 DOI: 10.1002/masy.201100229

Thermal, Mechanical and Morphological Properties of Composites Developed from Glycerol and Dicarboxylic Acids Reinforced with Piassava Fiber

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Summary: Vegetable fibers are being widely used as reinforcement in polymer composites. These composites can be applied in several fields, such as automotive, packaging and even construction. The polymer matrix used was synthesized from glycerol with phthalic and terephthalic acids in order to open future perspectives in the use of glycerin generated from the production of purified biodiesel. Composites with 2, 5, 10 wt% untreated and treated piassava fiber were obtained. Thermal, morphological and mechanical properties were evaluated. The tensile stress-strain curve of the polyester synthesized and composites was typical of a ductile material. SEM of the surface of fracture showed that the adhesion between fiber and matrix was enhanced after chemical treatment. However, the fiber content was more efficient than the superficial treatment when incorporated into the matrix. Therefore, the material under study is promising for the industrial marketplace, due to its good compatibility with natural fibers.

Keywords: composites; glycerol; piassava fiber; polyester; synthesis

Introduction

Due to environmental and economic concerns, the study and use of raw materials from renewable sources and industrial wastes have been growing significantly in recent years. Interest in biodegradable polymers with potential properties and natural fibers as strength in polymer matrices has been growing worldwide.[1,2]

Cellulose fibers have many features which make their use attractive such as low-cost, low density, high specific strength and modulus, they are not abrasive and do not wear out process equipment, they are not toxic, they can be easily modified by chemical agents, and they are plentiful and come from renewable sources. Their mechanical properties are comparable to other commonly used reinforcements.[3] Vegetable fibers are more affordable than synthetic ones and can replace them in many applications where cost is a more important factor than strength and stiffness. Vegetable fibers such as bananas,[4,5] jute,[6] sisal,[7,8] coconut,[9,10] piassava,[11–13] curauá,[14,15] cane sugar,[16] pineapple,[17] cumbaru,[18] hemp[19–21] and wood[22] have been used as reinforcement in polymer matrices.[23] Among those fibers, the use of waste piassava fiber, called sludge, is particularly interesting because it has good chemical and mechanical properties and can be used as reinforcement in polymer matrices, adding value.[24]

Nowadays, investment is being made in research into expanding the marketing and use of glycerol to manufacture plastics with biodegradable properties. When the glycerol structure reacts with dicarboxylic acids it produces polyesters from condensation polymerization.[1,25–28]

The matrices have the main purpose of transferring the stress imposed on the

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composite material to the fibers as well as providing support and protection. In general, a thermoplastic matrix is used in composites. One of the great difficulties in incorporating natural fibers is their interaction with the matrix because most thermoplastic matrices are nonpolar while the fibers are polar. New materials are being developed which require a low processing temperature and have polar properties for favorable matrix/fiber interface.[24]

The strength and modulus of short fiber reinforced composites depend mainly on the stress transfer efficiency of the matrix to the fibers. The efficiency of tension transfer depends on the fiber length and the magnitude of the interactions in the fiber-matrix interface. In short fiber reinforced composites a critical fiber length is required so that the ultimate strength (stress transfer) can be achieved. The critical aspect ratio depends on the fraction volume of the fibers and also the ratio between the fiber modules and matrix. The processing also influences the final properties of composites. The incorporation of short fibers into the matrix through extrusion leads to excessive fiber breakdown, which can be avoided by using a mixed solution. However, the extrusion process leads to the alignment of short fibers providing composite improvements in strength and modulus.[29]

The aim of this study was to incorporate piassava waste fiber into a polymer matrix produced from glycerol, phthalic and terephthalic acids to improve its thermal, mechanical and morphological properties to produce a competitive product for the commodities market. The study was also designed to maximize the concentration of biodegradable components obtained from renewable sources to produce a product mainly consisting of raw materials derived from renewable sources, thus contributing to environment sustainability.

Experimental Part

Materials

In this work piassava fiber waste (*Attalea Funifera Mart*), kindly donated by a broom factory located in Ilhéus, in the southern state of Bahia was used. Terephthalic acid, dibutyltin dilaurate from Sigma-Aldrich, phthalic acid from Vetec and sodium hydroxide and glycerol from Merck were also used.

