



Journal of Materials and Engineering Structures

Research Paper

Thermo mechanical characteristics of Sisal fibre reinforced composites after treatment with potassium permanganate and stearic acid

Subramanya Raghavendra ^{a,*}, Manjunatha Kuntanahalli Narayanappa ^b, Chandra Shekar Anjinappa ^c

^a Department of Mechanical Engineering, Sai vidya institute of Technology, Bangalore, Visvesvaraya Technological University, India

^b Department of Mechanical Engineering, SJC institute of Technology, Chikaballpura, Visvesvaraya Technological University, India

^c Department of Mechanical Engineering, Bangalore institute of Technology, Bangalore, Visvesvaraya Technological University, India

ARTICLE INFO

Article history :

Received : 10 October 2021

Revised : 16 January 2022

Accepted : 22 January 2022

Keywords:

Sisal Fibre

Stearic acid

Composites

Scanning Electron Microscopy

ABSTRACT

This paper presents an experimental study of epoxy and sisal fibre composites with and without potassium permanganate and stearic acid treatment. A compression moulding technique was used to develop the composites. Differential Scanning Calorimetry (DSC), tensile and flexural tests, and scanning electron microscopy were used to investigate the thermal and mechanical behaviour of these composites. SEM images of sisal fibres revealed improvements in the fibre's surface topography further to the surface stearic acid treatment process. X-ray diffraction (XRD) analysis reveals that sisal fibre is crystalline in nature. When sisal fibre was treated with stearic acid, the tensile strength increased to 43.45 MPa. Potassium permanganate-treated fibre reinforced composites demonstrated high potential flexural strength. SEM analysis revealed that stearic acid-treated fibre improved interfacial adhesion between the fibres and matrix.

1 Introduction

The materials researches have a direct impact on scientific and technological developments. Metals and polymers are used in a variety of applications in daily life, and these technological advancements are largely dependent on advances in the field of material science. A composite is made up of one or more discontinuous phases embedded in a continuous phase. The

* Corresponding author. Tel.: +91 9880642862.

E-mail address: rvs.sdly@gmail.com

discontinuous phase is generally harder and stronger than the continuous phase and is referred to as the reinforcement or reinforcing material, whereas the continuous phase is referred to as the matrix. The properties of composites are primarily determined by the properties of their constituent materials. Natural fibres such as banana, coir, sisal, hemp, and others are now widely used by material scientists in the development of polymer matrix composites. Because these natural fibres are derived from plant sources and are eco-friendly in nature. Furthermore, the strength of these fibres is relatively high. The strength of these natural fibres can be increased by modifying the surface of the fibres. One among in this, the Sisal fibre is one of the most commonly used natural fibres and is very easily cultivated. Sisal fibre obtained from the sisal plant that is commonly known as agave sisalana. sisal plant having a short growing period, widely available, easy to cultivate sisal fibres shows the excellent physical and mechanical characteristics. Normally sisal plant able to produce about 200-500 leaves and each leaf consists of 1000-1200 fibre bundles. Before using natural fibres in a polymer composite, there are some issues and constraints to consider. One of the most serious issues with natural fibre is its hydrophilic nature. Because of this hydrophilic nature, fibres swell and fungi can be attacked [1, 2]. The chemical nature of plant-based natural fibres is critical and differs from fibre to fibre. The aspect/ratio and cellulose content of the fibre materials have the greatest impact on fibre performance. The concentration of cellulose, hemicellulose, and lignin in plant-based fibres has a major impact on the overall efficiency [3]. Sisal fibres are suitable for construction industries for a wide range of reasons, such as ease of cultivation, good thermal and acoustic insulation capabilities, and great toughness and abrasion resistance [4]. The main disadvantage of these fibres is that they have poor interfacial adhesion between polar and hydrophilic matrix. When natural fibres are reinforced with matrix, they exhibit poor wetting properties, resulting in a weak interface in the composite. If these interfaces are weak, load distribution is not uniform and effective load distribution cannot be achieved. The mechanical properties of the composite can be varied [5]. The following literatures provide the details on fibre chemical treatment, and to improve the fibre matrix interface.

