

CHARACTERIZATION OF THERMOPLASTIC POLYURETHANE
ELASTOMER COATED PINEAPPLE LEAF FIBER

HAZWANI BINTI HASAN

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Polymer)

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

JULY 2019

DEDICATION

To my beloved husband, parents, family and friends

ACKNOWLEDGEMENT

In preparing this thesis, I was in contact with many people, researchers, academicians and practitioners. They have contributed towards my understandings and thoughts. A sincere appreciation belongs to my main supervisor, Associate Professor Dr. Wan Aizan Wan Abdul Rahman for encouragement, guidance, critics and friendship. I am also very thankful to my co-supervisor, Dr. Jamarosliza Jamaluddin for their guidance, advices and tolerance. Without their continued support and interest, this thesis would not have been the same as presented here.

I am also indebted to Universiti Teknologi Malaysia (UTM) for funding my master study. Librarians at UTM, officers at Malaysia Agriculture Research and Development, (MARDI) Pontian, Johor and officers at Malaysia Pineapple Industrial Board (MPIB) also deserved special thanks for their assistance in supplying the relevant informations.

My fellow postgraduate students should also be recognised for their support. My sincere appreciation also extends to all my colleagues, laboratory assistants and others who have provided assistance at various occasions. Their views and tips are useful indeed. Unfortunately, it is not possible to list all of them in this limited space. I am grateful to all my beloved family members.

ABSTRACT

Pineapple leaf fibers (PALFs) have several advantages such as low cost, eco-friendly and high specific strength but their brittleness limit the application. To overcome this limitation, PALFs were coated with thermoplastic polyurethane elastomer (TPU) to enhance their elasticities and flexibilities. TPU was synthesized using a two-stage route method which consists of polyurethane (diisocyanate react with polypropylene glycol), forming pre-polymer (polyurethane with short chain), and to increase the chain length, chain extender was added into pre-polymer. Prior to this coating, PALFs were treated with sodium hydroxide at 5% concentration to improve their surface areas of the PALF. Three parameters were varied during the preparation of TPU coated PALF which were dipping times (5 min, 10 min, 15 min and 20 min), curing temperatures (30 °C, 55 °C, and 85 °C) and curing times (6, 12 and 24 hours). From scanning electron microscope it was found that sample with 10 minutes dipping time showed a clean and rough surface which favorable for coating with TPU. These were supported by tensile strength that showed sample with 10 minutes high in modulus around 900 MPa with 30% elongation at break. The formation of hydrogen bonding was thought contributed to the increase as shown by the plots of Fourier Transform Infrared at 3300 cm^{-1} and at 1530 cm^{-1} indicates PALF fully coated with TPU. Thermal analysis has been studied by using differential scanning calorimetry. The existence of hydrogen bonding had increased the thermal stability as measured with thermogravimetric analysis at around 500 °C of end set temperature. It was found that there is a formation of hydrogen bonding between PALF and TPU. The optimum requirement of TPU coated PALF were 10 minutes dipping time at 85 °C curing temperature and for 6 hours curing time in order to enhance the elasticity and flexibility of the fiber due to their brittleness. As a conclusion, coated PALF with TPU with optimum condition have improved the properties of an elastic yarn.

ABSTRAK

Serat daun nanas (PALF) mempunyai beberapa kelebihan seperti kos rendah, mesra alam dan kekuatan yang tinggi tetapi kerapuhan mereka telah menghadkan penggunaannya. Untuk mengatasi masalah ini, PALF telah disalut dengan elastomer poliuretana termoplastik (TPU) untuk meningkatkan keanjalan dan kebolehlenturan. TPU telah disintesis menggunakan satu kaedah jajaran dua peringkat yang mengandungi poliuretana (diisosianat bertindak dengan polipropilena glikol), menjadi pra-polimer (poliuretana dengan rantai pendek) dan untuk menambahkan panjang rantai, penyambung rantai ditambah ke dalam pra-polimer. Sebelum salutan ini, PALF telah dirawat dengan natrium hidroksida pada 5% kepekatan untuk memperbaiki luas permukaan PALF itu. Tiga parameter telah dianalisa semasa penyediaan TPU menyalut PALF iaitu masa celupan (5 min, 10 min, 15 min dan 20 min), suhu pematangan (30 °C, 55 °C dan 85 °C) dan masa pematangan (6 jam, 12 jam dan 24 jam). Dapatan dari morfologi mikroskop elektron imbasan mendapati 10 minit adalah masa celupan, menunjukkan permukaan yang bersih dan kasar yang sesuai untuk salutan dengan TPU. Ini telah disokong melalui kekuatan tegangan yang menunjukkan 10 minit masa celupan mempunyai modulus yang tinggi sekitar 900 MPa dengan 30% pemanjangan pada waktu putus. Pembentukan ikatan hidrogen telah menyumbang peningkatan seperti ditunjukkan plot spektroskopi inframerah Fourier pada 3300 cm^{-1} dan pada 1530 cm^{-1} menunjukkan PALF disalut sepenuhnya dengan TPU. Analisis terma telah dikaji dengan menggunakan kalorimeter imbasan pembezaan. Kehadiran ikatan hidrogen telah meningkatkan kestabilan terma kepada 500 °C suhu set hujung yang diukur dengan analisis termogravimetri. Ia menunjukkan bahawa terdapat pembentukan ikatan hidrogen antara PALF dan TPU. Keperluan optimum untuk TPU menyalut PALF adalah masa mencelup 10 minit pada suhu pematangan 85 °C dan selama 6 jam masa pematangan bagi meningkatkan keanjalan dan kebolehlenturan serat disebabkan oleh kerapuhan mereka. Kesimpulannya, PALF bersalut TPU pada keadaan yang optimum telah menambahbaik sifat-sifat untuk benang elastik.

