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SYNTHESIS AND CHARACTERISATION OF NON-EDIBLE OIL FATTY ACID BASED THERMOSET RESIN SUITABLE FOR NATURAL FIBRE REINFORCED COMPOSITE

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ABSTRACT

Novel bio- based polymer was synthesised from naturally available Maravetti oil. Oligomeric polytriglyceride Fumerate (O-PTF) was prepared by insitu glycerolysis of the Maravetti oil followed by condensation. Biobased thermoset resins were prepared by maravetti oil fatty acid with hydrogen peroxide and then maleic anhydride. The polymer was prepared by resin react with styrene. The structures of the products were studied by FT-IR. The cross-linking ability of the resins were checked by DSC analysis.TGA analysis was conducted to indentify the thermal degradation patterns. Mechanical properties analysis presented that tensile strength and impact strength were characterized. The resulted polymers have satisfied mechanical performance and fast curing speed.

INTRODUCTION

Issues of natural contamination brought about by polymer materials have currently attracted expanding attention. Research into ecologically friendly crude materials substitute for getting ready polymeric materials has turned out to be crying needs in the improvement of materials science. Many raw materials available in nature can be used to prepare polymer. Bio based thermosets have attracted more and more attention recently due to its sustainability and eco-friendly characteristics. They have several advantages such as environmental superiority, low cost, low density, lower manufacturing energy, low carbondioxide emission, renewability and biodegradability. Since they derive renewable resources, which can be replaced at equal or greater rate than their rate of consumption, undoubtedly, biobased thermosets will substitute the position of traditional petroleum derived materials. New biobased thermoset is on its rapid developing, however, it is much more complicated than thermoplastic, since it requires resin undergo cross-linking, which means the starting material for resin must contain reactive groups which can undergo cross-link by themselves, or reactive functional groups which can be introduced into the resin's molecules.

Plant oil is one of the most fascinating natural assets for the blend of polymers, as a result of the aliphatic chain and practical gatherings contribute as an essential component to the foundation of polymer. It has gotten much consideration as an inexhaustible asset for getting ready synthetics and polymers. The properties of polymer were constrained by the cross-connecting thickness, practical gathering and adaptability of the macromolecule chain.

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Hydroxyl gatherings, ester gatherings and twofold bonds in the plant oil particle make it accessible for changes and responses.

LITERATURE REVIEW

PLANT OIL

Plant oil which obtained from plant sources is quite abundant in nature.They are triglycerides which contain different fatty acids.Most plant oil is relatively cheap. Hydnocarpus Wightiana seed oil or chaulmoogra oil has been utilized in prescription as anti-microbials for the treatment of a few skin ailments and infection as a blend suspended in gum or as an emulsion.

CHEMICAL MODIFICATION OF PLANT OIL

Compound constituents of plant oil are Chaulmoogric corrosive, hydnocarpic corrosive, apigen in, hydnocarpin, fixed oils, tannins. The oil is irregular in not being comprised of straight chain unsaturated fats yet acids with a cyclic gathering toward the finish of the chain.

EXPERIMENTAL

3.1 RESIN SYNTHESIS

MATERIALS

Maravetti oil, Formic acid, Hydrogen peroxide were used in the first step modification. Maleic acid and Morpholine were used for futher modification of hydroxylated oil fatty acid in different synthesis schemes. Benzoyl peroxide was used as a radical initiator and N, N-Dimethyl aniline was used as accelerator in the curing process. Styrene was used as a monomer and Ethylenedimethacrylate was used as a cross-linker.

SYNTHESIS OF HYDROXYLATED MARAVETTI OIL FATTY ACID (HOMOFA)

Hydroxlylation of maravetti oil was carried out by using 100 ml of maravetti oil,100 ml of 97% formic acid and 55 ml of 30% hydrogen peroxide.Ice water bath was used externally to keep the temperature below 40 ^{o} C. The reaction was vigorously stirred over night. The resulting emulsion was poured into a separating funnel and extracted with ether. The aqueous layer was removed.The resulting ether layer was dried over anhydrous sodium sulphate and the ether was removed by a rotator evaporator. The resulting product was hydroxylated maravetti oil.

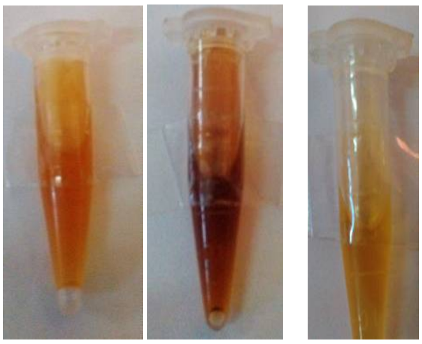
A b c

Figure 1.a)Maravetti oilb)Hydroxylated maravetti oilc) Resin

FURTHER MODIFICATION OF HYDROXYLATED MARAVETTI OILl

The above obtained hydroxylated maravetti oil was then reacted with maleic anhydride to get the resin. Morpholine was used as a catalyst.

CURING PROCESS

The curing process was carried out in two steps by first mixing the obtained resins with 2 wt% benzoyl peroxide as the catalyst and 0.5 wt% N, N Dimethylaniline as the accelerator. And the second step was the addition of 10 ml of styrene and 1 ml of cross – linker to the above resin and let them cure in room temperature.

PREPARATION OF POLYMERIC SHEET

The glass mould was spread out with silicon oil, the above cured resin was poured in to the glass mould, after a few hours we can get a polymeric sheet.

CHARACTERISATION OF RESINS

(FTIR) spectroscopy was used to characterize the synthesised resins in order to testify the chemical modification reactions. The FTIR analysis was carried out for maravetti oil, hydroxylated maravetti oil and also the resin.Cured samples were also checked to see the degree of curing.The Differential Scanning Calorimetry(DSC) analysis was done by a TA instrument.The ThermoGravimetric Analysis (TGA)was done by using TGA instrument.