Paramasivam, Abdulkalam et al [6] worked on sisal fibre reinforced epoxy composites. it is found that Tensile strength of sisal epoxy composites was found to be 250-300 Mpa, which can be compared with strength of fibre glass epoxy composites of the same composition. The unidirectional modulus of sisal epoxy composites was found to be about 8.5 Gpa. Also authors are fabricated some cylindrical components using sisal epoxy composites.

A. Valadez-Gonzalez et al. [7] studied the interfacial shear strength of silane chemical modified polyethylene matrix composites. Results shows that composites made using alkali treated fibres are higher when compared with untreated fibre reinforced silane polyethylene composites. These increases in the results are due to the better fibre wetting and adhesion between fibre and matrix.

Varghese et al. [8] have studied the effect of chemical treatment on the tensile, dynamic mechanical, electrical and ageing properties of the short sisal fibre reinforced LDPE composites. Treatments using chemicals such as sodium hydroxide, isocyanate, permanganate and peroxide were carried out to improve the bonding at the fibre polymer interface. It was observed that the treatments enhanced the tensile properties of the composites considerably. It has been observed that the cardanol derivative of toluene diisocyanate treatment reduced the hydrophilic nature of the sisal fibre and thereby enhanced the tensile properties of the sisal LDPE composites. They found that peroxide treated composites showed an enhancement in tensile properties due to the peroxide induced grafting. It was also found that permanganate treated composites also showed similar trend due to the permanganate induced grafting.

R.G. Raj et al. [9] investigated the influence of using various dispersing acids such as stearic acid and mineral oil and a coupling agent maleated ethylene. In cellulose fibre reinforced polypropylene composites tensile strength and modulus of the composites studied were found to increase with fibre content when either stearic acid or mineral oil 1% by weight of fibre were added as processing acids during the compounding. The properties also were found to be affected by the amount of processing acid used. Maximum increases in the properties were observed when the aid was added in 1% concentration by weight of the fibre.

Siby Varghese, et al. [10] have studied the mechanical properties of acetylated and untreated short sisal fibre reinforced natural rubber composites and found that acetylating improves the adhesion between the rubber and the fibre. They have investigated the effect of different bonding agents on the physical and mechanical properties of sisal fibre reinforced natural rubber composites. The treatments employed included alkali immersion at high temperature and use of bonding agent based on phenol formaldehyde resorcinol formaldehyde precipitated silica at different concentrations. They concluded that alkali treated fibre imparts better physical properties mixes than the untreated fibre.

The current study looked at the use of stearic acid and potassium permanganate for fibre surface modification and the ability of sisal fibre as a reinforcement material composite using epoxy as a matrix. Some of the fibres were treated with stearic acid, while others were treated with potassium permanganate to improve mechanical and thermal properties by increasing fibre-to-matrix adhesion when compared to untreated fibres. To describe the observed tensile properties of the fibres, morphology of the fibre surface and fractography studies of the surfaces of tensile tested specimens were also carried out.

A complete characterization of a material is very useful when searching for potential applications for it. Many interfacial phenomena such as adsorption, wetting, and adhesion are caused by the surface composition of the elements in polymer composites, so it is crucial to describe fibres before and after chemical treatment to assess the use of sisal fibre in biocomposites. Various analytic techniques were used to characterise sisal fibre in this study. The impact of various chemical treatments on the fibres was also studied. As a result, this work aims to address crucial fibre features in order to promote their expanding utility.

Various analytic techniques were used to characterise sisal fibre in this study. The impact of various chemical treatments on the fibres was also studied. As a result, our research aims to address essential fibre characteristics in order to facilitate their increased use in current and future applications such as polymeric biocomposites.