TABLE OF CONTENTS

	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	x
	LIST OF FIGURES	xi
CHAPTER 1	INTRODUCTION	1
1.1	Introduction	1
1.2	Problem Statements	2
1.3	Objective	4
1.4	Scope of Study	5
CHAPTER 2	LITERATURE REVIEW	7
2.1	Introduction	7
2.2	Natural Fiber	7
2.2.1	Advantages and Disadvantages of Natural Fiber	8
2.2.2	Application of Natural Fibers	10
2.2.3	Effect of Alkali Treatment on Crystalline Structure	15
2.2.4	Natural Fiber Extraction	16
2.2.5	Mechanical Treatment of Fiber	19
2.3	Pineapple Leaf Fiber	20
2.4	Polyurethane	25
2.5	Thermoplastic Polyurethane Elastomers	28
2.6	Polymer Coated Natural Fiber	33

2.7	Summary	36
CHAPTER 3	METHODOLOGY	37
3.1	Introduction	37
3.2	Materials	37
3.2.1	Pineapple Leaf Treatment	39
3.2.2	Thermoplastic Polyurethane Preparation	39
3.2.3	Coated Fiber Chemical Testing	39
3.3	Flow Chart of Research	40
3.3.1	Extraction of Pineapple Leaf	40
3.3.2	Alkaline Treatment of Pineapple Leaf Fiber	41
3.4	Synthesis of Thermoplastic Polyurethane Elastomer	41
3.5	Preparation of Thermoplastic Polyurethane Elastomer Coated Pineapple Leaf Fiber	42
3.5.1	Effect of Dipping Time	42
3.5.2	Effect of Curing Temperature	43
3.5.3	Effect of Curing Time	44
3.6	Characterization of Thermoplastic Polyurethane Elastomer Coated Pineapple Leaf Fiber	44
3.6.1	Fourier Transform Infrared Analysis	44
3.6.2	Tensile Test	45
3.6.3	Differential Scanning Calorimetry	45
3.6.4	Scanning Electron Microscopy	46
3.6.5	Thermogravimetric Analysis	46
3.6.6	Chemical Resistance	46
CHAPTER 4	RESULT AND DISCUSSION	49
4.1	Introduction	49
4.2	Fourier Transform Infrared Analysis	49
4.2.1	Fourier Transform Infrared Analysis of Untreated and Alkaline-Treated PALF	49
4.2.2	Fourier Transform Infrared Analysis of Untreated and Alkaline-Treated PALF Coated with TPU	51
4.3	Tensile Test	54

4.3.1	Effect of Dipping Time	54
4.3.2	Effect of Curing Time	58
4.3.3	Effect of Curing Temperature	60
4.4	Differential Scanning Calorimetry	63
4.5	Scanning Electron Microscopy	65
4.6	Thermogravimetric Analysis	66
4.7	Chemical Resistance	68
4.8	Summary	70
CHAPTER 5	CONCLUSION AND RECOMMENDATIONS	71
5.1	Conclusion	71
5.2	Recommendations	72
REFERENCES		73

LIST OF TABLES

TABLE NO.	TITLE	PAGE
Table 2.1	Advantages and disadvantages of natural fibers	9
Table 2.2	General properties of PALF	22
Table 2.3	Availability and composition of biofibers	24
Table 2.4	Structure and properties of biofibers	24
Table 3.1	List of materials	38
Table 3.2	List of materials for chemical testing	39
Table 3.3	Dipping time for thermoplastic polyurethane elastomer coated pineapple leaf fiber	43
Table 3.4	Curing temperature for thermoplastic polyurethane elastomer coated pineapple leaf fiber	43
Table 3.5	Curing time for thermoplastic polyurethane elastomer coated pineapple leaf fiber	44
Table 4.1	Summary of peak assignment of untreated and alkaline-treated PALF	51
Table 4.2	The FTIR analysis of the untreated and treated coated PALF	53
Table 4.3	DSC of pure TPU, untreated PALF coated with TPU and treated PALF coated with TPU for 20 minutes dipping time	59
Table 4.4	The chemical resistance test of untreated and treated PALF coated TPU	69

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
Figure 2.1	Classifications of natural fibers	8
Figure 2.2	Tensile properties of uncoated and polystyrene-coated Tamarind fiber	13
Figure 2.3	Scanning electron micrographs of (a) untreated, (b) alkali treated and (c) alkali with silane treated Tamarind fiber	14
Figure 2.4	Scanning electron micrographs of (a) untreated, (b) alkali treated and (c) alkali with silane treated polystyrene-coated Tamarind fiber	14
Figure 2.5	Reaction scheme of alkali treatment of natural fiber	17
Figure 2.6	Picture of (a) before and (b) after alkaline treatment of natural fiber	18
Figure 2.7	Picture showing a) Josaphine pineapple fruit and b) Pineapple leaf fiber	21
Figure 2.8	TG , DTA and DTG curves of raw pineapple leaf fiber	23
Figure 2.9	The chemical structure of TPU	26
Figure 2.10	Illustration of micro phase separation in TPU	27
Figure 2.11	The structure of TPU	28
Figure 2.12	The structure of polypropylene glycol	29
Figure 2.13	The structure of toluene diisocyanate	30
Figure 2.14	The structure of glycerol propoxylate	30
Figure 3.1	The flowchart of research work	40
Figure 3.2	Schematic diagram of TPU synthesis	42
Figure 4.1	The FTIR spectra of the untreated and treated PALF	50
Figure 4.2	The ATR-FTIR result from untreated & treated PALF coated with TPU	52

