers attribute its origin to Northern Asia. The absence of a detailed study of its characteristics and properties in the

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scientific literature make this fiber a material little described morphologically. However, vinylester matrix composites reinforced by fibers originated from the *L. cylindrica* fruit have not been reported yet. This composite system (vinylester resin—fibers of the *L. cylindrica* fruit) may represent an interesting alternative for Brazil in several applications due to the cultivation easiness, weather resistance, soil change, and short maturity cycle of this natural fiber allied to the attractive properties of the vinylester thermoset matrix such as high chemical and mechanical resistance in addition to its curing process at room temperature. However, little has been done to characterize and modify the plant, fruit, and seed through chemical treatments.²⁰

The main objectives of this study are the preparation and characterization of a composite system consisting of a vinylester thermoset matrix and a natural reinforcement agent: the fibers of the *L. cylindrica* (Brazilian sponge gourds) fruit. Surface chemo-physical modification treatments, as extraction in organic solvents, mercerization and a quite new esterification with BTDA dianhydrides were carried out on these surface fibers to ensure better results and improve wettability and adhesiveness by the polymeric matrix.

EXPERIMENTAL

Fiber preparation

The natural fiber (*L. cylindrica*) used in this study was cultivated in the rural zone of the municipality of Conselheiro Lafaiete—State of Minas Gerais, Brazil. The material was composed of thick, brittle, and brown color bark as a result of the fruit ripening process. The bark and seeds were removed, and the fibrous fruit was washed thoroughly with distilled water until the color of the water used in this procedure was colorless. Subsequently, it was dried in a stove for 24 h at $(100 \pm 5)^\circ\text{C}$ and stored in a desiccator with silica gel.

Characterization of fibers

The determination of the moisture content of the *L. cylindrica* fruit fibers was carried out according to the ASTM 1413-76 standard. The ash content of the *L. cylindrica* fruit fibers was determined by the TAPPI T211 om-93 standard. The content of soluble extractives in water was determined by the TAPPI T212 om-98 standard. The content of soluble extractives in organic solvents (ethanol/cyclohexane) was determined by the TAPPI T207 om-93 standard.

The content of insoluble Klason lignin was determined by the TAPPI T13 *m*-54 method (1991), being modified and adapted by Botaro et al.²¹ The filtrate obtained on the analysis of the insoluble Klason lignin content was analyzed by absorption spectroscopy

in the UV–vis region according to the TAPPI T13 *m*-54 standard, modified and adapted by Botaro et al.²¹ The holocellulose content was determined by the TAPPI T257 om-85 standard.

Surface modification treatments

Alkaline treatment (Mercerization)

Samples of the *L. cylindrica* fruit fibers, cut in layers of various dimensions, washed in distilled water, Soxhlet extracted with ethanol: cyclohexane (1 : 1, v/v) for 48 h and dried, were suspended in NaOH solution (Vetec Química Fina Ltd., Rua Pastor Manoel Avelino de Souza, 1.021 - Xerém - Duque de Caxias - RJ Brasil) at 2%. The samples were completely submerged in alkaline solution and kept in constant agitation on shaker, at room temperature for 2 h. Then, the samples were washed with distilled water, the water disposed was verified with universal indicator paper until presenting neutral pH and later the samples were dried.

Fiber esterification with BTDA (tetracarboxylic benzophenone dianhydride or 3,3',4,4'-benzophenonetetracarboxylic dianhydride 96%)

After mercerization (NaOH 2%) and complete drying in a stove at $(105 \pm 5)^\circ\text{C}$ for 24 h, the *L. cylindrica* fruit fibers were treated with BTDA (ζ -Aldrich, batch 12722BE-447). The ratio of reactants was 1.0 g fiber to 2.5 g BTDA and 1.5 mL triethylamine using acetone as solvent. After reaction, fibers were washed with abundant acetone until the removal of nonreacted adhered solids, and then dried in stove at $(105 \pm 5)^\circ\text{C}$ for 24 h.