2 Materials and methods

2.1 Sisal fibre

The sisal fibres which is used for the reinforcement is collected from the local sources. The fibres were mechanically comminuted to the size of diameter 0.5–2.0 mm.

2.2 Epoxy resin

In this work epoxy resin grade LY 951 has been used along with hardener HY951. These resins are thermosetting polymers and used as adhesives, these resins having properties such as low shrinkage, good adhesion, and resistance to the moisture. Both supplied from S&S polymers Bangalore.

2.3 Stearic acid

Stearic acid with acetone solution is used to modify fibre surfaces. The stearic acid chemical formula is represented by $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$. The carboxyl group of stearic acid reacts with hydroxyl groups of the fibre and improves the fibre and water resistant properties. Chemical treatment removes pectin, wax, oil covering materials from the fibre surface which results in more cellulose microfibrils are to appear on the fibre surface.

The following equation 1 shows the chemical reaction between the NaOH and fibre



In this reaction the OH groups of cellulose is converted into ONa groups increases the dimensions of molecules. Due to the washing with distilled water will remove the linked Na-ions that is Na^+ ions and new crystalline structure is formed.

2.4 Potassium permanganate treatment

The powdered fibres are immersed in 100 ml potassium permanganate and a 100 ml acetone solution for 30 minutes. Then the fibres are washed with distilled water and after washing, the fibres are allowed to dry in sunlight for 2 days

The following equation 2 shows the reaction between fibre OH group and potassium permanganate



This treatment results in formation of highly reactive permanganate ions they react with cellulose and forms cellulose magnate which initiates the polymerization process. This treatment provides the chemical interlocking at the interface and develops adhesions between fibre and matrix. Permanganate treatment reacts with the OH groups of lignin and removes them

from the fibre. Due to this treatment fibre surface becomes rougher there by mechanical interlocking with the matrix can be improved.

Composites containing 70% of Epoxy and 30% of natural sisal fibres. Melt mixing of short-cropped Sisal Fibres(SF) and epoxy(along with hardener) was carried out in a twin rotary mixer (XK-160B, Shanghai Rubber Machinery Factory, China) with a rotation speed of 60 rpm for 5 min at 180°C. After melt mixing, the composites with 10 wt% SF content were fabricated by compression moulding with flat vulcanizing machine (XLB-0350 x 350, Huzhou Dongfang Machinery, China). No pressure was applied for 5 min and then 10 GPa pressure was applied for 10 min at 180°C. Before demoulding, the samples were then cold pressed for 15 min down to about 60°C.

2.5 X-ray diffraction

An X-ray diffraction study was performed to determine the crystallographic nature and crystallinity of the selected fibres. A Bruker Diffractometer Model D8 with CuK radiation ($\lambda = 1.5406$) and a Ni filter, operating at 40 kV and 30mA, was used for this purpose.

2.6 Differential Scanning Calorimetry (DSC)

The equipment used was a Shimadzu DSC-60; all samples were analysed from 25 to 600 °C with a heating rate of 20°C/min.

2.7 Mechanical testing

The tensile test was performed as per the ASTM standard D638. Universal testing machine (make KIC-2-1000-c) used for the tensile test. Tensile specimen is placed on the universal testing machine and the tensile load is applied gradually. The flexural test was performed as per the ASTM standard D-5943. Universal testing machine (make KIC-2-1000-c) used for a flexural test. Flexural test is a three-point bend test. Flexural specimen is placed in the universal testing machine. When the load is applied the specimen bends the computer generate the graphs and all the properties of the specimen.

2.8 Scanning electron microscopy

Scanning electron microscopy (SEM) observations were made on a ZEISS EVO 40 microscope. Voltage between the electrodes was 17.2 kV. Observations were performed of the cleavage surfaces of the composite samples, coated with sputtered gold film to increase contrast.