Surface Treatment of Piassava Fiber

The fiber was washed with fresh distilled water and cut into 5 mm. The process of piassava fibers mercerization was performed as follows: a NaOH 10% (m/v) solution was prepared and piassava fibers were immersed in it for 1 h at room temperature. Then the fibers were washed with water until they reached a pH of seven and then washed with distilled water. After this step, the fibers were dried at 100 °C for 48 h.

Synthesis of the Polymeric Matrix

The synthesis of polyesters was carried out using 1:1.5 stoichiometric molar ratio of glycerol (1) and phthalic/terephthalic acid (1.5), respectively. The glycerol was put into a reactor and heated to 70 °C under fixed mechanical stirring. Subsequently, the acids were added and the mixture was heated to 120 °C, then two drops of dibutyltin dilaurate catalyst were added and the temperature was raised to 220 °C. The mass ratio of phthalic and terephthalic acids in the polyesters was 75 and 25%, respectively. The matrix was molded by removing it before the formation of polyester and it was placed into silicone molds.

Preparation of Composites

The preparation of the composites followed the same method described above. When the polymer reached the sol-gel state, the cut piassava fiber was added to the reaction with fixed stirring for 5 minutes and then molded. The composites were prepared using the washed fiber in the following ratio: 2, 5 and 10 wt% cut fiber, the composite classification was comp 2%, comp 5% and comp 10%, respectively, as illustrated in Figure 1. Composites were also prepared with a content of 5 wt% fiber treated with NaOH 10% cut in 5mm; the

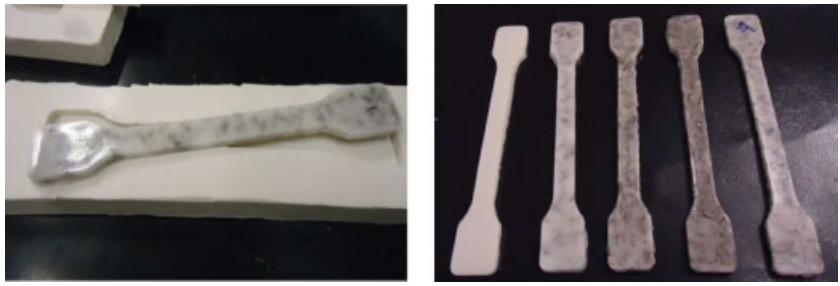

Figure 1.
Samples of matrix and composites.

composite was named comp 5% T (see Figure 1).

Techniques Used in Material Characterization

Thermo-Gravimetric Analysis (TGA)
The analyses were performed in a TGA (Shimadzu TG-50) thermo-balance operating at a scanning rate of 20 °C/min in the range of 25 to 600 °C under nitrogen flow. The analysis data were obtained directly from the software provided by the TGA manufacturer.

Differential Scanning Calorimetry (DSC)
The equipment used was a Shimadzu DSC-60, all samples were analyzed from 25 to 600 °C with a heating rate of 20 °C/min.

Tensile Test
Tensile tests were performed according to ISO 527 using a universal testing machine (EMIC, DL2000) with a displacement speed of 2 mm/min, 500 N load cell and distance between the grips equal to 100 mm. The t-Student test was the mean values obtained from eight individual test results the statistical method used to express the confidence interval. Large discrepancies in reported tensile strength and Young's modulus of natural fibers can be found in the literature as there is no simple means of obtaining the cross-sectional areas of natural fibers due to their non-regular cross-section and variability in length. There are different methods of estimating the cross-sectional of these fibers available. The existence of luminal cavities in vegetal fibers contributes to the large porosity. The non-circular cross sectional area of the fibers affects the understanding of mechanical proprieties of natural fibers. SEM, optical microcopy, optical laser equipment or micrometer caliper have been usually used to measure a fictional diameter. In this work the area (A) of each fiber was estimated based on weight (w), length (l) and density (ρ) (Eq. 1). The density 1.10 g/cm^3 was evaluated using Helium gas pycnometer.

$$A = w.(1.\rho)^{-1} \quad (1)$$

Scanning Electron Microscopy (SEM) Analysis
The analyses of fracture of composites after the tensile test were performed in a SS-550 Shimadzu scanning electron microscope. The samples were previously dried under vacuum and coated with gold in a Shimadzu IC-50 ion coater.