Fiber analysis characterization techniques

To execute the analytical instrumental techniques, it was necessary to spray the samples of *L. cylindrica* fruit fibers before and after treatments. A Fritsch disc spray (Vibrating Cup Mill Pulverisette) was used by adding 20 g of fiber for about 4 min. The fourier transform infrared spectroscopy (FTIR) absorption spectra were obtained from *Luffa* fruit fibers previously pulverized, in the form of tabs with KBr spectroscopic grade. The thermogravimetric analyses were carried out with heating speed of 5°C min^{-1} at room temperature up to 800°C , under N_2 atmosphere (100 mL min^{-1} flow). The micrographs obtained by electronic scanning of fibers before and after modification treatment were carried out after coating the samples with carbon vaporization. The X-ray diffraction analyses were carried out in the 14° – 35° (2θ) region and at 2 degree per minute speed according to the method proposed by Segal and colleagues (1959).

Preparation of composites

About 40 mL of the commercial resin Dion See 9100 (Reichold) were used for matrix synthesis. The resin was transferred to a 250-mL beaker, and 4 drops of dimethylaniline were added. The system was then subjected to mechanical stirring for homogenization at 100 rpm. After 10 min, 8 drops of Cobalt 6% accelerator were added and the system was again subjected to shaking for 20 min. In the sequence, 20 g of aluminum hydroxide (Hydrogard GP—ALCOA, SA) were incorporated, and the system was kept under agitation for another 20 min. After this time interval, 12 drops of ethylmethylketone peroxide (Centerox ADM 90) were added and the mixture was stirred for 10 min. The preparation of the composites was executed in 30 cm × 30 cm × 4 cm standardized steel molds. After the thermosetting resin synthesis, fibrous layers of the *L. cylindrica* fruit before and after modification treatment were pressed and added in a ratio of 15% compared to the matrix. The composite cure was performed at room pressure and temperature for about 120 min.

Techniques of composite characterization

The water absorption test of composites was carried out according to the ASTM D570 standard. The density was calculated from the mass and geometry of the specimens. The dynamic thermomechanical tests were performed in dynamic thermomechanical analysis (DMA) Q800 equipment from TA Instruments in accordance with the ASTM D5023 standard. Specimens were prepared in dimensions of approximately 50 mm × 12.8 mm × 3.2 mm. The three point bending clamp flexion methodology (DMA multi-frequency strain—ramp/temp frequency sweep) was employed. The experimental conditions used in the first heating cycle were: 10 μm amplitude, 1 Hz frequency, 25–170°C temperature range and 2 °C min⁻¹ heating speed. Due to the clamp used, the sample was subjected to an initial 1 N (static force) load and to a self-strain of 150% (force track or autostrain). The glass transition temperature of the vinyl ester thermoset matrix and the temperature of the composites were identified and determined in a second heating cycle, consecutive to the first cycle, after cooling the samples to room temperature, under the same experimental conditions, by the temperature at the maximum tan δ point where there is the largest variation between the storage modulus and the loss modulus. The tensile test of composites was carried out according to ASTM D638 (Type IV) by using a universal testing machine Instron 5869 equipped with force transducer of 5.0 kN and Bluehill software. The thickness of the specimens was approximately 3.2 ± 0.4 mm and length 130 mm. The dis-

TABLE I
Characterization of the Constituents Present in the Microstructure of the Fibers of the Fruit of *L. cylindrica*

Analysis	Composition (%)
Water content	9.10
Ash	0.41
Water extractives (70°C)	2.34
Organic extractives	4.86
Klason soluble	0.81
Klason insoluble	8.12
Klason Total	8.93
α-cellulose	67.23
Holocellulose (α-cellulose + hemicelluloses)	88.42

tance between the grips was 65 mm and the stressing of 25.4 mm min⁻¹.

RESULTS AND DISCUSSION

L. cylindrica fruit fiber samples were initially subjected to two pre-extraction processes: in water and mixture of organic solvents. Table I shows the results obtained for the characterization of constituents present in the microstructure of *L. cylindrica* fruit fibers. The values showed in Table I are consistent and within the range of values reported in literature for *L. cylindrica*.²⁰ Figure 1 shows a scheme for the reaction among BTDA and hydroxyl groups present in cellobiose, which forms the cellulose structure.

Table II shows the Crystallinity index (%) (CI) data for natural, extracted with organic solvents, mercerized, and esterified fiber. The calculations were based on the works of Segal and colleagues (1959) for native celluloses mentioned by Focher et al., 2001.²²

Luffa fruit fibers have an approximate 8.93% rate of lignin and 21.2% rate of hemicelluloses which constitute the amorphous portion of this material. The partial removal of these compounds by extraction in ethanol/cyclohexane resulted in a CI increase from 51.8% in the natural fiber to 58.4% in the fiber extracted by these organic solvents. The reaction with hydroxide enables the alkaline penetration in the cellulose structure and promotes the crystallinity decrease transforming cellulose I into II which resulted in a CI decrease from 58.4% to 49.8%. During mercerization, the alkali penetrates into the lignocellulosic fibers causing the rearrangement of the crystal packing of native cellulose chains, aligned in parallel, for cellulose II where chains are antiparallel. This change is irreversible and usually accompanied by a crystallinity decrease²³ and a reduction in the polymerization degree due to the hydrolysis of β-glucosidic bonds.