Figure 4.3	FTIR spectra of alkaline-treated PALF coated with TPU at different dipping time	53
Figure 4.4	FTIR spectra of untreated PALF coated with TPU at different dipping time	54
Figure 4.5	The ultimate tensile strength of untreated and treated PALF/TPU with different dipping time	55
Figure 4.6	The percentage of elongation at break of untreated and treated PALF with different dipping time	56
Figure 4.7	The Young's modulus of untreated and treated PALF/TPU with different dipping time	57
Figure 4.8	The ultimate tensile strength of untreated and treated PALF/TPU with different curing time	58
Figure 4.9	The percentage of elongation at break of untreated and treated PALF with different curing time	59
Figure 4.10	The Young's modulus of untreated and treated PALF/TPU with different curing time	60
Figure 4.11	The ultimate tensile strength of untreated and treated PALF/TPU with different curing temperature	61
Figure 4.12	The percentage of elongation at break of untreated and treated PALF with different curing temperature	62
Figure 4.13	The Young's modulus of untreated and treated PALF/TPU with different curing temperature	63
Figure 4.14	Differential scanning calorimetry of pure PALF, untreated PALF/TPU and treated PALF/TPU	64
Figure 4.15	Scanning electron micrograph of (a) untreated PALF, (b) alkaline-treated PALF, (c) untreated PALF coated with TPU and (d) alkaline-treated PALF coated with TPU at a magnification of 500 x at 10 minutes dipping time	65

Figure 4.16	(a) DTG/TGA of PALF and (b) TG curves of PALF/TPU under synthetic air atmosphere and heating rate of 10 °C min ⁻¹	66
Figure 4.17	The percentage of improvement in chemical resistance of untreated and treated coated PALF	69

CHAPTER 1

INTRODUCTION

1.1 Introduction

In the recent years, biofibers have gained considerable attention from researchers and industrial players all over the world because natural fibers are renewable, biodegradable, creating a greener environment impact and causing less health hazards. Natural fibers can be generally classified according to their origins such as leaf, seed, fruits, wood, stalk, grass and bats which includes jute, flax, hemp and kenaf. In tropical countries, biofibers can be easily, even from agricultural crops. One of them is the agro waste, which are abundant and has low price to obtain biofibers. The unique composition, properties and structure of agro waste like biofibers make them suitable material for several applications such as composite, textile, pulp and paper manufacturing. On top of that, biofibers are also suitable materials to produce fuel, chemicals, enzymes and food, (Mohammad et al, 2009). An example of tropical plant that provides biofibers is pineapple. This plant from the Bromeliaceous family is one of an important fruit in Malaysia and can be found abundantly. Moreover, this plant is harvested for its flesh or pulp, leaving behind the leaves and trunks. Manufacturers and farmers tend to discard these wastes by means of incineration or burning, which leads to serious environmental problems, (Sena Neto et al, 2013).

Pineapple wastes especially the leaves can be benefited as they are natural cellulose fiber source for textiles as their long fiber, composites and paper. In textile application, cotton is a famous sources but it was under short fiber. As the individual cells in pineapple and also banana fibers are relatively longer in size, they are suitable for the production of long fibers. This is a point worth to be taken as the length to diameter ratio (L/D) of individual cells in a fiber affects the flexibility and resistance to rupture of the fibers and the products produced from them especially textiles and papers. Pineapple leaf fiber also produces a silky and soft long fiber just like silk, (Yusof and Yahya, 2013).

1.2 Problem Statements

Currently, a major challenge in the pineapple industry is the environmental issue arising from it. In some countries, paper industries using pineapple fiber are facing great pressure to reduce pollutant emissions (Rahman, 2011). Method of incinerating these wastes creates environment issues. To overcome this problem, pineapple leaves are usually extracted mechanically or chemically for their fiber. The leaves are of the lower lignin content than other fiber which can undergo bleaching quite easily therefore low usage of chemicals during alkaline treatment (Kumar and Siddaramaiah, 2005).

Conventionally, this type of pineapple fiber is commonly used as thread and textile in some country like Philippine as reported from Textile Today by Tinyla L. (2014), but recent modifications in term of fiber treatments have improved the properties of pineapple leaf ; fibers for example their brittleness, making them in trend with current textile industry and commercial textile materials. The brittleness of the fiber need to have some improvement or treatments in order to suit with industrial environment. This is because the production lane need a specific parameter such as temperature and concentration. Normal processing of wood fiber shows a loss of production at the output parts because the virgin fiber itself will loss during processing. Therefore its need some treatments are needed in order to entangle the full capacity of wood fiber with added some acetone during