Results and Discussion

Thermo-Gravimetric Analysis (TGA) Results

Figure 2 show the TGA curves for the composites with the matrix and piassava fiber. The composite with washed and treated fibers showed thermogravimetric profile similar to the polymer matrix with thermal stability of up to 250 °C and this did not change with the fiber content, with mass loss around 95–99%.

By analyzing the DTG curves of the composites with washed fibers (Figure 3), it

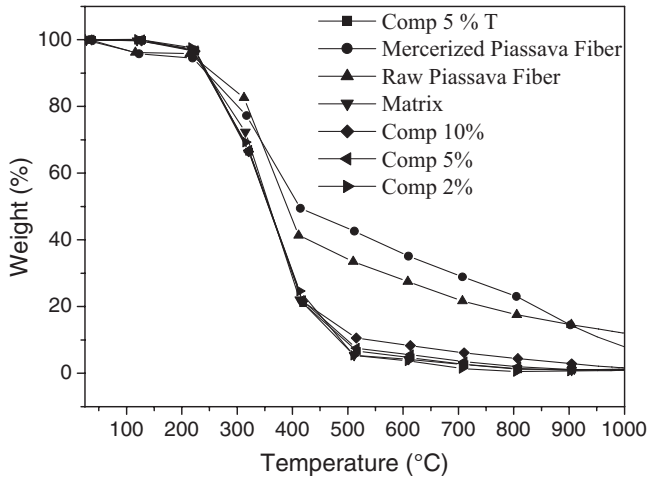

Figure 2.
TGA curves for the matrix, composites and fiber.

was observed that the matrix showed four events.The first and the second event, with maximum at 250 and 326 °C, can be attributed to the evaporation of residual monomers and also the loss of CO_2 from the carboxyl group of phthalic and terephthalic acids. The third event with maximum at 397 °C is attributed to the decomposition of the polymer chains and the glycerol + phthalic. The fourth event with maximum at 442 °C is attributed to the decomposition of the polymer chains of the glycerol + terephthalic. When comparing composites DTG curves with washed fiber a displacement of the second and third event with increasing fiber content was observed, with maximum temperatures equal to the piassava fiber. It can therefore be inferred that there was an interaction between the matrix and the fiber. This interaction between the matrix and fiber was expected due to their polarity. By

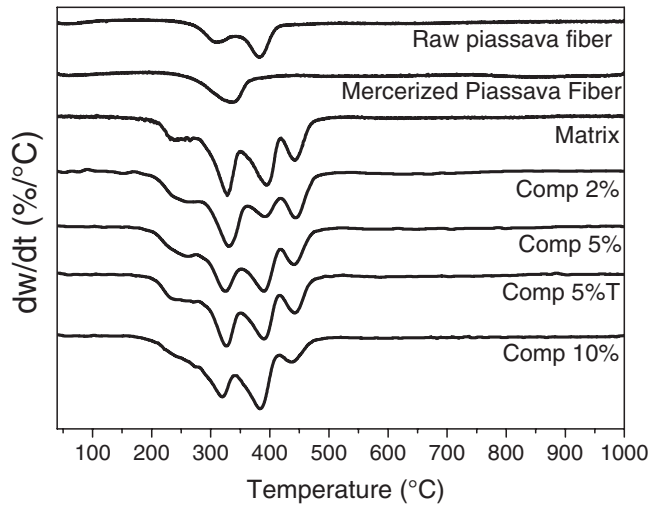

Figure 3.
Derivative curve of thermal decomposition profile for matrix, composite and fiber.

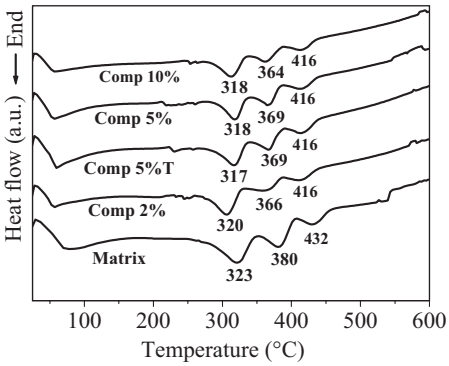

Figure 4.
DSC curves for the matrix and composite.

analyzing the DTG curves (Figure 3) of the treated fiber this shift was not clear as the event of fiber and composite is overlapped.