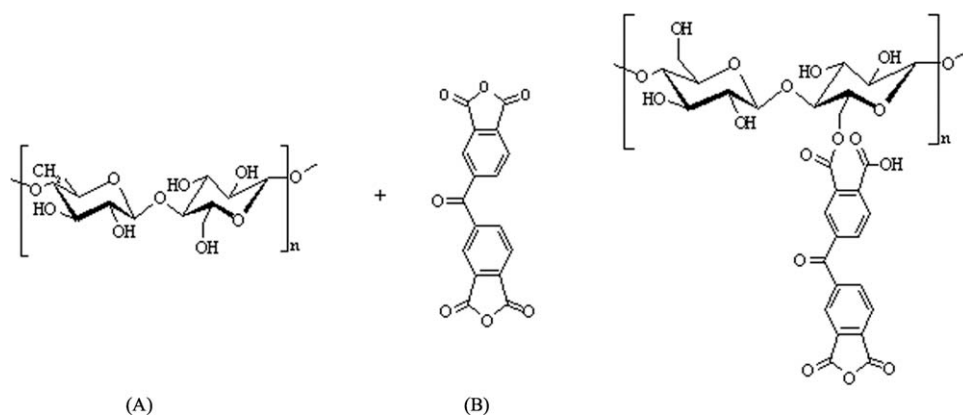


Figure 1 Esterification reaction between cellobiose (A) and the dianhydride BTDA (B).

Esterification has only provoked a slight change in the CI of the fibers. One reason would be the parameters and conditions employed in these treatments that resulted in changing only the surface hydroxyl groups, preserving the internal structure of the fibers. This result was also observed by other authors in the esterification of natural lignocellulosic fibers with anhydrides.^{24,25}

Figure 2 shows the FTIR spectra of natural *L. cylindrica* fruit fibers, after extraction in ethanol/cyclohexane and mercerized with NaOH (2%).

The presence of the absorption band in the 1733 cm^{-1} region in the sample with no treatment decreases after extraction in ethanol/cyclohexane and disappears after mercerization. This absorption band is attributed to the C=O axial deformation, acetyl groups in xylose (component of polyoses), and also lignin chemical groups.^{20,24} The reduction and disappearance of this band are related to the extraction of polyoses, lignin fragments of low molecular weight, and lignans after treatment with the mixture of organic solvents used. It was possible to observe the decrease of the band in the region of about 1245 cm^{-1} in the samples after extraction in ethanol/cyclohexane and mercerization. The absorption bands at about 2922 and 1378 cm^{-1} present in the sample with no treatment are related to stretching and deformation vibration of C—H, respectively.¹

TABLE II
Crystallinity Index of Samples of Natural Fibers and Modified

Treatments	I_{002}	I_{am}	Crystallinity index (%)
Luffa	105.5	50.9	51.8
Extracted fiber with organic mixture	244.2	101.6	58.4
Mercerized fiber	144.8	72.7	49.8
Fiber esterified with BTDA	64.9	31.6	51.3

Figure 3 shows the FTIR spectra of the fibers after esterification with the BTDA dianhydride.

The mercerization of the fibers practically provokes the disappearance of the band at about 1240 cm^{-1} relating to the O=C—O—C asymmetric axial deformation. This band reappears after treatment with BTDA dianhydrides. A justification for this fact would be the incorporation of this group with the esterification reaction. After treatments with BTDA, there are increases in the absorption bands at about 892 cm^{-1} , when compared to the mercerized fiber, attributed to the asymmetric stretch out of phase of aromatic rings.²⁰ Such event may be correlated to a possible esterification reaction of the fiber and the incorporation of aromatic groups, since these are present in the structures of this dianhydride.

