Proceedings of the

6th Brazilian Conference on Composite Materials

ISBN 978-65-00-49386-3

Part of ISSN 2316-1337

Organised & Edited by R.J. da Silva & T.H. Panzera

Content available at: doi.org/10.29327/566492

Mechanical properties of castor-oil polyurethane laminates reinforced with papaya bast fibre cellular layers

G.L.C. Coura[(a)], R. T. S. Freire[(b), *], A. J. B. Campuzano[(c)], J. C. dos Santos[(d)], F. Scarpa[(e)], T. H. Panzera[(f)]

(a) 0000-0002-8139-988X (Federal University of São João del-Rei – Brazil)

(b) 0000-0001-5206-5939 (Federal University of São João del-Rei – Brazil)

(c) 0000-0002-7241-6836 (Federal University of São João del-Rei – Brazil)

(d) 0000-0002-7485-491X (Federal University of São João del-Rei – Brazil)

(e) 0000-0002-5470-4834 (University of Bristol – United Kingdom)

(f) 0000-0001-7091-456X (Federal University of São João del-Rei – Brazil)

* Corresponding author: rfreire@ufsj.edu.br

Keywords: Papaya bast fibre, castor-oil polyurethane, sustainable composite, honeycomb-like structure, mechanical properties

Abstract: This work aims to manufacture and characterise a bio-composite material reinforced with natural papaya fibres using castor-oil polyurethane as the matrix phase. Samples are fabricated through hand lay-up and uniaxial compaction. Papaya fibres are extracted as laminas of a honeycomb-like structure, whose elongated cells line up in a single preferred direction. These laminas present a set of quasi-periodic holes along its surface, owing to the emergence of stems during the growing cycle of the plant. The influence of these holes on the mechanical properties of the laminates was investigated, as well as different morphologies (without holes, alternating holes, coincident holes and randomly oriented ground fibres (length ranging from 5-20 mm). The data are analysed via Analysis of Variance (ANOVA) to assess the influence of the different morphologies on the tensile and flexural modulus and strength of the fabricated composites. Results reveal the potential of papaya fibres as a reinforcement phase in polymeric composite materials.

1. Introduction

The scientific and technological interest in composite materials has lately grown, considering its diverse applications in industrial sectors such as aeronautics, automotive and biomedical. In particular, sustainability and environmental issues have recently intensified the research on natural fibres in material science and engineering, owing to their low cost, moderate mechanical resistance, low specific weight, biodegradability and obtention from renewable resources [1].

The most versatile natural polymer is castor oil, widely used as a raw material in the production of various products, such as paints and lubricants [2]. Castor bean (*Ricinus communis*) is abundant in Brazil and can be found in tropical and subtropical regions with low humidity. According to Milanese, 2008 [3], the leading producers of castor oil are Brazil, China and India. Tests carried out on polyurethane foams prove the good biodegradability of this material in the presence of fat-degrading microorganisms [4]. Castor-oil-based polyurethanes are thus an attractive alternative renewable material, according to the concept of sustainable development [5].

Carica papaya, a species of the Caricaceae family, is widely cultivated in tropical and subtropical regions. Brazil is the world's second-largest producer of this fruit, surpassed only by India [6]. Even though *Carica papaya* does not contain wood, these plants can reach up to 10 meters in height [7]. The strength of the stem is provided by fibre layers that constitute the bark. Each layer consists of a fibre mesh with an anisotropic, honeycomb-like cellular structure, where the elongated cells align in a preferential direction. [7-9].

Kempe et al. [8] reported that papaya bast fibres present tensile modulus and strength of up to 10 GPa and 100 MPa, respectively. Although these values are comparatively lower than those of natural fibres in general [10-11], the density of the papaya fibre is one of the lowest in the plant kingdom (approximately 0.86 ± 0.07 g/cm³) [8-12], and this makes the specific properties of the fibre attractive to produce sustainable composite materials.

To the best of these author's knowledge, this work represents the first attempt to investigate fully sustainable composites with papaya fibres and castor-oil-based biopolymer considering different types of fibre morphologies. One-way ANOVA and Tukey's test were used to evaluate the effects of the different morphologies on the tensile and flexural properties of the fabricated composites.