cleaning or surface treatment (Richard et al, 2011). The variety of surface treatment such as mechanical using decorticator, chemical using alkaline treatment, physically using hand scrapping or biologically using retting process by microbes which applied on the leaves to gain their fiber will decide the quality of the long fiber later on. Thus, it is important for the natural fiber coated with the polymer to make easy to handle manually or by machinery as reduce their fiber brittleness. The result of tensile test or observations only were not enough to ensure their fiber's quality. The processing of pineapple leaves also quite complicated which need specific machinery to handle the fibers. This has driven the textile manufacturers to seek for new approaches to produce environmental friendly products, especially green, recyclable and biodegradable textile materials and easy to handle for further processing. In previous research study, bamboo fiber has been coated with polyurethane and polystyrene to provide better result which improved their tensile properties. Alternatively, pineapple fiber was studied without modification to evaluate its strength, (Barikani and Barmar, 1996, Tye A. L and Richard D. G, 2012). Herein, modifications are made on pineapple leaf fibers using thermoplastic polyurethane elastomer to investigate its properties and reusability. It also known as a polymer that has high tensile strength, good resistance to abrasion, oil, fuel and solvents, low temperature flexibility, heat resistance and high adhesion to many substrates. Polyurethane material is widely utilized in industry and daily lives due to its versatile chemistry and relatively easy handling (Barikani and M. Barmar, 1996; Wu et al, 1995).

The pineapple leaf fiber (PALF) is a good fiber obtained after mechanical and chemical extraction process of the leaves. These two methods are commonly used as they were easy steps required and processed in a short period (John and Thomas, 2008). Thermoplastic polyurethane elastomer is a versatile polymer in the market that plays important roles in our daily lives. The use of thermoplastic elastomer polyurethane (TPU) as one of the matrix possesses numerous advantages as this material is an excellent abrasion resistant, good mechanical property in order modifying the brittle fiber to have elastic material (Rahman, 2011). In addition, it exhibits rubber-like elasticity and tear resistance. Therefore, natural long fiber such as PALF obtained from Josapine cultivar was chosen as fiber in textile application

due to its enhanced mechanical properties together with the characteristics offered by TPU through two stage method to produce homogeneous TPUs with constant quality. The samples were differentiated with some parameters which are dipping time, curing time and curing temperature in modifying the fiber to behave elastically. Previously, these three parameters were not really defined yet. Kenaf fiber has a dipping time of 5 minutes and its curing temperature is room temperature. The curing time was not stated as it takes several hours (Abu A. S. et al, 2012, Barikani and Barmar, 1996). Therefore, PALF was characterized with Fourier transform infrared analysis (FTIR), Scanning Electron Microscope (SEM), Differential scanning calorimetric (DSC), thermo gravimetric analysis (TGA). For the mechanical analysis, tensile test (ASTM D3822) was carried out to evaluate the Young modulus, tensile strength and elongation at break. Meanwhile the chemical analysis was done to observe the resistance of coated PALF with several chemicals.

1.3 Objective

The objectives of this study are:

- i. To obtain the treated fiber from pineapple leaves using mechanical and chemical methods and to synthesize TPU using a two stages method.
- ii. To choose the optimum pre-determined dipping time, curing time and curing temperature of TPU coated PALF.
- iii. To characterize and evaluate the mechanical and chemical properties of TPU coated PALF.

1.4 Scope of Study

PALF from Josephine cultivar used was obtained from MARDI Pontian. This type of species was chosen because of their characteristics such as long and strong which is suitable for textile applications. These fibers were first undergo mechanical extraction and followed by chemical treatment using sodium hydroxide. TPU was prepared by a two-stage route using toluene diisocyanate (TDI) as isocyanate, poly (propylene) glycol (PPG) as diols and glycerol propoxylate (GPO) as chain extender. PALF was coated with TPU solution by dipping method to obtain the elastic properties. Dipping times were varied from 5 min to 30 min in this study. Different curing times ranging from (6 hours, 12 hours, and 24 hours) and different curing temperatures ranging from (30 °C, 55 °C, and 85 °C) were also evaluated on the fiber samples to gain the optimum condition. Characterisation using ATR was conducted in order to identify the presence of –OH functional group in the fiber and the presence of functional group for PALF after alkaline treatment and after coated with TPU. Next, SEM was run to study the morphology of the treated and coated fiber. DSC also has been conducted for thermal analysis. Then, TGA was run to find the range of usage temperature on the samples. Several testing were also evaluated in this research for mechanical and chemical analysis to evaluate PALF coated TPU. First of all, tensile test (ASTM D3822) was run for mechanical testing. Then, chemical analysis was conducted to find the chemical interaction with thermoplastic polyurethane coated on the fiber (Wu et al, 1995).

REFERENCES

- Abu A.S., Siti H. N, Lim J.L, (2012), Characterization of Kenaf coated with polyaniline, *Journal of Polymer*, Vol 3, 183-189.
- Adam A. and Yusof Y. (2013) Review on PALF extraction machines and its properties amongst natural fibers. *Scientific.net, Advances in Chemical Engineering III*. 2699-2703.
- Alawar, A., Hamed, A. M. and Al-Kaabi, K. (2009). Characterization of treated palm tree fibre as composites reinforcement. *Composites: Part B*, 40, 601-606.
- Alves, M.E., Castro, T., Martins, O. da F., de Andrade, F. and Toledo, R. (2013) the effect of fiber morphology on the tensile strength of natural fibers. *Journal of Materials Research and Technology 2* (2), 149–157.
- Arib, R.M.N., Sapuan, S.M., Ahmad, M.M.H.M., Paridah, M.T. and Zaman, H.M.D.K. (2006) Mechanical properties of pineapple leaf fibre reinforced polypropylene composites. *Materials & Design 27* (5), 391-396
- Asim, M., Abdan, K., Jawaid, M., Nasir, M., Dashtizadeh, Z., Ishak, M.R. and Hoque, M.E. (2015) A review on pineapple leaves fibre and its composites. *International Journal of Polymer Science* (2015), 1-16.
- ASTM 1695-77. (2001). *Cellulose and Cellulose Derivatives*. West Conshohocken PA: ASTM International.
- ASTM D3039/D3039M-14. (2014). *Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials*. West Conshohocken: ASTM International.
- ASTM E1758-01. (2015). *Standard Test Method for Determination of Carbohydrates in Biomass by High Performance Liquid Chromatography*. West Conshohocken: ASTM International.
- American Society for Testing and Materials (2010). *ASTM D790-10, Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials*. West Conshohocken: ASTM.

