

Synthesis and Evaluation of anhydride based polyester and their composites from punnal oil

T. J. Sasikala, A. Malar Retna*

*Department of Chemistry, Scott Christian College (Autonomous), Nagercoil-3, Tamil Nadu, India.

(Affiliated to Manonmanium Sundaranar University, Abishekapatti, Tamil Nadu, India)

malarscott@gmail.com

Abstract - This research aims to study the effects on the synthesis and characterization of punnal oil based polyester and their composites. Punnal oil is the seed oil of the *Calophyllum inophyllum* tree. This oil is readily available and inexpensive, used for the synthesis of various polymers. Punnal oil based polyester sheet was synthesised by treating punnal oil with peroxyacetic acid followed by the addition of phthalic anhydride. The obtained polyester resin was cured in the presence of benzoyl peroxide and dimethyl aniline. The coir and banana fibre reinforced polyester composites were synthesised using punnal oil based polyester resin with coir fibre of varying compositions. The physico-chemical properties, spectral analysis such as FTIR and ¹H NMR analysis, crosslink density, mechanical properties such as tensile, Young's modulus and elongation at break and chemical resistance were evaluated. It has been evaluated that the variation of composition of fibres influences the mechanical properties.

Key words: Punnal oil, phthalic anhydride, crosslink density, mechanical properties, polyester, composites

I. INTRODUCTION

In olden days, polymers are synthesised from petroleum feed stocks. The decline of petroleum based resources for the polymer industry and difficulties of disposal of waste from the petrochemical feed stocks, there is a need of naturally available renewable resource for the development of polymers. Plant oil is one of the most important renewable resources that can be used as starting material to produce new products with a wide variety of applications. It is eco-friendly, less pollution emission, cheap and readily available when compared to the petroleum based polymers[1-2]. The naturally and abundantly occurring vegetable oil is the punnal oil. It is extracted from the seed of the *Calophyllum inophyllum* tree. Punnal oil is non-edible oil and comes under the category of non-drying oils. It generally contains 92% triglycerides and the remaining 6.4% glycolipids and 1.6% phospholipids. The major fatty acids present in punnal oil are palmitic acid, palmitoleic acid, stearic acid, oleic acid, linoleic acid and linolenic acid[3]. The double bonds present in the punnal oil acts as a reaction site for the chemical modification of the oil. The high performance bio-based materials and green composites have been developed for structural applications using vegetable oil based polyester resin.

Coir is the natural fibre found between the hard, internal shell and the outer coat of a coconut palm. Coir fibre is environmentally friendly, biodegradable, abundantly available and cheap[4]. Coir consists of cellulosic fibres with hemicellulose and lignin as the bonding materials for

the fibres[5]. Banana fibre is extracted from the plant *Musa sapientum*[6]. The chemical composition of banana fibre is cellulose, hemicellulose, and lignin[7]. It is a strong fibre having smaller elongation and has a shiny appearance depending upon the extraction and spinning process. It is a light weight and strong moisture absorption quality. The coir and banana fibres are used for making composites with the newly synthesized polyester based on punnal oil.

The present work deals with the spectral and mechanical properties of punnal oil based polyester and their composites with coir and banana fibres.

II. EXPERIMENTAL

A. Materials

Punnal oil was procured from local company. Glacial acetic acid (Merck), 30% hydrogen peroxide (Merck), phthalic anhydride (Merck), triethyl amine (Sigma-Aldrich), triethylene glycol dimethacrylate (Sigma-Aldrich), benzoyl peroxide (Sigma-Aldrich) and dimethyl aniline (Sigma-Aldrich) were used without further purification. Coir and banana fibre was procured from local sources.