Differential Scanning Calorimetry (DSC) Results

Analyses made by differential scanning calorimetry from matrix and composites (Figure 4) revealed the presence of endothermic peaks corroborating the events of the DTG. The first event was related to moisture, the second event was related to the degradation of the fatty chains, the third and the fourth event were related to the degradation of the polymer chains. By Comparing the DSC curves of the composite and matrix, was observed an offset of events at lower temperatures due to the presence of the fiber. Thus, an interaction between the fiber/matrix can be inferred.

Tensile Test Results

The polyester stress-strain curves show that there was no repeatability of the curve profile (Figure 5) as this, is a new matrix that still requires several steps in order to optimize its processing. It was observed that by adding piassava fibers into the matrix, the behavior of the material under tensile tests became uniform. The composite curve behavior showing an initial elastic deformation followed by yielding (Figure 5b) is typical of plastic materials.

Table 1 shows the Young's modulus and the tensile strength and elongation at break of fiber, matrix, and composites. The increase in the fiber volume from 2%, 5% and 10% wt resulted in an increased composite strength and decreased strain. Composites made up of 2% and 10% fiber volume showed a reduction in the strain at failure. Similar work in the literature reported that adding sugar cane bagasse and buriti fibers into ductile matrixes reduced the failure strain of the composites when compared to the matrix. Fibers with a higher stiffness than the matrix results in an increase in the elastic modulus and toughness, but a decrease in elongation at failure.[30,31]

The matrix compared to composities with a 2% fiber content fraction did not show a significant change in strength and Young's modulus was lower than the

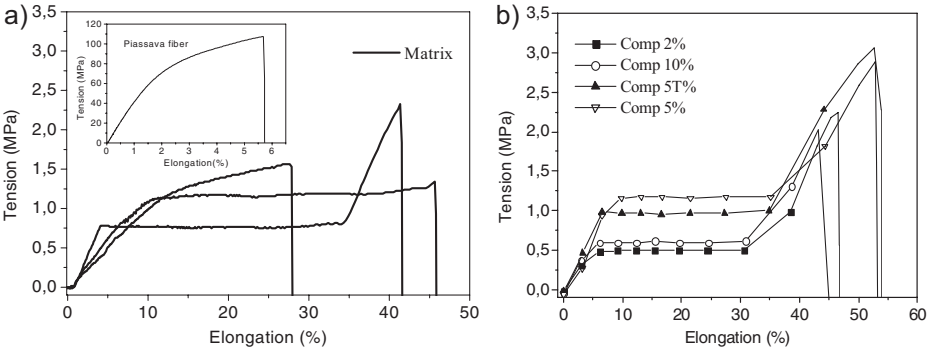

Figure 5.
Tensile test stress-strain curves of a) matrix and b) composites.

Table 1.
Values of tensile strength (σ_r), elongation at break (ε_r) and Young's modulus (E) of the piassava fiber, matrix and composites.

Sample	σ_r (MPa)	E (MPa)	ε_r (%)
Matrix	1.73 ± 0.68	1319 ± 606	50.71 ± 21.01
Raw Piassava	134,5 ± 13,0	6095,4 ± 966,2	3,4 ± 0,5
Mercerized Piassava	117,0 ± 7,3	4845,8 ± 500,3	5,2 ± 0,9
Comp 2%	2.20 ± 0.35	1098 ± 408	63.41 ± 27.21
Comp 5%	2.59 ± 0.46	1293 ± 354	59.29 ± 14.23
Comp 5% T	2.33 ± 0.78	1914 ± 534	47.12 ± 8.59
Comp 10%	3.02 ± 0.78	2247 ± 702	49.33 ± 9.05

matrix. When comparing the tensile strength of the composites with 5% untreated piassava fiber content and the 5% treated piassava fiber content it can be seen that the treated fibers reduced the tensile strength of the composites slightly. However, these results are not statistically significant. The fiber treatment decreased the strength and failure strain and increased Young's modulus which is an important parameter during design. The increase in Young's modulus is due to the improvement in the fiber-matrix interface induced by the fiber treatment. Similar effects have been reported with mercerized curauá fibers which showed a decrease in fiber strength after undergoing polyester matrix decohesion.[32]

The initial composite stiffness was analyzed with regard to the physical and chemical interactions on the fiber-matrix interface and the fiber content. Young's modulus increased with fiber content, to a maximum of 10% wt. The treated 5% fiber content composites show increased stiffness due to the increased surface roughness leading to an increased surface contact between the fiber and matrix. The increased roughness can be seen in Figure 6. The alkali treatment cleans the fiber surface providing a better grip with the matrix. Figure 6 shows the part of the polymer adhered to the piassava fibers.