- Araujo, J.R., Waldman, W.R. and De Paoli, M.A. (2008). Thermal properties of high density polyethylene composites with natural fibres: Coupling agent effect. *Polymer Degradation and Stability*, 93, 1170-1775.
- Arbelaiz, A., Fernandez, B., Ramos, J.A. and Mondragon, I. (2006). Thermal and crystallization of short flax fibre reinforced polypropylene matrix composites: Effect of treatment, *Thermochimica Acta*, 440, 11-121.
- Aubert, Robert Shanks and Ink Kong (2004) Thermoplastic Elastomers. Intech Open. Vol. 8, (1) 137-144.
- Barikani and M. Barmar (1996), Thermoplastic Polyurethane Elastomers, Synthesis, and Study of Effective Structural Parameters. *Iranian Polymer Journal* Vol. 5 No.4
- Brigida, A.I.S., Calado, V.M.A., Goncalves, L.R.B. and Coelho, M.A.Z. (2010). Effect of chemical treatments on properties of green coconut fibre. *Carbohydrate Polymers*, 79, 832-838.
- Berins, M.L. (ed.) (1991) SPI Plastics Engineering Handbook of the Society of the Plastics Industry, Inc. Boston: Springer US
- Callister, W.D. and Rethwisch, D.G. (2010) Materials science and engineering: an introduction. 8th ed. Hoboken: John Wiley & Sons.
- Chollakup, R., Tantatherdtam, R., Ujjin, S. & Sriroth, K. (2011) Pineapple leaf fiber reinforced thermoplastic composites: Effects of fiber length and fiber content on their characteristics. *Journal of Applied Polymer Science* 119 (4), 1952-1960.
- Cooper S. L. and Tobolsky A. V. (1966) Properties of linear elastomeric polyurethanes. *Journal of Applied Polymer Science*. Vol. 10, (12), 1837-1844.
- D. Sun (2005) Investigating the plasma modification of natural fiber fabrics-the effect on fabric surface and mechanical properties, *Text Res J.*, Vol. 75, pp. 639-44
- De Rosa, I.M., Kenny, J.M., Puglia, D., Santulli, C. and Sarasini, F. (2010). Morphological, thermal and mechanical characterization of okra (*Abelmoschus esculentus*) fibres as potential reinforcement in polymer composites. *Composites Science and Technology*, 70, 116-122.
- Devi, L.U., Bhagawan, S.S. and Thomas, S. (1997) Mechanical properties of pineapple leaf fiberreinforced polyester composites. *Journal of Applied Polymer Science* 64 (9), 1739-1748.

- Devallencourt, C., Saiter, J.M. and Capitaine, D. (1996). Characterization of recycled cellulose: Thermogravimetry/Fourier transform infra-red coupling and thermogravimetry investigations. *Polymer Degradation and Stability*, 52, 327-334.
- Doan, T.T.L., Brodowsky, H. and Mader, E. (2007). Jute fibre/polypropylene composites II. Thermal hydrothermal and dynamic mechanical behaviour. *Composites Science and Technology*, 67, 2707-2714.
- Elsevier (2015). Scopus. Elsevier. <http://www.scopus.com>
- El- Shekeil, Sapuan and Khalina (2012) Influence of chemical treatment on the tensile properties of kenaf fiber reinforced thermoplastic polyurethane composite. *Polymer Letters*. Vol. 6, No. 12, 1032- 1040.
- FAO. (2015). Statistical database of the FAO. <http://faostat3.fao.org/home/E>
- George, J., Bhagawan, S.S. and Thomas, S. (1996). Thermogravimetric and dynamic mechanical thermal analysis of pineapple fibre reinforced polyethylene composites. *Thermal Analysis*, 47, 1121-1140.
- George, J., Bhagawan, S.S. and Thomas, S. (1997) Improved interactions in chemically modified pineapple leaf fiber reinforced polyethylene composites. *Composite Interfaces* 5 (3), 201-223.
- Hujuri, U., Chattopadhyay, S.K., Uppaluri, R. and Ghoshal, A.K.. (2008) Effect of maleic anhydride grafted polypropylene on the mechanical and morphological properties of chemically modified short-pineapple-leaf-fiber-reinforced polypropylene composites. *Journal of Applied Polymer Science* 107 (3), 1507-1516.
- Hidayat P. (2008) Teknologi Pemanfaatan Serat Daun Nanas Sebagai Alternatif Bahan Baku Tekstil. *Teknoin*, 31-35
- Jawaid M. and H.P.S., Abd Khalil (2011), *Cellulosic/Synthetic Fibre Reinforced Polymer Hybrid Composites: A Review*. *Carbohydrates Polymer*; 86: 1-18.
- Jen M., Yosuke N., Toshiyuki Y., Tetsuko K. and Takeshi K., (2016) Influence of types of alkali treatment on mechanical properties of hemp fiber reinforced polyamide. *Journal of Applied Polymer Science* 107 (2), 152-156.
- John and Thomas (2008) Application and extraction of natural fiber. *Journal of Natural Fiber*, Vol. 2, 23-29.
- John D. , William S. and Sara M. (2013) The characterization of bambo coated with natural fiber for industrial applications. *Journal of composite*, Vol.2, 55-60.