B. Synthesis of coir and banana fibre reinforced anhydride based polyester composites

Punnal oil (1 M) was placed in a 500 ml three neck flask equipped with a Liebig condenser, mechanical stirrer and thermometer containing acetic acid (0.5 M) and few drops of sulphuric acid. Then 30% hydrogen peroxide (1.5 M) was added drop wise with continuous stirring for about 1 h. Thereafter, the temperature of the reaction mixture was

raised to 60°C for a period of 8 h. The obtained epoxidised punnal oil was washed with warm water and then extracted with ether. The epoxidised punnal oil was heated with phthalic anhydride and triethyl amine at about 120°C for 2 h to yield yellowish brown viscous resin. The synthesised anhydride based epoxidised punnal oil was treated with 1 ml of triethylene glycol dimethacrylate (crosslinking agent) in the presence of benzoyl peroxide (initiator) and dimethyl aniline (accelerator) with coir and banana fibres of varying compositions (5, 10 and 15wt. %). The mixture was stirred in a plastic cup using glass rod and casted in a clean silicone oil spreaded glass plate. The cast was cured in vacuum oven at 80°C for 6 h. The obtained anhydride based polyester sheet was coded as POPC. The 5%, 10% and 15% coir fibre reinforced composites were coded as POPCF5, POPCF10 and POPCF15. The 5%, 10% and 15% banana fibre reinforced composites were coded as POPBF5, POPBF10 and POPBF15.

C. Spectral analysis

Fourier transform infrared spectral analyses (FTIR) of the punnal oil and the synthesised resins were carried out by KBr pellet method using Shimadzu FTIR-8400S spectrophotometer. ¹H NMR spectra of the synthesised resins were recorded using CDCl₃ with tetramethylsilane as an internal standard. The spectrum was recorded using Bruker Avance H 500 MHz spectrometer.

D. Crosslink density

The crosslink density of polyester and their composites was determined using Flory Rehner equation [8],

$$\chi = \frac{-[V_r + \chi V_r^2 + \ln(1 - V_r)]}{d_r \cdot V_0 \left(V_r^{1/3} - \frac{V_r}{2} \right)} = \frac{1}{M_c}$$

where V_r is the volume fraction of polyester in swelled polymer, V_0 is the molar volume of the solvent, M_c is the molecular weight between two crosslinks, d_r is the density of the polyester.

E. Determination of solvent absorptivity percentage

Swelling behaviour of polyesters and their composites were also studied[9]. Each polyester sheet was put in 3 ml of different solvents for 24 h. After 24 h, the excess solvent present on the surface of polyester sheet was removed by using filter paper. Then it was weighed and the solvent absorptivity percentage was calculated using the following equation,

$$\text{Solvent absorptivity percentage} = \frac{W_2 - W_1}{W_1} \times 100$$

Where

W_1 = Weight of the dry sample

W_2 = Weight of the sample after absorption of the solvent.

F. Determination of mechanical properties

Tensile strength of the polyesters and their composites were determined in Universal Testing Machine at a cross head speed of 100 mm/min using rectangle shaped specimens (10 x 1 cm) punched out from polyester sheets as per ASTM D6100. The gauge length was fixed at 3 cm in each test. The tensile strength, Young's modulus and elongation at break were calculated using standard formulations. Shore A hardness of polyesters and their composites were determined as per ASTM D2240. Hardness tester durometer was used. Polyester sheets of 5 mm thickness were used for hardness measurements.

G. Chemical resistance of polyester and their composites

The degradation of polyesters and their composites in hostile acidic, basic and oxidant medium was studied. Dilute hydrochloric acid (1 N), sodium hydroxide (1 N) and hydrogen peroxide (30%) were used. The medium was changed and fresh medium was added at an interval of one week. The samples were removed at the end of exposure, dried in vacuum oven and then weighed.

III. RESULTS AND DISCUSSION

A. Physico-chemical properties

Punnal oil is a mixture of triglyceride consisting of unsaturated and saturated fatty acids. The unsaturated fatty acids present in punnal oil are oleic acid (41.4%) and linoleic acid (29.7%) and the saturated fatty acids are palmitic acid (14.5%) and stearic acid (12.9%). The possible triglyceride structure for punnal oil is,

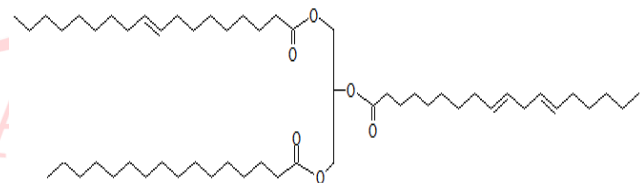


Fig. 1 Triglyceride structure of punnal oil[10]