Figure 4 shows the thermogravimetical analyses (TGA) and Derived TG curve (DTG) curves for the natural fibers, after extraction in ethanol/

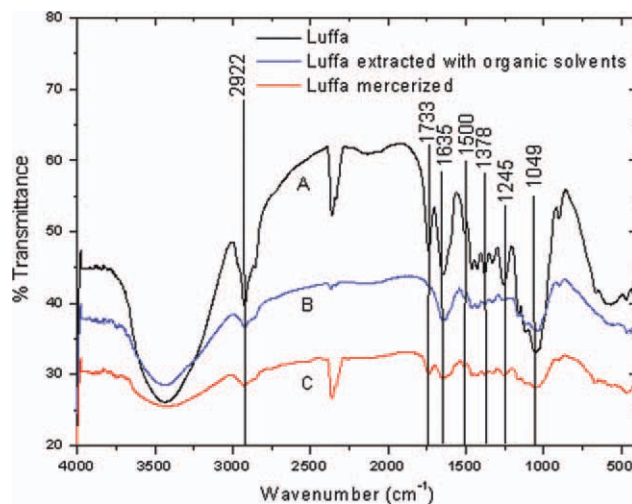


Figure 2 Absorption spectra in the region IV of the samples of fibers from the fruit of *L. cylindrica* natural (A), after extraction in ethanol/cyclohexane (B), and mercerized (2% NaOH) (C). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

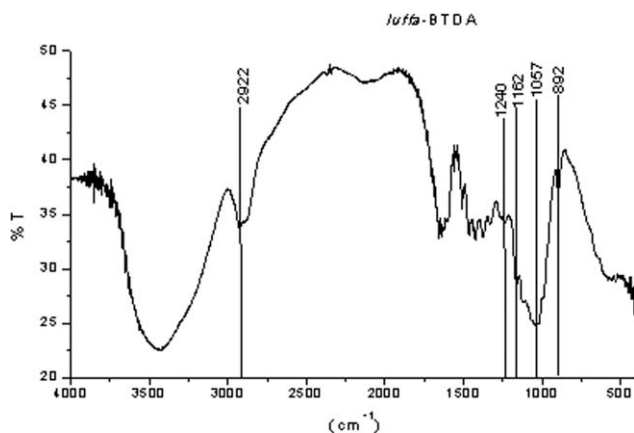


Figure 3 FTIR spectra from the fruit of *Luffa* esterified with the dianhydride BTDA.

cyclohexane and mercerized. TGA curves showed similar mass loss profiles in their entire extension.

The slightly higher moisture absorption of the fiber extracted in ethanol/cyclohexane when

compared to the natural fiber is due to the removal of extractives such as terpenes, volatile oils, aromatic compounds (aldehydes, acids, alcohols, flavonoids, etilbenos, quinones, and tannins), fatty acids, waxes, long chain alcohols, steroids, etc., that in a first degradation stage provoke the appearance of pores in the structure of the fibers where water molecules may be stored. The lower moisture absorption presented by the mercerized fiber may be justified by the removal of polyoses, which are also responsible for moisture absorption in natural fibers.¹ After 600°C it was possible to observe mass loss of about 81.3, 85.6, and 79.7% for natural fibers, fibers extracted, and fibers mercerized, respectively.

Figure 5 shows the TGA and DTG curves obtained for the fibers after alkali treatment and BTDA esterification. *L. cylindrical*: it is pointed out by literature that one of the critical factors in the use of natural fibers as reinforcement in composites materials is their low thermal stability.²⁶ In this sense, the thermal stability of *L. cylindrical* fibers was investigated