3 Result and discussions

3.1 X-ray diffraction

Powdered sisal fibre was placed in a sample holder and scanned continuously in the 10°-80° range at a rate of 20° per minute. Following R. Nayak, et al. [11] to determine the crystallinity index (CI) of the fibre, first the area under the peaks (shaded area figure 1) and the total area in the obtained XRD spectrum were determined using Solid Edge CAD software. Then, crystallinity index (in %) was obtained using the formula.

$$\frac{(\text{Area of Crystalline Fraction})}{(\text{Area of crystalline Fraction} + \text{Area of amorphous Fraction})} \times 100 = \text{Crystallinity}(\%) \quad (3)$$

The spectra are distinguished by a strong peak (a broad hump) at 2 values at 16.5 °, a very strong peak at 22.7 °, and another peak at 15.4 °. The narrow peak in the graph, which could be due to contamination in the fibre, most likely from an inorganic substance [12]. Calculated crystallinity index of sisal fibres of Karnataka obtained from Fig. 1 was found to be about 53%.

3.2 Differential Scanning Calorimetry (DSC)

Figure 2 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, and 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 fibre. Thus, an interaction between the fibre/matrix can be inferred [13, 14].

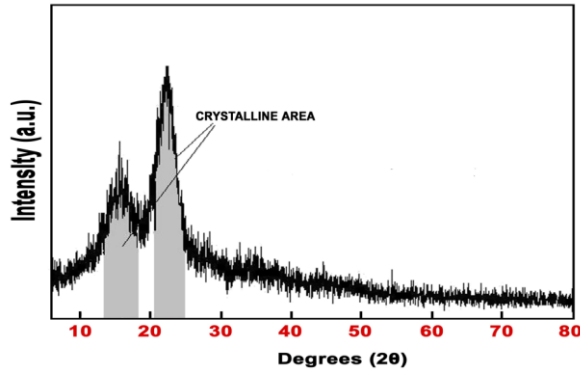


Fig. 1 – X-ray diffraction spectrum of Sisal fibre

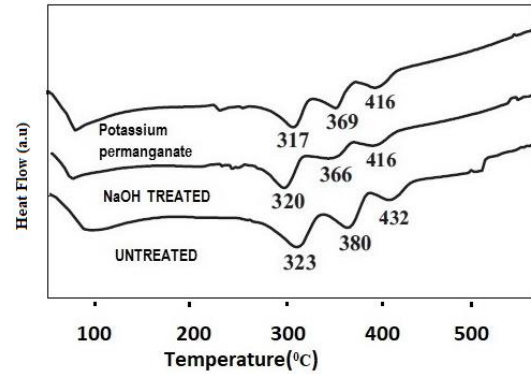


Fig. 2 – DSC curves of the untreated and treated sisal fibres

3.3 Tensile and flexural test

The variations in the tensile strengths of both the composites are shown in below table. The tensile strength of the KMnO₄(potassium permanganate) treated sisal fibre epoxy composite is 29.58 N/mm² while Stearic acid treated composite shows 43.45 N/mm² and from this result we concluded that stearic acid treated sisal fibre reinforced composites shows better tensile strength as compared to potassium treated sisal fibre reinforced composite. Therefore, stearic acid treated sisal fibre epoxy composite significantly improves the load carrying capacity and with stands the tensile stresses.

Table 1: Results of Tensile and flexural strength of sisal Untreated and Treated fibre composites

Sample	Tensile strength (MPa)	Flexural strength (MPa)
Untreated fibre+ epoxy (30%wt+70%wt)	22.76	96.41
Potassium permanganate treated specimen 1 (30%wt+70%wt)	29.58	109.32
Potassium permanganate treated specimen 2 (30%wt+70%wt)	29.59	109.32
Potassium permanganate treated specimen 3 (30%wt+70%wt)	29.58	109.11
Stearic acid treated 1 (30%wt+70%wt)	43.39	103.36
Stearic acid treated 2 (30%wt+70%wt)	43.45	103.36
Stearic acid treated 3 (30%wt+70%wt)	43.42	103.36