In the present study, the reduction in iodine value indicates the oxidation of double bonds during epoxidation [11]. Both specific gravity and viscosity of epoxidised punnal oil are higher than the punnal oil. It is due to the increase in the number of epoxy linkages which corresponds to the decrease in the unsaturated bonds of the oil [12]. This may also be caused due to the change in molecular weight, polarity and intermolecular forces [13]. The decrease in iodine value in anhydride based epoxidised punnal oil reveals the consumption of epoxy groups. On the other hand, the addition of anhydride groups to the epoxy chain results in high molecular weight and high viscosity compared to that of the punnal oil. The following table shows the physico-chemical properties punnal oil and the synthesised resins.

Table 1 Physico-chemical properties punnal oil and the synthesised resins

Properties	Punnal oil	Epoxidised punnal oil	Anhydride based epoxidised punnal oil
Colour	Dark green	Pale yellow	Yellowish brown
Specific gravity	0.91	1.19	1.1
Acid value	35	-	-
Saponification value	182	-	-
Iodine value	71	48	44
Viscosity	0.03	0.04	0.05
Molecular weight	860	900	1150

B. FTIR spectral analysis

The FTIR spectrum of punnal oil shows a maximum absorbance at 3006 cm^{-1} due to the presence of non conjugated unsaturation of linoleic acyl groups. A pair of peaks observed at 2924 cm^{-1} and 2852 cm^{-1} is due to the symmetric stretching vibration of the aliphatic -CH_2 groups. A strong and sharp band at 1743 cm^{-1} is due to the ester carbonyl group. The peak at 1462 cm^{-1} reveals the presence of -C-H bending of unsaturated methylene groups and the peak at 1115 cm^{-1} is for -C-O stretching of ester group. A band at 725 cm^{-1} is due to the stretching vibration of -CH-CH- groups. The disappearance of 3006 cm^{-1} band in epoxidised punnal oil shows -C=C- has been used for the epoxidation. The appearance of the band around 910 cm^{-1} is due to the formation of epoxy groups confirmed the success of epoxidation[14]. The FTIR spectrum of anhydride based epoxidised punnal oil shows that the peak around 1628 cm^{-1} is attributed to the carbonyl stretch of the aromatic acid which indicates the asymmetric cleavage of the phthalic anhydride by the addition of triethyl amine catalyst. The epoxy peak in epoxidised punnal oil at 910 cm^{-1} is disappeared in anhydride based epoxidised punnal oil. This shows that phthalic anhydride is substituted in the epoxy ring. The following figure shows the FTIR spectrum of punnal oil, epoxidised punnal oil, anhydride based epoxidised punnal oil and the polyester

sheet.

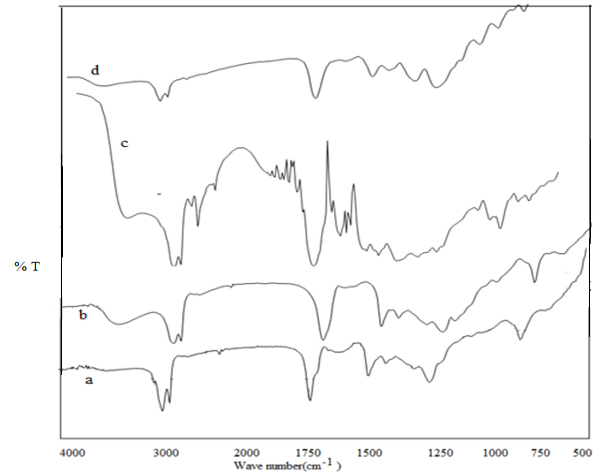


Fig 1 a. FTIR spectrum of punnal oil, b. FTIR spectrum of epoxidised punnal oil, c. FTIR spectrum of anhydride based epoxidised punnal oil, d. FTIR spectrum of anhydride based polyester sheet.