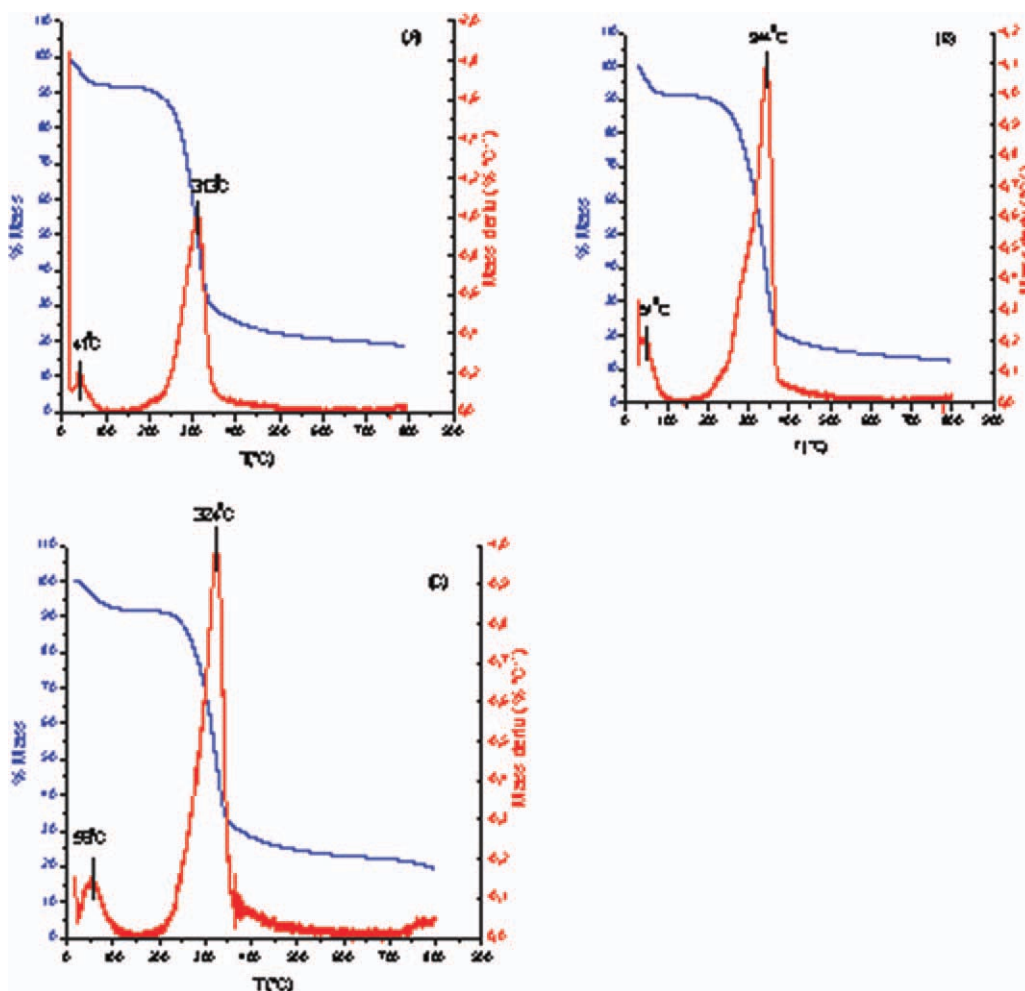


Figure 4 TGA and DTG curves of samples of fibers with heating rate of 5 °C min⁻¹ under an atmosphere of N₂ for natural fiber (A), extracted in ethanol/cyclohexane (B), and mercerized (2% NaOH) (C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

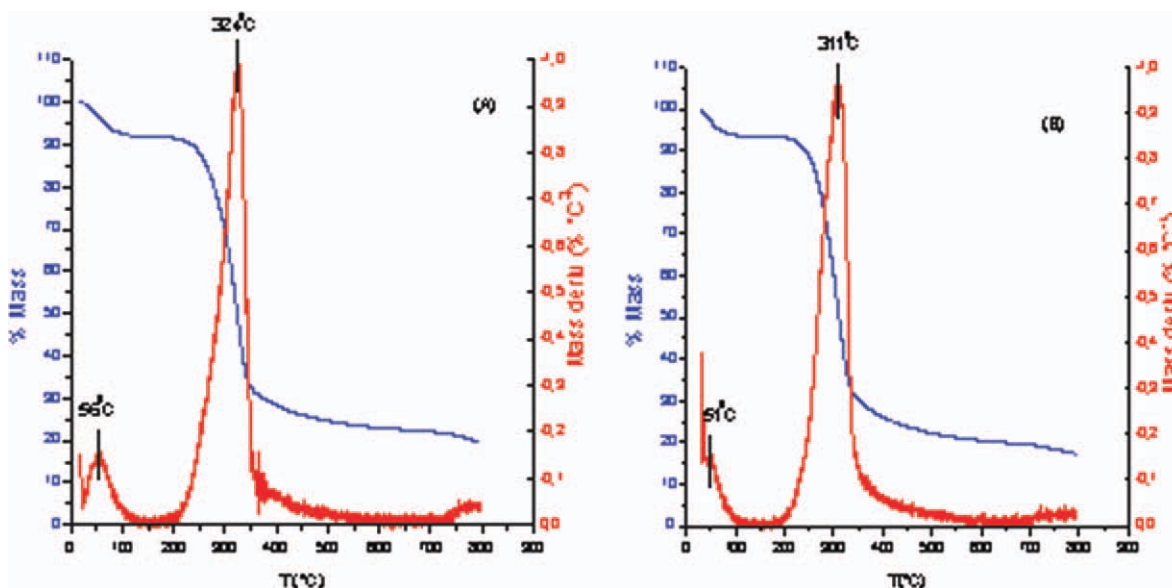


Figure 5 TGA and DTG curves obtained with heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ under an atmosphere of N_2 for samples of fiber mercerized (2% NaOH) (A) and esterified with BTDA (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