The injection process used to obtain the composites limits the maximum fiber content to 10%. These 10% fiber content composites showed increased stiffness and strength. The density of fibers is lower than the polymer matrix and therefore the composites are lighter in weight. These composites also presented a lower dispersion of results. This is associated with the compatibility of the fibers with the matrix which is influenced by the restricted mobility of the macromolecular chains promoting an increase in the mechanical properties of the composites.

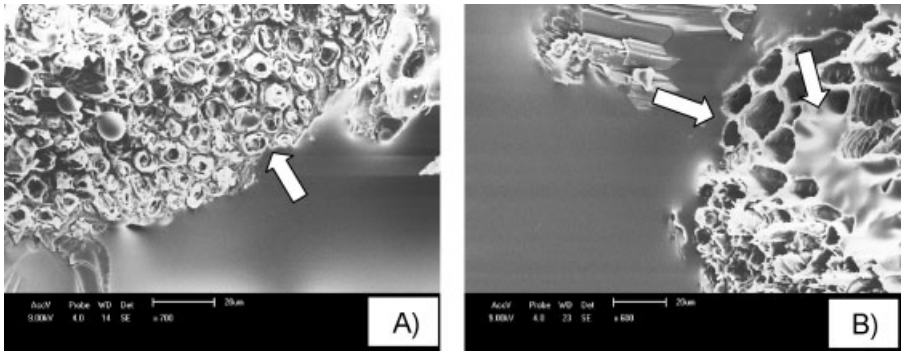

Figure 6.
SEM micrographs of composite in 700× (A) and 600× (B).

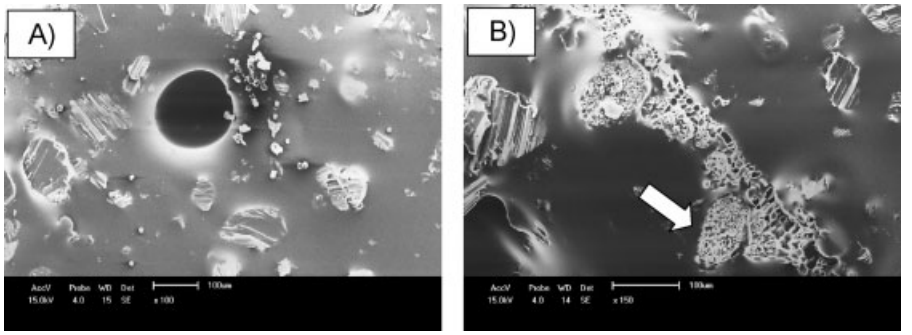

Figure 7.
SEM micrographs of Comp 2% in 100× (A) and 150× (B).

Scanning Electron Microscopy (SEM) Analysis Results

By analyzing the micrographs of the composites fracture with 2% and 5% piassava fiber content after fracture (Figure 7 and 8), possible events related to the pull-out effect, where the fiber is drawn from the matrix were observed. However, there is also good adhesion between fiber and matrix because the fiber has the interfacial part of the matrix after the landslide.

By analyzing the micrographs of the composite fracture with 10% fiber (Figure 9) fiber disruption after material rupture was observed, followed by a good adhesion

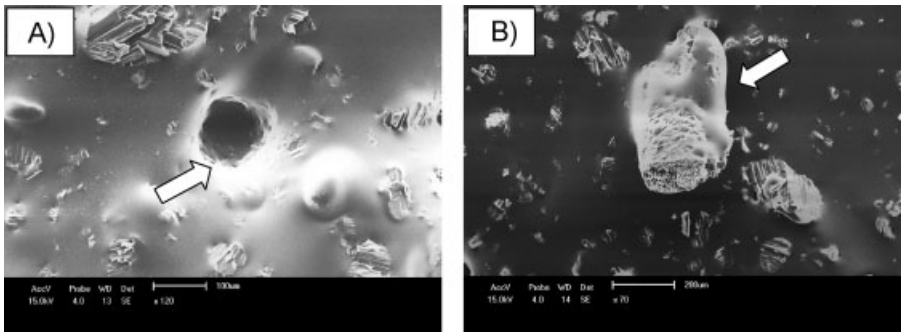

Figure 8.
SEM micrographs of Comp 5% in 120× (A) and 70× (B).