C. ^1H NMR spectral analysis

The ^1H NMR spectral analysis of punnal oil is shown in Fig 2. It reveals that the peak at $0.75\ \delta$ corresponds to the hydrogen ending methyl groups ($\text{CH}_3\text{-(CH}_2)_n\text{-}$). Peak appeared at $1.2 - 1.4\ \delta$ indicate the aliphatic methylene hydrogens ($\text{-CH}_2\text{-}$)[15]. The peak at $2.05\ \delta$ attributes the allyl hydrogen ($\text{-CH}_2\text{-CH=CH-}$). The peak around $2.7\ \delta$ is originated from the hydrogen of two double bonds ($\text{-CH=CH-CH}_2\text{-CH=CH-}$). The peaks at $4.1 - 4.3\ \delta$ is due to the protons in the methylene groups of the triglyceride. The peak sited at $5.2 - 5.5\ \delta$ indicates the presence of olefinic protons of the punnal oil.

The ^1H NMR spectral analysis of epoxidised punnal oil is shown in Fig 3. The presence of epoxide ring in the epoxidised punnal oil is confirmed at $2.8\ \delta$ that mean the double bond is replaced by the epoxy group. The peak at $3.2\ \delta$ shows -CH- hydrogen between two epoxy groups. The allyl hydrogen of punnal oil at $2.05\ \delta$ is shifted to $1.45\ \delta$ in epoxidised punnal oil.

The ^1H NMR spectra of anhydride based epoxidised punnal oil is shown in Fig 4. It reveals that the new peak at $7.54 - 7.71\ \delta$ correspond to the aromatic proton of phthalic anhydride. The disappearance of epoxy band at $2.8\ \delta$ shows that phthalic anhydride is added to the epoxy ring. The peak at $1.4\ \delta$ corresponds to the long chain methylene groups and the peak at $0.95 - 2.3\ \delta$ is attributed by aliphatic side chain.