by thermogravimetric analysis. The initial weight loss (10%) observed between 25 and 110°C is attributed, mainly, to the vaporization of the water present into the fibers. The onset degradation for the fibers occurs at higher temperature, precisely after 210°C . Above this temperature it can be seen that the thermal stability decreases in a large scale and the degradation occurs. The literature²⁶ has pointed out that the first stage, normally between 220 and 310°C , is attributed to the thermal depolymerization of hemicellulose, pectin, and the cleavage of glycosidic linkages of cellulose. The degradation of α -cellulose present in the fiber occurs in the range of 310 – 390°C and corresponds to an important weight loss. Due to the complex structure of the lignin, generally, the decomposition occurs slowly within the whole temperature range. As shown in Figure 5, fibers esterified with BTDA showed a first peak of mass loss of 51°C and 50°C , with stabilization at 100°C and with massive loss of 6.4% and 6.9% respectively, in the DTG curves. The formation of ester bonds after modification with BTDA, may have contributed to a lower thermal stability of the esterified fibers due to the lower thermal stability of ether linkages present.

Figure 6 shows the scanning electron microscopy (SEM) micrographs of the natural *L. cylindrica* fruit fiber obtained under different magnifications. Its fibrous nature and the considerable roughening of the surface may be observed. In general, lignocellulosic fibers are present covered with a surface layer rich in fats and waxes, in addition to solids embedded in the form of salts-like pointed out by Botaro et al.²¹ The micrographs obtained after extraction treatment in

ethanol/cyclohexane presented lower roughness and lower content of encrusted solids adhered to surface.

Figure 6 shows the SEM micrographs obtained after mercerization treatment where it was also possible to observe the removal of encrusted material from the surface of the fibers. Despite the microstructure alteration including cellulose I changes with parallel orientation to antiparallel cellulose II, the destruction of the surface integrity of microfibrils in the conditions used was not found. Works reported in the literature found, through micrographs obtained by SEM, that these fibers are already badly affected in the surface after treatment with alkaline NaOH solutions at 5 and 10% concentrations.²⁷ Figure 6 shows also the micrographs of the fibers after BTDA esterification treatments. It may be noticed that these treatments maintain the natural fibrous integrity of the lignocellulosic structure unlike other surface modification treatments such as, for example, with methacrylamide, where it is possible to notice through SEM that fibers are severely degraded onto the surface.²⁰

Characterization of the composites

A ratio of fibers to allow the obtainment of moldable, bound bodies, free of cracks, excess of bubbles and porosity was used in the preparation of the composites. This ratio was set at 15% which caused a reduction in density of about 1.33 g cm^{-3} of the matrix to 0.715 g cm^{-3} in the material of the composite reinforced with the natural *L. cylindrica* fruit fibers and after modifications. This 46.2% density decrease in the composites is extremely significant