The above table shows the flexural strengths of the both the composites. The potassium permanganate treated sisal fibre epoxy composite shows the flexural strength of 109.32Mpa and stearic acid treated sisal fibre epoxy composites shows the flexural strength of 103.36 Mpa. From the results it is cleared that potassium permanganate treated sisal fibre epoxy composites shows better flexural strength when compared to stearic acid sisal fibre epoxy composites. The lignocellulosic fibres seem to responsible for the reduction in deformation capability. The epoxy matrix is ductile, whereas the lignocellulosic fibres are brittle, resulting in a loss of toughness in the composite material.

The tensile and flexural strengths of untreated sisal epoxy composites were significantly lower than those of treated sisal epoxy composites (from table 1). This pattern can be explained by the fact that the fibre surface became rough after treatment with potassium permanganate and stearic acid. As seen in the SEM images (Fig 3b, 3c and 3d), the epoxy matrix wetted around the sisal fibre, resulting in better load transfer in the fibre [15, 16]. Similar trend found in Seetha Girish et al, [17] Evaluated treated and untreated coir fibre reinforced vinyl ester composites and found that NaOH treated fibre increased tensile strength and tensile modulus by 10% over untreated fibre composites.

3.4 Scanning electron microscopy

Figure 3 (a) shows scanning electron micrograph of the longitudinal section of the untreated sisal fibre, while Figure 3(b) shows the fractured surface of potassium permanganate treated sisal fibre. Longitudinal section of the fibre figure 3(a) shows smooth surface covered with cellulose and other wax substances. Whereas Figure 3(b) shows rough surface, that a layer of extractives was removed after the potassium permanganate treatment. Figure 3(c) shows the stearic acid treated fibre morphology. In this fibre pull-out as well as holes resulting from fibre delamination were observed regardless the nature of the fibre. Figure 3(d) shows The fractured surfaces of each composite revealed extensive interfacial delamination between the fibre and the matrix. It indicates that lignocellulosic fibres were hardly wetted by the epoxy matrix with a gap developing around the fibres. These could be reason for the variation in observed different strength values.