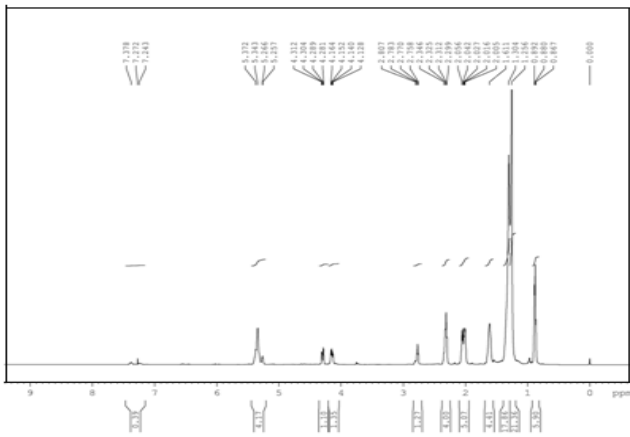


Fig 2 ¹H NMR spectra of punnal oil

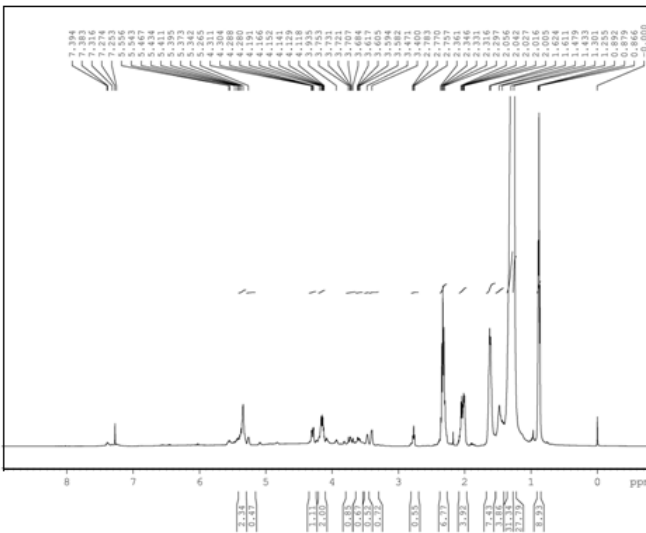


Fig 3 ¹H NMR spectra of epoxidised punnal oil

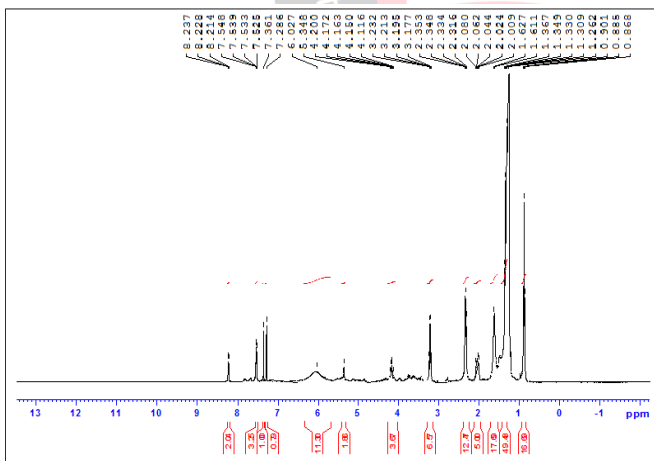


Fig 4 ¹H NMR spectra of anhydride based epoxidised punnal oil

D. Crosslink density

Crosslink density is the factor to determine the properties of cured polyester and their composites and is reported as an average molecular weight between crosslinks. The crosslink density increases as the molecular weight between crosslinks decreases. In the present study, the crosslink density, molecular weight between crosslinks of polyester and their composites are presented in Table 2.

In the present study, the swelling coefficient is maximum in neat polyester sheet. It reveals that the 15% coir fibre reinforced polyester composites possess higher crosslink density than the remaining composites and the neat polyester sheet. As the fibre content increases, the crosslink density also increases[16]. When compared the coir and banana fibre reinforced anhydride based polyesters and their composites, the crosslink density is higher in coir fibre reinforced composites than the banana fibre composites. Accordingly, the molecular weight between crosslinks was found to be higher in neat polyester sheet and the crosslink density is lower. It is due to the steric hindrance of the anhydride groups present in the polyester sheet.

Table 2 Crosslink density of polyester and their composites

Polyester and their composites	Density (g/cc)	Swelling coefficient in DMA (Q)	Crosslink density (x10 ⁻³)	Molecular weight between crosslinks (mole ⁻¹)
POPC	1.21	1.20	1.31	763.36
POPCF5	1.23	1.16	1.39	719.42
POPCF10	1.24	1.14	1.42	704.23
POPCF15	1.24	1.11	1.48	678.68
POPBF5	1.26	1.19	1.31	763.36
POPBF10	1.28	1.17	1.33	751.88
POPBF15	1.29	1.15	1.35	740.74

E. Solvent absorptivity percentage (SA %)

The solvent absorption is used to test whether the polyester and their composites are capable of withstanding exposure to a variety of organic solvents. In the present investigation, solvent absorptivity percentage is carried out in different solvents such as ethyl methyl ketone (EMK), chloroform, dimethyl acetamide (DMA), dimethyl formamide (DMF), ethanol, and glycerol. These datas are presented in Table 3. From the data, it is found that the solvent absorptivity percentage of all the polyesters and their composites increases from non-polar to polar solvents. This indicates that these polyesters are hydrophobic in nature. Maximum swelling is observed for all the polyesters in polar aprotic solvents like dimethyl formamide (DMF) and dimethyl acetamide (DMA). Solvent absorptivity percentage of various polyester and their composites are shown in bar chart and the datas are presented in Table 3..