- John and R. D. Anandjiwala (2008), Recent developments in chemical modification and characterization of natural fiber-reinforced composites, *Polymer Composite*, Vol. 29, 187-207.
- John and Thomas (2008), Biofibers and biocomposites. *Carbohydrate Polymers*, Vol. 4, 69-76.
- Kalia, S. and Kaith, B.S. (eds.) (2011) *Cellulose fibers: bio- and nano-polymer composites; green chemistry and technology*. Berlin: Springer
- Kayode Feyisetan Adekunle (2015) Surface treatments of natural fibers - A review: Part 1. *Open Journal of Polymer Chemistry*, Vol. 5 , 41-46.
- Kengkhetkit, N. and Amornsakchai, T. (2012) Utilisation of pineapple leaf waste for plastic reinforcement: 1. A novel extraction method for short pineapple leaf fiber. *Industrial Crops and Products* 40, 55-61
- Kovacevic S. (2010) *Coated Textile Materials. Woven Fabric Engineering*. Intech.
- Krauss, B.H. (1949) Anatomy of the vegetative organs of the pineapple, *Ananas comosus* (L.) Merr. (Continued) II. The Leaf. *Botanical Gazette* 110 (3), 333-404
- Kumar and Siddaramaiah (2005) Study of chemical and tensile properties of PU and PU/PS coated bamboo fibers, *Polymer plastic technology and engineering*, 44:7, 1369-1377
- Lee K.J, Lim S.J. and Ong K.I (2009), The surface treatments of baggase for packaging applications. *Crops and Products* 35, 55-59
- Leduc (2000) Plant material processing system. US006079647A
- Luz, S.M., Del Tio, J., Rocha, G.J.M., Goncalves, A.R. and Del'Arco Jr., A.P. (2008). Cellulose and cellulignin from sugarcane bagasse reinforced polypropylene composites: Effect of acetylation on mechanical and thermal properties. *Composites Part A. Applied Science and Manufacturing*, 39, 1362-1369.
- M. R. Sanjay, G. R. Arpitha, L. Laxmana Naik, K. Gopalakrishna and B. Yogesha (2016) Applications of natural fibre and its composites : An overview. *Natural Resources*. Vol. 7, 108-114.
- Maheswari, Reddy, E. Muzenda and A.V. Rajulu (2012), Tensile and thermal properties of polycarbonate-coated Tamarind fruit fibers. *International Journal Polymer Analysis*, Vol. 17, 578-589.

- Maheswari, Chidige, Kanchireddy, Muzenda, and Edison (2013) Tensile properties of polystyrene-coated Tamarind fruit fiber, *International Journal Polymer Analysis*, Vol. 19, 223-237.
- Manfredi, L.B., Rodriquez, E.S., Przybylak, M.W. and Vasquez, A. (2006). Thermal degradation and fire resistance of unsaturated polyester, modified acrylic resins and their composites with natural fibres. *Polymer Degradation and Stability*, 91, 255-261.
- Maniruzzaman, M., Rahman, M.A., Gafur, M.A., Fabritius, H. and Raabe, D. (2012) Modification of pineapple leaf fibers and graft copolymerization of acrylonitrile onto modified fibers. *Journal of Composite Materials* 46 (1), 79-90.
- Maleque, M. A., Belal, F. Y. and Saupam, S. M. (2007). Mechanical properties study of pseudo-stem banana fiber reinforced epoxy composites. *Arabian Journal for Science and Engineering*, 32, 359–364
- Manikandan, V., Ponnambalam, S. G. and Sabu Thomas, V. R. (2004). Mechanical properties of short and uni-directional palmyrafiber reinforced composite. *International PlasticsTechnology*, 8, 205–216.
- Mariatti, M., Jannah, M., Abu Bakar, A. and Abdul Khalil, H. P. (2007). Properties of banana and pandanus woven fabric reinforced unsaturated polyester composites. *Journal of Composite Materials*, 42, 931–941
- Matthews, F.L., and Rawlings, R. D. (2005). *Composite materials: Engineering and science* (pp. 169–173)
- Mohammad A. R. , Sapuan S. M., Shahjahan M., and Khalina A. (2009) Characterization of pineapple leaf fibers from selected Malaysian cultivars, *Journal of Food, Agriculture and Environment*, Vol. 7 (1), 235-240
- Mohanty, A.K., Misra, M. and Drzal, L.T. (2005) *Natural Fibers, Biopolymers, and Biocomposites*. Boca Raton: Taylor & Francis.
- Nilza, G., Virgo, J. S. J., and Buchanan, V. (2008). Potential of Jamaican banana, coir, bagasse fiber as composite materials. *Materials Characterization*, 59, 1273–12738.
- Nair, K.C.M., Thomas, S. and Groeninckx, G. (2001). Thermal and dynamic mechanical analysis of polystyrene composites reinforced with short sisal fibres. *Composites Science and Technology*, 61, 2519-2529.