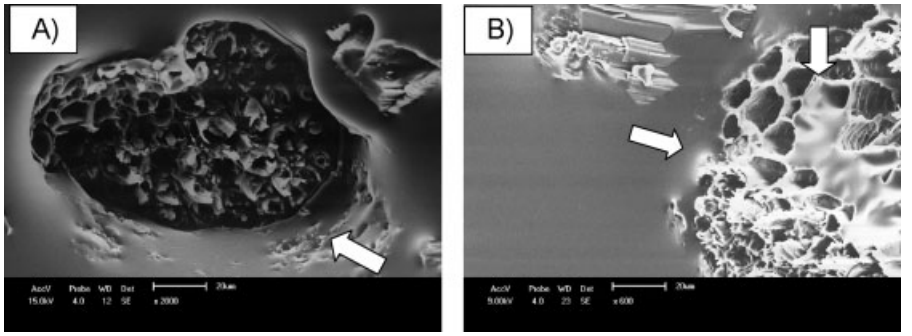

Figure 9.
SEM micrographs of Comp 10% in 2000× (A) and 600× (B).

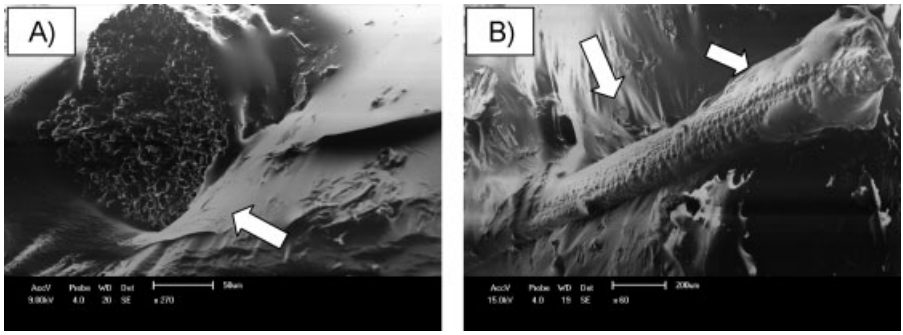

Figure 10.
SEM micrographs of Comp 5% T in 270× (A) and 60× (B).

between fiber and matrix. This proves the compatibility between the matrix and fiber which favored the improvement in the mechanical behavior of the matrix.

By analyzing the composites micrographs with 5% mercerized piassava fibers (Figure 10) there was better interpenetration of the matrix in the fiber bundles, indicating the partial breakdown of the fibers present in the beam treated providing better fiber/matrix adhesion compared to the untreated fiber composites. However, this effect is outweighed by the deterioration of the fiber with the treatment, reducing the capacity of the fiber to resist tensile strength after its final release from the matrix. Therefore, there was a decrease in tensile strength for the composite made with treated fiber.

Conclusion

From the results it can be seen that the stress at break is influenced by the fiber content. Considering the mean values, the 10% washed fiber sample showed a tensile stress at failure 74.5% higher than the matrix.

However, although the treatment led to the extraction of fiber components as shown by SEM, the mechanical properties such as tensile strength were not significantly changed. Therefore, the fiber content was more efficient at increasing the mechanical properties than the superficial treatment of the fibers when incorporated in the matrix.

It can therefore be concluded that the material under study is promising for the market due to its good compatibility with natural fibers and its potential to expand the applications of natural fibers and glycerol. The replacement of polymer volume with natural fiber materials also results in more environmentally and socially appropriate material. Future work will focus on improving the properties of the product in order to participate in the more competitive commodities market.

Acknowledgements: The authors thank FAPESB (Foundation for Research of State of Bahia) for financial support and scholarship.

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