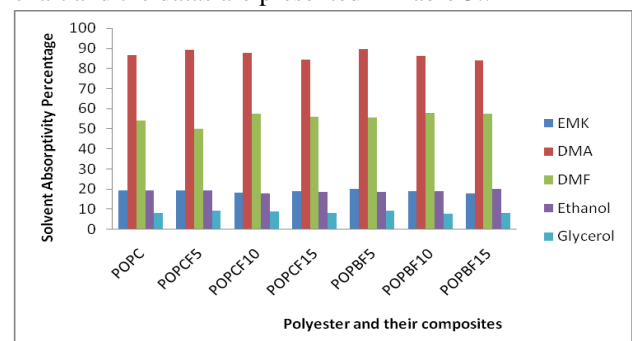


Table 3 Solvent absorptivity of polyester and their composites

Polyester and their composites	Solvent absorptivity (%)				
	EMK	DMA	DMF	Ethanol	Glycerol
POPC	19.51	86.45	54.28	19.28	8.14
POPCF5	19.28	89.23	50.00	19.54	9.21
POPCF10	18.18	87.5	57.5	17.98	8.88
POPCF15	18.95	84.2	55.91	18.74	8.2
POPBF5	20.25	89.4	55.65	18.68	9.5
POPBF10	18.99	86.32	57.98	19.00	7.89
POPBF15	18.07	84.12	57.52	20.00	8.2

F. Mechanical properties

The alkali treated coir and banana fibre reinforced polyester composites shows higher tensile strength and Young's modulus than the neat polyester sheet due to its high crosslink density. Alkali treatment increases the effective surface area available for wetting by the matrix resin[17]. Alkali treatment removed the cementing substances like lignin and hemicelluloses present in coir and banana fibre. Therefore, increasing the fibre content may improve the interface adhesion and increase the mechanical properties[18].

Coir fibre and banana fibre possess good mechanical properties. As the content of coir and banana fibres are increased, more fibres shared the tensile stress to improve the tensile strength and Young's modulus greatly. When compared, the coir fibre reinforced polyester composites having higher percentage fibre possess higher tensile strength and Young's modulus than the banana fibre composites and neat polyester sheet due to improved mechanical properties of coir fibre. But the elongation at break decreases. The banana fibre is a light weight fibre. Thus 15% of banana fibre reinforced polyester composites cannot be prepared because the fibres could not distribute evenly and the defects of the composites increases and also it cannot be removed from the mould. The hardness of coir and banana fibre reinforced composites increases with the increase in the percentage of fibre due to high crosslink density.

Table 4 Mechanical properties of polyester and their composites

Polyester and their composites	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Shore-A hardness
POPC	2.5	115	2.17	35
POPCF5	5.4	113	4.78	38
POPCF10	8.9	112	6.74	42
POPCF15	13.73	110	10.56	51
POPBF5	3.7	112	3.3	43
POPBF10	6	107	5.61	45
POPBF15	Brittle			

G. Chemical resistance of polyester and their composites

The chemical resistance of polyester and their composites are presented in bar chart and Table 5. The newly

synthesized polyester and their composites seem to exhibit higher weight loss in NaOH than the acid and oxidant medium because the polyester with ester linkages can be easily hydrolysed in the presence of alkalis[19]. When compared the coir and banana fibre reinforced polyester composites, the neat polyester sheet poses higher degradation than the remaining composites. Thus the present polyester and their composites are stable towards acid and oxidant medium than the base medium.

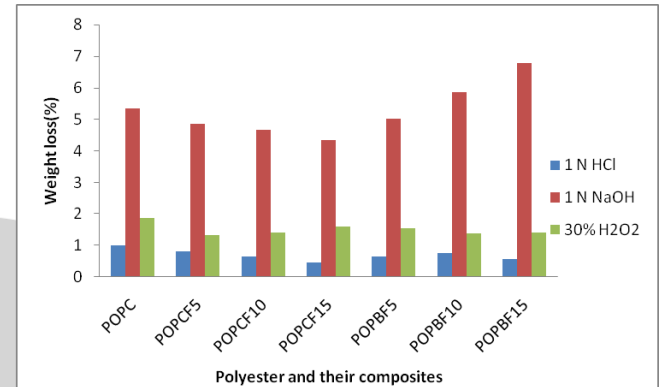


Table 5 Chemical resistance of polyester and their composites

Polyester and their composites	Weight loss (%)		
	Acid 1 N HCl	Base 1 N NaOH	Oxidant 30% H ₂ O ₂
POPC	0.99	5.35	1.87
POPCF5	0.82	4.86	1.33
POPCF10	0.65	4.67	1.42
POPCF15	0.45	4.34	1.59
POPBF5	0.64	5.03	1.54
POPBF10	0.77	5.86	1.37
POPBF15	0.56	6.79	1.42

IV. CONCLUSION

The epoxidised punnal oil, anhydride based epoxidised punnal oil were synthesised successfully. The synthesised resins were confirmed by FTIR and ¹H NMR spectral analysis. The mechanical and chemical resistance properties were studied. The synthesized polyester and their composites were found to exhibit good mechanical and chemical resistance properties. When compared, the coir fibre reinforced composites were found to possess good mechanical properties and chemical resistance properties than the banana fibre reinforced composites and the neat polyester sheet. This is due to its high crosslink density. Increasing the fibre content improves the mechanical properties.