2. Methodology

2.1. Materials

Castor oil-based polyurethane (AGT 1315) was supplied by Imperveg (Brazil). Papaya fibres are extracted from papaya trees in the midwest region of the state of Minas Gerais (Brazil).

2.2. Fibre extraction & Composites manufacturing process

The extraction of papaya bast fibres follows the process described by Kumaar et al. [13]. The fibre extraction process from *Carica papaya* plants consists of cutting the stem and immersing it in water for 15 days to remove the core (parenchyma) of the stems. This material is removed manually and discarded, while the remaining bark is again immersed in water for an additional period of 15 days, after which fibre layers can be manually extracted, water-rinsed and dried in the shade for a week. This extraction process is environmentally friendly, and no chemicals are required. Papaya fibre layers are initially cut (or ground, in the case of short fibres) according to the dimensions required by the standards of the respective tests. Short fibres are ground in a knife mill, with an approximate size of 5-20 mm. The fibre layers are pre-compacted at 20 MPa for 10 minutes before use.

Composite laminates are manufactured according to the levels of the morphological factors (Table 1), using hand lay-up followed by cold uniaxial compaction. The fibre grammage is fixed at 0.15 g/cm², determining the number of layers used. The corresponding fibre mass fraction varies from 40 to 60% (fibre volumetric fraction from 46 to 66%). Each layer is placed one by one in a metallic mould (300 × 300 mm²), pouring part of the total volume of the biopolyurethane adhesive to ensure proper wetting. This biopolymer is a two-component adhesive that consists of a prepolymer (methylene diphenyl diisocyanate) and a polyol mixed respectively in a 1:1.2 mass ratio, according to the manufacturer's recommendations. The mould is previously covered with a plastic film to provide a better surface finish. A lid closes the mould, and a pressure of 654 kPa is applied for 24 hours, after which the composite plate is demoulded and wrapped in plastic for post-cure to avoid moisture absorption. Subsequently, these samples were sent to the Bristol Composites Institute (University of Bristol, UK), where individual samples were laser-cut and tested according to the respective ASTM standards.

Table 1. Experimental conditions investigated.

Experimental Condition	Morphology
NoH	No holes
AltH	Alternating holes
CoH	Coincident holes
Rnd	Randomly oriented ground fibres

3. Results and Discussions

Table 2 presents the mean value and standard deviation for all mechanical responses analysed, considering three samples and two repetitions for each experimental condition. Table 3 shows the parameters obtained via Analysis of Variance (ANOVA) for the means of these response variables.

Table 2. Descriptive statistics of the response variables investigated.

Experimental conditions		Tensile		Flexural	
		Strength (MPa)	Modulus (MPa)	Strength (MPa)	Modulus (GPa)
Replica 1	NoH	100±52	11.01	40.1±5.2	0.46±0.17
	AltH	87±40	15.0±4.7	35.6±2.5	0.40±0.13
	CoH	114±38	16.1±3.3	39.3±1.0	0.44±0.03
	Rnd	26.1±4.5	2.43±0.26	13.8±5.2	0.11±0.04
Replica 2	NoH	77.79	14.5±7.7	47±16	0.50±0.30
	AltH	94±35	14.5±4.3	38.8±9.5	0.39
	CoH	121±17	16.0±2.0	42.7±5.7	0.44±0.09
	Rnd	31.0±1.2	2.96±0.39	13.28	0.09

Table 3. One-way ANOVA for response variables.

	Tensile			Flexural	
Experimental Factor: Morphology	Strength	Modulus	Poisson's ratio	Strength	Modulus
P-value ≤ 0.05	0.002	0.001	0.202	0.002	0.000
R^2_{adj}	93.74%	95.13%	38.62%	94.84%	98.92%
P_{AD}-value ≥ 0.05	0.612	0.076	0.684	0.904	0.986

The factor under analysis is the morphology of the composites (Table 1), considered significant for the response variable when the P-value is less than or equal to 0.05, that is, at a 95% confidence level. The R^2_{adj} values associated with the response variables for which the morphology has a significant effect are greater than 88%, indicating good predictability of the underlying linear statistical model used in ANOVA. The Anderson-Darling normality test is used to validate the statistical analysis; P-values should be greater than or equal to 0.05, indicating that the data follow a normal distribution. All the averages presented in the graphs of the effects of the response variables are analysed using a multiple-comparison (Tukey's) test to assess equivalence between average pairs; equal letters represent equivalent means.