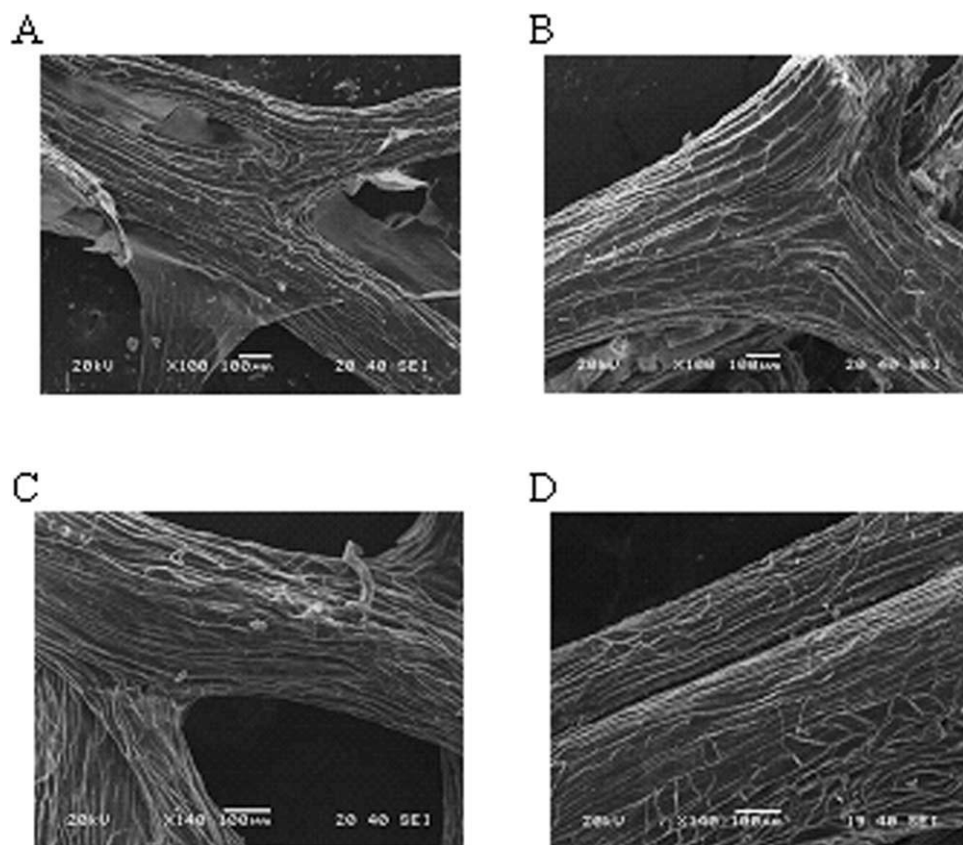


Figure 6 SEM micrographs of fibers from the fruit of *L. cylindrica* (A), after extraction in ethanol/cyclohexane (B), after mercerization in 2% NaOH (C), and modified by esterification with BTDA (D).

and opens up tremendous prospects for the use of this material in applications requiring lightness and performance. Table III shows the absorption values (in percentage) after 24-h immersion.

Through this experimental procedure it was possible to verify the low percentage of water absorption of this thermoset polymer when compared to others such as phenol–formaldehyde resin.¹ The highest percentage of water absorption, about 4.3%, was also observed for the composite prepared from vinyl ester resin and natural *L. cylindrica* fruit fibers. This result is due to the hydrophilic character of natural lignocellulosic fibers and the lower adhesion between fiber–matrix due to a poor compatibility with the polymer, which allows greater penetration of water inside the material when compared to other composites. After the extraction process in organic solvents, there is a reduction in the percentage of absorption to 1.6% due to the polyoses extraction in the structure of the fibers that are mainly responsible for water absorption.

A very important result was the decrease of water absorption after mercerization and esterification of fibers. These results indicate an improvement in compatibility between fiber and matrix after surface modification. DION[®] 9100 is a modified Bisphenol-A epoxy vinyl ester resin that presents extremely chemi-

cal compatibility with the modification agent, BTDA considering the presence of aromatic rings in its structure. In contrast, the inclusion of unreacted anhydrides onto fiber surface will allow future studies involving the reaction of these anhydrides with, as example, polymers bearing hydroxyl reactive groups.

Table IV shows the results of DMA tests obtained at 30°C and the tensile strength obtained for the matrix and composites. An increase in the storage modulus may be observed after the second heating cycle for all samples and, in general, the behavior of the loss modulus has also shown the same trend. In order that the processing of polymeric materials is competitive it is necessary that

TABLE III
Values of Water Absorption for the Composites After 24 h of Immersion

Material	Water absorption (%)
Esthervinilic matrix	0.46
NLC	4.3
OLC	1.6
MLC	0.92
ELC	0.62

NLC: natural *Luffa* composite; OLC: organic extracted *Luffa* composite; MLC: mercerized *Luffa* composite; ELC: esterified *Luffa* composite.