REFERENCES

- [1] L. Montero De Espinosa, and M. A. R. Meier, "Plant oils: the perfect renewable resource for polymer science," European Polymer Journal, vol. 47, no. 5, pp. 837-852, 2011.

- [2] M. A. Mosiewicki, and M. I. Aranguren, "A short review on novel biocomposites based on plant oil precursors," *European Polymer Journal*, vol. 49, no. 6, pp. 1243-1256, 2013.
- [3] A. Adeyeye, "Studies on seed oils of *Garcinia kola* and *Calophyllum inophyllum*," *Journal of the Science of Food and Agriculture*, vol. 57, no. 3, pp. 441-442, 1991.
- [4] S. Taj, M.A. Munawar, and S. Khan, "Natural fibre-Reinforced Polymer Composites," *Proceedings of Pakistan Academy of Science*, vol. 44, no. 2, pp. 129-144, 2007.
- [5] H.N. Tran, O.T. Shinji, H. T. Nguyen, and K.A. Satoshi, *Comps.*, vol. 42, pp. 1648, 2011.
- [6] D. P. Ray, L. Ammayappan and L. K. Nayak, *Agricultural reviews*, vol. 33, pp. 37, 2011.
- [7] D. Mohapatra, S. Mishra and N. Sutar, *Journal of Scientific and Industrial Research*, vol. 69, no. 5, pp. 323, 2010.
- [8] S. Katoch, V. Sharma and P.P. Kundu, *Diffusion Fundamenta*. 2011.
- [9] S. Amar Singha and K. Ashvinder Rana, *Bulletin of Materials Science*, vol. 35, no. 7, pp. 1099, 2012.
- [10] T. J. Sasikala, R. K. Samuel and A. M. Retna, *Green Chemistry and Technology Letters*, vol. 1, no. 1, pp. 33, 2015.
- [11] S. Ramesh, G.B. The, R. F. Louh, Y. K. Hou, P. Y. Sin and L. J. Yi. 2010. *Sadhana*. 2010.
- [12] E. A. Ismail, A. M. Motawie and E. M. Sadek. 2011. *Egyptian Journal of Petroleum*. 2011
- [13] P. Panigrahi, X. Li, P. Panigrahi and R. L. Kushwaha. 2009. *SAE International Journal of Commercial Vehicles*. (Apr 2009), ISSN 1407-7353 print / 2255-8713
- [14] L.J. Bellamay, *The infrared spectra of complex molecules*. In: *Ethers, peroxides and ozonides*, Methuen and company Ltd, London, UK. volume I, 3rd edition, 133, 1975.
- [15] C.V. Mythili, A.M. Retna, and S. Gopalakrishnan, *Bull. of Mat. Sci.*, vol. 27, no. 3, pp. 235, 2004.
- [16] T. J. Sasikala, A.M. Retna, *International Journal of Scientific Research in Science, Engineering and Technology*, vol. 3, no.8, pp. 299, 2017.
- [17] V.A. Patel, and P.H. Parsania, *J. of Rein. Plast. And Comp.*, vol. 29, no. 1, pp. 52, 2010.
- [18] H.C. Obasi, N.C. Iheaturu, F.N. Onuoha, C.O. Chike-Onyegbula, M.N. Akanbi, and V.O. Ezech, *Amer. J. of Eng. Resear.*, vol. 3, no. 2, pp. 117, 2014.
- [19] T. J. Sasikala, A.M. Retna, *Materials Today proceedings*, vol. 5, no.2, pp. 6217, 2018.