3.1. Tensile Tests

The tensile strength values vary from 26 to 122 MPa, while the modulus of elasticity values range from 2.4 to 16 GPa (Table 2). Such values are comparable, although generally lower, to those obtained for the longitudinally oriented papaya-epoxy composites (investigated elsewhere [14]), a fact attributed to the matrix properties since the tensile properties of castor-oil biopolyurethane are inferior when compared to epoxy [15]. However, it is worth mentioning that papaya fibres provide an efficient reinforcement. The tensile modulus is 6.8 – 40 times higher, and the tensile strength is 2.6 – 10.6 times higher relative to the pure resin (0.4 GPa and 11.1 MPa, respectively [15]). Moreover, the use of biopolyurethane results in a fully sustainable and biodegradable composite.

3.2. Flexural Tests

The flexural strength of the laminates varied from 13.28 to 47 MPa and, the modulus of elasticity, from 0.1 to 0.48 GPa (Table 2). These values are lower than those found for the papaya epoxy composite with longitudinal fibres, a fact attributed to the matrix properties [14].

Table 4 presents the mean value for the mechanical responses investigated for each experimental condition considered. It is noteworthy that laminates made with continuous laminas with or without holes present statistically equivalent means, except for flexural modulus, which is higher for laminates without holes. Laminates with randomly oriented fibres display a significant reduction in tensile (and flexural) strength and modulus relative to other morphologies, as most fibres are not oriented in the load direction. The ANOVA was also performed excluding the level with randomly oriented ground fibres since this morphology is dramatically different from the others. The analysis, including Tukey's test, also leads to the same conclusions drawn above from Table 4

Table 4. Mean values and Tukey's test for the mechanical responses analysed.

Experimental condition	Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)
NoH	89 (A)	12.8 (A)	44 (A)	0.48 (A)
AltH	91 (A)	14.8 (A)	37.2 (A)	0.40 (B)
CoH	118 (A)	16.1 (A)	41.0 (A)	0.44 (AB)
Rnd	28.6 (B)	2.70 (B)	13.5 (B)	0.10 (C)

4. Conclusions

Papaya bast fibres provide an efficient reinforcement to castor-oil polyurethane. The tensile modulus (strength) is 6.8 – 40 (2.6 – 10.6) times higher relative to the pure resin (0.4 GPa and 11.1 MPa, respectively). Randomly oriented fibres offer inferior results for tensile and flexural properties (60%-80% lower relative to morphologies with continuous fibrous laminas). Moreover, the use of biopolyurethane results in a fully sustainable and biodegradable composite. Tukey's test shows that the mean values for tensile and flexural strength as well as for flexural modulus are equivalent for the three types of morphology with continuous fibrous laminas (alternating, coincident and without holes). Such findings imply that holes do not play a significant role in reducing the mechanical properties of the composite laminates. This observation is important as the presence of holes is an intrinsic characteristic of papaya fibre laminas. The selection of large regions without holes is complex and would lead to the disposal of most of the material. Similar observations have already been reported elsewhere for papaya-epoxy laminates.

Declaration of Competing Interests

The authors declare no conflicts of interest.

CRediT author statement

G.L.C. Coura: experiments, data analysis, writing – original draft. **R. T. S. Freire:** conceptualisation, supervision, review, discussion of results. **A. J. B. Campuzano**: writing and review. **J. C. dos Santos**: data analysis, experimental technical support and discussion of results. **F. Scarpa:** review, resources, discussion of results. **T. H. Panzera:** resources, supervision, review and discussion of results.