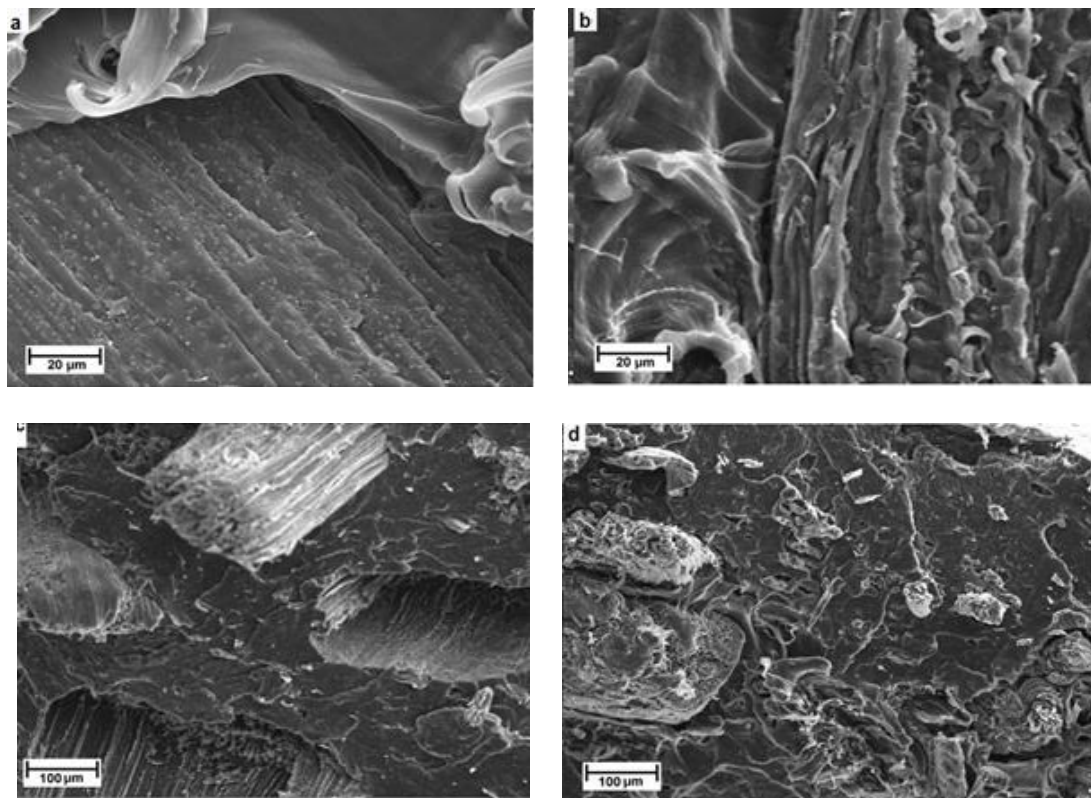


Fig. 3 – Scanning electron micrograph of the longitudinal section of, 3(a) untreated sisal fibre, 3(b) fractured surface of potassium permanganate treated sisal fibre, Figure 3(c) Fibre pull outs in stearic acid treated fibre morphology and 3(d) interfacial delamination between the fibre and the matrix in stearic acid treated fibre morphology

4 Conclusion

This study showed that by using the compression moulding technique it was possible to process highly filled composites. XRD results indicated the fibre to have mainly the Cellulose I structure and crystallinity index of about 53%. DSC of sisal fibre revealed the thermal degradation details of sisal fibre samples and also their thermal stability.

All of these tensile and flexural strength values are greater than the untreated sisal fibre composite sample. It is attainable that the treated fibres used in this study have a higher strength. Morphology studies revealed the number of defects along the length of the fibre, while fractured surface exhibited flat surface with intracellular fractures clearly indicating brittle nature of the fibre.

Acknowledgement

The support of the Sai vidya institute of Technology, Bangalore and Visvesvaraya Technological University, Belagavi is gratefully acknowledged.

Disclosure statement

No potential conflict of interest was reported by the authors.