TABLE IV
Storage Modules and Loss Obtained at 30°C for the Matrix and Composite Reinforced with *Luffa* Before and After Modification

Material	Storage modulus (MPa) (1st cycle)	Loss modulus (MPa) (1st cycle)	Storage modulus (Mpa) (2nd cycle)	Loss modulus (MPa) (2nd cycle)	Tensile strength (Mpa)
MATRIX	2541	340	3010	315	14.0 ± 0.5
NLC	2870	324	3189	426	15.9 ± 1.3
OLC	2909	298	3231	310	17.3 ± 1.0
MLC	3064	370	3411	330	17.4 ± 1.4
ELC	4649	454	6209	709	21.2 ± 0.7

NLC: natural *Luffa* composite; OLC: organic extracted *Luffa* composite; MLC: mercerized *Luffa* composite; ELC: esterified *Luffa* composite

its production is made with extremely short molding cycles. However, the economic interest of the transformer may lead to future losses in the form of excessive internal frozen stress in the molded part which become points of fragility of the material causing premature fracture. The temperature of the mixture and the mold, as well as the rapid increase in the viscosity of the vinyl ester resin may have led to resin curing at a speed higher than needed to provoke a sufficient relaxation of the chains. The higher wettability and adhesion of the surface of modified fibers, mainly after esterification with dianhydride, may have also contributed to the increase in storage and loss modulus due to the greater difficulty of mobility of polymeric chains that become more compatible with the surface of the fibers increasing the composite material resistance. As noted in Table IV, there was considerable increase in maximum tensile of all composites compared to unreinforced matrix. The largest increases were observed by the composites reinforced with fibers of the fruit of *Luffa* esterified with BTDA. This fact of great significance can be explained by a better adhesion and wettability of the surface of modified fibers with the matrix provoked by esterification reaction. Despite the treatments, it can be concluded that chemical modifications have caused little degradation in the integrity of the fibers. Finally, the esterified fibers have showed remarkable potential to act as reinforcing agents in the prepared composites.

Table V shows the values of the glass transition temperature (T_g) determined by temperature peaks in the Tan delta ($\tan \delta$) curves after the first and second heating cycles and the $\tan \delta$ value in T_g after the 2nd cycle of the vinyl ester matrix and vinyl ester matrix composite materials reinforced by *Luffa* fruit fibers before and after surface modification treatments.

Comparing the temperatures at which there are the peaks in the $\tan \delta$ curves in the 1st and 2nd heating cycle it is possible to observe, in addition to the relaxation of the internal tensions with the dis-

appearance of the shoulder observed during the 1st cycle, the T_g shift to higher values during the 2nd heating cycle. This fact is related to the after-curing process of the sample, due to the passage through T_g during the first heating cycle, which allows the polymeric chains to reorganize and reduce internal frozen stresses raising the T_g value in the 2nd cycle due to the increase of crosslinking density of the polymeric chain. The transition temperature of a given phase, defined and identified through the $\tan \delta$ maximum, is related to the internal characteristics of the transition phase at this temperature and/or characteristics induced by the external phase involved in this same transition phase. If the characteristics imply in an impediment of molecular motion, temperature shifts to higher values. If, on the other hand, it tends to facilitate the molecular motion, it is reflected in a transition temperature reduction.²⁸

Among the composite materials, the composite reinforced by *Luffa* fruit fibers esterified with BTDA was the one that showed the lowest value for the $\tan \delta$ at T_g . This fact is consistent with the values obtained for the storage and loss modulus of these materials. The greatest adhesion and wettability of the fibers esterified with the BTDA by the matrix hampers the motion of the polymeric chains with the temperature raise, resulting in an increase in the storage modulus and the consequent reduction of the internal damping or $\tan \delta$ in T_g during the 2nd heating cycle.

TABLE V
Values of the Maximum Temperatures at the Maximum of Tan Delta (T_g) After 1 and Two Cycles of Warming and Tan Delta Value of the T_g After the 2nd Heating Cycle

Material	T_g (°C) (1st cycle)	T_g (°C) (2nd cycle)	$\tan \delta$
Matrix	61.8	113	0.983
NLC	69.0	115	0.822
OLC	56.0	111	0.746
MLC	58.9	110	0.737
ELC	57.1	111	0.557

CONCLUSIONS

Luffa fruit fibers were characterized by electron microscopy and FTIR. Their thermal degradation behavior was investigated through TGA and DTG curves. A vinyl ester thermoset matrix composite material was reinforced by fibers of the natural *Luffa cylindrica* fruit after modification treatments. The higher wettability and adhesion of the surface of modified fibers, mainly after esterification with dianhydride has provoked considerable increase in maximum tensile of composites compared to unreinforced matrix. It can be concluded that chemical modifications have caused little degradation in the integrity of the fibers. Finally, the esterified fibers have showed remarkable potential to act as reinforcing agents in the prepared composites.

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