Acknowledgements

G.L.C. Coura acknowledges the Brazilian Research Agencies, FAPEMIG (MSc scholarship) and CNPq (PQ - 309885/2019-1) for the financial support provided.

References

[1] M. Ramesh, K. Palanikumar, K. H. Reddy. Plant fibre-based bio-composites: sustainable and renewable green materials, Renew. Sust. Energ. Rev. 79, (2017), 558-584. https://doi.org/10.1016/j.rser.2017.05.094

[2] D. S. Ogunniyi. Castor oil: A vital industrial raw material, Bioresource Technology, 97, 1086-1091, 2006. https://doi.org/10.1016/j.biortech.2005.03.028

[3] A. C. Milanese, A. C. Caracterização de compósitos de matrizes poliméricas reforçados com fibra de sisal e vidro, Dissertação de Mestrado- Universidade Estadual Paulista, Guaratinguetá, 2008.

[4] J. M. Cangemi. Biodegradação de Poliuretano Derivado de Óleo de Mamona, São Carlos 2006, Tese (Doutorado em Ciências) – Universidade de São Paulo.

[5] H. Mutlul., M. A. R. Meier. Castor oil as a renewable resource for the chemical industry,Eur, J, Lipid Sci, Technol, 112,10–30, 2010. https://doi.org/10.1002/ejlt.200900138

[6] E. A. Evans, F. H. Ballen, An overview of global papaya production, trade, and consumption, FE913- University of Florida, (2012).

[7] A. Kempe, T. Lautenschläger, A. Lange, C. Neinhuis. How to become a tree without wood- Biomechanical analysis of the stem of Carica papaya L. Plant Biology 16(1), (2014), 264-271. https://doi.org/10.1111/plb.12035

[8] A. Kempe, A. Göhre, T. Lautenschläger, A. Rudolf, M. Eder, C. Neinhuis, Evaluation of bast fibres of the stem of Carica papaya L. for application as reinforcing material in green composites, Research and Review in Biology, 6(4), (2015), 245-252. https://doi.org/10.9734/ARRB/2015/15407

[9] V. M. Jiménez, E. M. Newcomer, M. V. G. Soto. Biology of the Papaya Plant, Genetics and Genomics of Papaya, Plant Genetics and Genomics: Crops and Models 10, 17-33, 2014.

[10] L. G. Thygesen, M. Eder, I. Burgert. Dislocations in single hemp fibres - investigations into the relationship of structural distortions and tensile properties at the cell wall level. Journal of Materials Science, 42, (2007) 558-564. https://doi.org/10.1007/s10853-006-1113-5

[11] T. Gurunathan, S. Mohanty, S. K. Nayak. A review of the recent developments in biocomposites based on natural fibres and their application perspectives, Composites: Part A- Applied Science and Manufacturing, 77, 1-25, 2015. https://doi.org/10.1016/j.compositesa.2015.06.007

[12] A. K. Bledzki, W. Zhang, A. Chate. Natural-fibre-reinforced polyurethane microfoams, Composites Science and Technology, 61(16), 2405-2411, 2001. https://doi.org/10.1016/S0266-3538(01)00129-4

[13] A. Saravana Kumaar, A. Senthilkumar, T. Sornakumar, S. S. Saravanakumar, V.P. Arthanariesewaran, Physicochemical properties of new cellulosic fibre extracted from Carica papaya bark, Journal of Natural Fibres, 16(2), (2019), 175-184. https://doi.org/10.1080/15440478.2017.1410514

[14] G. L. C. Coura, R. T. S. Freire, J. C. D. Santos, L. A. Oliveira, F. Scarpa, T. H. Panzera. Tensile and flexural properties of epoxy laminates with natural papaya bast fibre cellular layers. Composites Part C: Open Access, v. 2, p. 100017, 2020. https://doi.org/10.1016/j.jcomc.2020.100017

[15] P. R. Oliveira, M. May, T. H. Panzera, F. Scarpa, S. Hiermaier. Reinforced biobased adhesive for eco-friendly sandwich panels. International Journal of Adhesion and Adhesives. v.98, 102550, 2020. https://doi.org/10.1016/j.ijadhadh.2020.102550