REFERENCE

- [1]- K.G. Satyanarayana, K. Sukumaran, A.G. Kulkarni, S.G.K. Pillai, P.K. Rohatgi, Fabrication and properties of natural fibre-reinforced polyester composites. *Composites*, 17(4) (1986) 329-333. doi:10.1016/0010-4361(86)90750-0.
- [2]- G. Kalaprasad, B. Francis, S. Thomas, C.R. Kumar, C. Pavithran, G. Groeninckx, S. Thomas, Effect of fibre length and chemical modifications on the tensile properties of intimately mixed short sisal/glass hybrid fibre reinforced low density polyethylene composites. *Polym. Int.*, 53(11) (2004) 1624-1638. doi:10.1002/pi.1453.
- [3]- A. Atmakuri, A. Palevicius, L. Kolli, A. Vilkauskas, G. Janusas, Development and Analysis of Mechanical Properties of Caryota and Sisal Natural Fibers Reinforced Epoxy Hybrid Composites. *Polymers*, 13(6) (2021) 864. doi:10.3390/polym13060864.
- [4]- B. Bahja, A. Elouafi, A. Tizliouine, L.H. Omari, Morphological and structural analysis of treated sisal fibers and their impact on mechanical properties in cementitious composites. *J. Build. Eng.*, 34 (2021) 102025. doi:10.1016/j.job.2020.102025.
- [5]- S. Kalia, B.S. Kaith, I. Kaur, Pretreatments of natural fibers and their application as reinforcing material in polymer composites—A review. *Polym. Eng. Sci.*, 49(7) (2009) 1253-1272. doi:10.1002/pen.21328.
- [6]- T. Paramasivam, A. Kalam, On the study of indigenous natural-fibre composites. *Fibre Sci. Tech.*, 7 (1974) 85-88. doi:10.1016/0015-0568(74)90020-7.
- [7]- A. Valadez-Gonzalez, J.M. Cervantes-Uc, R. Olayo, P.J. Herrera-Franco, Effect of fiber surface treatment on the fiber–matrix bond strength of natural fiber reinforced composites. *Composites Part B*, 30(3) (1999) 309-320. doi:10.1016/S1359-8368(98)00054-7.
- [8]- S. Varghese, B. Kuriakose, S. Thomas, K. Joseph, Effect of Adhesion on the Equilibrium Swelling of Short Sisal Fiber Reinforced Natural Rubber Composites. *Rubber Chem. Technol.*, 68(1) (1995) 37-49. doi:10.5254/1.3538730.
- [9]- R.G. Raj, B.V. Kokta, F. Dembele, B. Sanschagrain, Compounding of cellulose fibers with polypropylene: Effect of fiber treatment on dispersion in the polymer matrix. *J. Appl. Polym. Sci.*, 38(11) (1989) 1987-1996. doi:10.1002/app.1989.070381103.
- [10]- S. Varghese, B. Kuriakose, S. Thomas, A.T. Koshy, Mechanical and viscoelastic properties of short fiber reinforced natural rubber composites: effects of interfacial adhesion, fiber loading, and orientation. *J. Adhes. Sci. Technol.*, 8(3) (1994) 235-248. doi:10.1163/156856194X01086.
- [11]- R. Nayak, I.L. Kyratzis, Y.B. Truong, R. Padhye, L. Arnold, G. Peeters, M. O'Shea, L. Nichols, Fabrication and characterisation of polypropylene nanofibres by meltblowing process using different fluids. *J. Mater. Sci.*, 48(1) (2013) 273-281. doi:10.1007/s10853-012-6742-2.
- [12]- R. Subramanya, K.G. Satyanarayana, B. Shetty Pilar, Evaluation of Structural, Tensile and Thermal Properties of Banana Fibers. *J. Nat. Fibers*, 14(4) (2017) 485-497. doi:10.1080/15440478.2016.1212771.
- [13]- J.L. Guimarães, F. Wypych, C.K. Saul, L.P. Ramos, K.G. Satyanarayana, Studies of the processing and characterization of corn starch and its composites with banana and sugarcane fibers from Brazil. *Carbohydr. Polym.*, 80(1) (2010) 130-138. doi:10.1016/j.carbpol.2009.11.002.
- [14]- P.H.F. Pereira, K.C.C.C. Benini, C.Y. Watashi, H.J.C. Voorwald, M.O.H. Cioffi, Characterization of high density polyethylene (HDPE) reinforced with banana peel fibers. *BioResources*, 8(2) (2013) 2351-2365. doi:10.15376/biores.8.2.2351-2365
- [15]- M. Idicula, K. Joseph, S. Thomas, Mechanical Performance of Short Banana/Sisal Hybrid Fiber Reinforced Polyester Composites. *J. Reinf. Plast. Compos.*, 29(1) (2010) 12-29. doi:10.1177/0731684408095033.
- [16]- Akash, K.V. Sreenivasa Rao, N.S. Venkatesha Gupta, D.S. Arun kumar, Mechanical Properties of Sisal/Coir Fiber Reinforced Hybrid Composites Fabricated by Cold Pressing Method. *IOP Conference Series: Materials Science and Engineering*, 149 (2016) 012092. doi:10.1088/1757-899x/149/1/012092.
- [17]- A.V.S. Girish, B. Vijaya, S. Arjun, S. Raghavendra, Manufacturing and mechanical characterization of coir fibre composites based on vinyl ester. *Adv. Mater. Process. Tech.*, (2021) 1-10. doi:10.1080/2374068X.2021.1878711.