- Oliveira, F. B., Gardrat, C., Enjalbal, C., Frollini, E., & Castellan, A. (2008). Phenol-furfural resins to elaborate composites, reinforced with sisal fibers – Molecular analysis of resin and properties of composites. *Journal of Applied Polymer Science*, 109(4), 2291–2303. [https://doi.org/10.1002/\(ISSN\)1097-4628](https://doi.org/10.1002/(ISSN)1097-4628)
- Pickering K.L. (2008). *Properties and Performances Natural Fibres Composites*. UK: Woodhead Publication Limited
- Rahman M. A. (2011), *Study on modified pineapple leaf fiber*, Vol 7 , issue 2 , Bangladesh.
- Ramesh, M., Palanikumar, K., and Hemachandra Reddy, K. (2013). Mechanical property evaluation of sisal-jute-glass fiber reinforced polyester composites. *Composites Part B: Engineering*, 48, 1–9. <https://doi.org/10.1016/j.compositesb.2012.12.004>
- Rao, K. M. M., Rao, K. M., and Prasad, A. R. (2010). Fabrication and testing of natural fiber composites: Vakka, sisal, bamboo and banana. *Material Design*, 31, 508–813.
- Razak S. I. A. (2016) Effect of mercerization on the properties of paper produced from Malaysian pineapple leaf fiber, IJET-IJENS, Vol.13, No.4, Malaysia.
- Reddy and Yang (2005) Biofibers from agricultural byproducts for industrial applications. *Trends in biotechnology*. Vol. 23, No. 1.
- Reddy, M. Shukla, Maheswari, and A. V. Rajulu (2012), Evaluation of mechanical behaviour of chemically modified Borassus fruit short fiber/unsaturated polyester composites. *Journal of Company Mater*, Vol. 46, 2987-2998
- Reddy, M. Shukla, Maheswari, J.I. Song and A. V. Rajulu (2013), Tensile and structural characterization of alkali treated Borassus fruit fine fibers. *Journal of Company Mater*, Vol. 44, 433-438.
- Reis, P.N.B., Ferreira, J.A.M., Antunes, F.V. and Costa, J.D.M. (2007). Flexural behaviour of hybrid laminated composites. *Composites Part A: Applied Science and Manufacturing*, 38, 1612-1620.
- Ren, H., Sun, J. Z., Zhao, Q., and Zhou, Q. Y. (2008). Synthesis and characterization of a novel heat resistant epoxy resin based on N, N0-bis(5-hydroxy-1-naphthyl) pyromellitic diimide. *Polymer*, 49, 5249–5253. <https://doi.org/10.1016/j.polymer.2008.09.047>

- Richard J., Sara M. and Jin Z. (2011) The overview: Wood fiber in paper industry. *Properties and Performances Natural Fibres Composites*. UK: Woodhead Publication Limited
- Rimduisit, S., Damrongsakkul, S., Wongmanit, P., Saramas, D., and Tiptipakorn, S. (2011). Characterization of coconut fiberfilled polyvinyl chloride/acrylonitrile styrene acrylate blends. *Journal of Reinforced Plastic and Composites*, 30(20), 1691–1702. <https://doi.org/10.1177/0731684411427484>
- Sapuan, S. M., and Bachtiar, D. (2012). Mechanical properties of sugar palm fibre reinforced high impact polystyrene. *Composites Procedia Chemistry*, 4, 101–106. <https://doi.org/10.1016/j.proche.2012.06.015>
- Satyunarayana , G.C.C. Arizaga and Wypych F., (2009) *Biodegradable composites based on lignocellulosic fibers an overview*, *Progre Polym Sci* , Vol. 34, pp 982-1021.
- Schollenberger C. S. and Dinbergs K. (1975) Thermoplastic Urethane Chemical Crosslinking Effects. *Journal of Polymer Science*. (64)1, 351-368.
- Sena Neto (2013) Evaluation of the micropropagation potential of curaua pineapple. *Journal of Applied Agriculture*. Vol. 12, 321-330.
- Soucek, M. D. and Ren, X. (2015). UV-Curable Coating Technologies. In Atul, T. and Alexander, P. *Photocured Materials*. (15-46). United Kingdom: Royal Society of Chemistry.
- Studer, K., Decker, C., Beck, E. and Schwalm, R. (2003). Overcoming Oxygen Inhibition in UV-Curing of Acrylate Coatings by Carbon Dioxide Inerting, Part I. *Progress in Organic Coatings*, 48, 92–100.
- Subasri, R., Madhav, C. S., Samaraju, K. R. C. and Padmanabham, G. (2012). Decorative, Hydrophobic Sol-Gel Coatings Densified using Near-Infrared Radiation. *Surface and Coatings Technology*, 206 (8–9), 2417–2421.
- Taki, K., Watanabe, Y., Ito, H. and Ohshima, M. (2014). Effect of Oxygen Inhibition on the Kinetic Constants of the UV- Radical Photopolymerization of Diurethane Dimethacrylate/ Photoinitiator Systems. *Macromolecules*, 47, 1906–1913.
- Tasic, S., Bozic, B. and Dunjic, B. (2004). Synthesis of New Hyperbranched Urethane-Acrylates and Their Evaluation in UV-Curable Coatings. *Progress in Organic Coatings*, 51 (4), 321–328.

- Tehfe, M. A., Lalevée, J., Morlet-Savary, F., Blanchard, N., Fries, C., Graff, B., Allonas, X., Louerat, F. and Fouassier, J. P. (2010). Near UV-Visible Light Induced Cationic Photopolymerization Reactions : A Three Component Photoinitiating System Based on Acridinedione / Silane / Iodonium Salt. *European Polymer Journal*, 46 (11), 2138–2144.
- Tehfe, M. A., Louradour, F. and Lalevée, J. (2013). Photopolymerization Reactions: On the Way to a Green and Sustainable Chemistry. *Applied Sciences*, 3 (2), 490–514.
- Tehfe, M. A., Dumer, F., Graff, B., Morlet-Savary, F., Fouassier, J. P., Gignes, D. and Lalevée, J. (2012). Trifunctional Photoinitiators Based on a Triazine Skeleton for Visible Light Source and UV LED Induced Polymerizations. *Macromolecules*, 45 (21), 8639–8647.
- Tinya L. Textile Today. Textile from Pineapple Fibers. Philippine.2014.
- Tissera, N. D., Wijasena, R. W., Perera, J. R., De Silva, K. M. N. and Amarahtuge, G. A. J. (2015). Hydrophobic Cotton Textile Surfaces using an Amphiphilic Graphene Oxide (GO) Coating. *Applied Surface Science*, 324, 455–463.
- Threepopnatkul, P., Kaerkitcha, M. and Anthipongarporn. (2009). Effect of surface treatment on performance of pineapple leaf fibre-polycarbonate composites. *Composites: Part B*, 40, 628-632.
- Tappi Method T204 cm-97. (1988). Solvent extractives of wood and pulp. Atlanta, GA: TAPPI PRESS.
- Tappi Method T222 om-02. (1988). Acidinsoluble lignin in wood and pulp. Atlanta, GA: TAPPI PRESS
- Tappi Method T207 om-88. (1988). Water solubility of wood and pulp. Atlanta, GA: TAPPI PRESS
- Tecnon Orbichem. (2014). Global Fibers Overview. http://www.orbichem.com/userfiles/APIC2014/APIC2014_Yang_Qin.pdf
- Thejvidi, M., Shekaraby, M. M., Motiee, N., and Najafi, S. K. (2006). Effect of chemical reagents on the mechanical properties of natural fiberpolypropelene composites. *Journal of Polymer Science Part*, 27(5), 563–569.
- Trigui, A., Karkri, M., Pena, L., Boudaya, C., Candau, Y., Bouffi, S., and Vilaseca, F. (2013). Thermal and mechanical properties of maize fibers-high density

- polyethylene bio composites. *Journal of Composite Materials*, 47, 1387–1397. <https://doi.org/10.1177/0021998312447648>
- Tye A. L. and Richard D. G. (2012) Influence of nitric acid treatment time on the mechanical and surface properties of high- strength carbon fibers. *Journal of Composite Materials*. 1-18.
- UNE 57050:2003. (2003). Papel, cartón y pastas. Determinación del residuo de ignición. Madrid: Asociacion Espanola de Normalizacion.
- Vilaplana, F., Ribes-Greus, A. and Karlsson, S. (2007). Analytical strategies for the quality assessment of recycled high impact polystyrene: A combination of thermal analysis, vibrational spectroscopy, and chromatography. *Analytica Chimica Acta*, 604, 18-28.
- Venkateshwaran, N., Ayyasamy, E., Alavudeen, A., and Thiruchitrambalam, M. (2011). Mechanical and water absorption behaviour of banana/sisal reinforced hybrid composites. *Materials Design*, 32, 4017–4021. <https://doi.org/10.1016/j.matdes.2011.03.002>
- Villain, G., Thiery, M. and Platret, G. (2007). Measurement methods of carbonation profiles in concrete: Thermogravimetry, chemical analysis and gammadensimetry. *Cement and Concrete Research*, 37, 1182-1192.
- Weida Z. (2004) Pineapple Leaf Fiber Extractor. *Journal of Agriengineering*. Vol. 2, 39-44.
- Wood, A. S. (1989). Big buildup in polycarbonate supply big buildup in polycarbonate values. *Modern Plastics*, 66, 34–37.
- Wu Z., Charles U. P., Steven D. G (1996) Nitric acid oxidation of carbon fibers and the effects of subsequent treatment in refluxing aqueous NaOH. *Journal of Carbon*. Vol. 2, 156-164.
- Yang, G. C., Zeng, H. M., Jian, N. B., and Li, J. J. (1996). Properties of sisal fiber/glass fiber reinforced PVC hybrid composites. *Plastics Industry*, 1, 79–81.
- Youssef, H. A., Ismail, M. R., Ali, M. A. M., and Zahran, A. H. (2009). Studies on sugarcane bagasse fiber-thermoplastics composites. *Journal of Elastomers and Plastics*, 41, 245– 262. <https://doi.org/10.1177/0095244308095014>
- Yusof and Yahya (2013) Applications of agriculture byproducts. *Journal of Modern Agriculture*. Vol 9, 34-39.

- Zah, R., Hischer, R., and Leao, A. L. (2007). Curauafibers in the automobile industry – A sustainability assessment. *Journal of Cleaner Production*, 15, 1032–1040. <https://doi.org/10.1016/j.jclepro.2006.05.036>
- Zaid, A., and Jimenez, E. J. A. (1999). Date palm cultivation (vol. 156). FAO Plant Production and Protection.
- Zarate, N., Aranguren, M. I., Reboredo, M. M. 2003. Studies on influence of fibre volume fractions and aspect ratio in *resol-sisal composites*, 89, 2714–2722.