RESULT AND DISCUSSION

FTI Ranalysis

The FTIR spectra of maravetti oil, HT resin, o-PTF resins are recorded between 500 cm to 4000 cm.

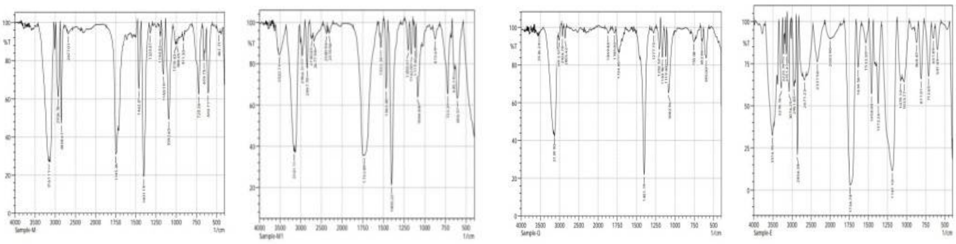

Figure 2.IR spectra of maravetti oil, Hydroxylated oil,Resin and sheet

Table 1.FT-IR probable assignment

Probable assignment	**Maravetti oil (cm^{-1})**	**Hydroxylated Maravettioil(cm$^{1)}$**	**Resin (cm^{-1})**	**Sheet(cm^{-1})**
-CH_2 Group	2926.78	2966.31	2926.78	2951.85
-C- OGroup in GM	2848.67	2847.7	-	2856.38
C=O in esters	1745.46	1733.89	1734.85	1736.78
TerminalCH_3Groups	1194.82	1200.61	1202.53	1372.26
CarboxylGroupofacids	1160.10	1163	1163.96	1187.1
-CH-CH-Stretching	1092.60	1084.88	1082.96	1079.1
CH2-sequences of the aliphatic chains	720.36	722.29	755.08	712.65
-OH Group	3161.11	3522.74	3536.24	3516.95

UV ANALYSIS

The UV spectra of the oil and hydroxylated triglyceride oil tars and for the O-PTF bio polyester saps have been explored (220 nm - 800 nm).The oil test demonstrated an electronic assimilation band around 239 nm .The hydroxylated sap showed a blue move when contrasted and the comparing guardian oil which is ascribed to the substitution of hydroxyl bunch at the unsaturated moiety. There is likewise decline in the absorbance in examination with that of parent oil is because of the substitution of the hydroxyl bunch at the olefinic twofold bond and furthermore twisting of geometry. The significant red move in electronic ingestion showed in (O-PTF) biopolyester tar because of the substitution of the fumarate gathering and furthermore because of the mutilation in geometry of the particle by the presentation of fumarate gathering.

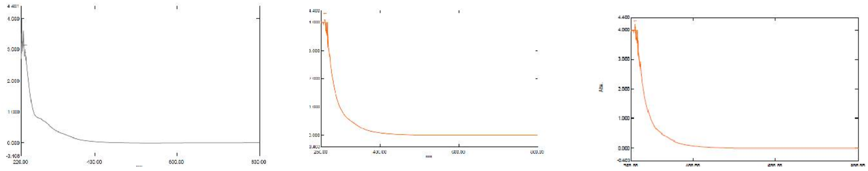

Figure 3.UV spectra of Maravetti oil, Hydroxylated oil and Resin

XRD PATTERN OF MARAVETTI OIL

This module provides an introduction to X-ray Diffraction (XRD), which is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of materials.

XRD CRYSTALLITE SIZE CALCULATOR

Using Scherrer **equation** one can calculate crystallite size from XRD data

$$D_p = \frac{0.94\lambda}{\beta_{1/2}\cos\theta} .$$

Where Dp = Average Crystallite size,

β = Line broadening in radians.

ϑ = Bragg angle

λ = X-ray wavelength

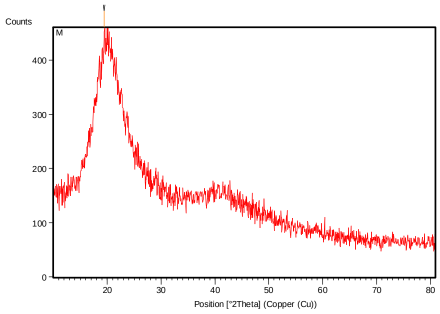

Figure 4.XRD Pattern of the sheet

Average crystallite size is 7.02 nm. Peak isnarrow, hence the sample is crystalline.

FTIR-ATR ANALYSIS

The samples were analysed over the range of 400 cm-1-4000 cm-1 with a spectrum resolution of 4 cm-1.All spectra were averaged over64 scans. The cross linking was confirmed through the AT-IR spectral studies.

WITH CROSS LINKER

The strong peaks observed at 1737.76 cm-1 indicate that the surface of the sample with cross linker is comprised predominantly with ester linkages.

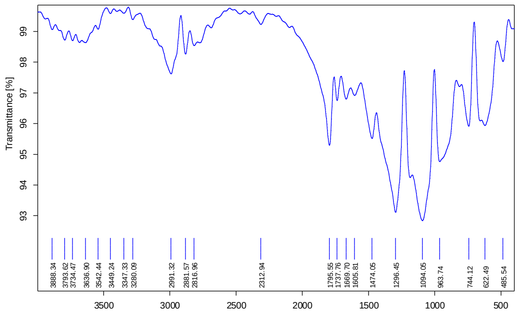

Figure 5.ATR Spectrum of sample with cross linker

WITHOUT CROSSLINKER

The strong peaks observed at 1754.23 cm-1 indicate that the surface of the sample without cross linker is comprised predominantly with ester linkages.

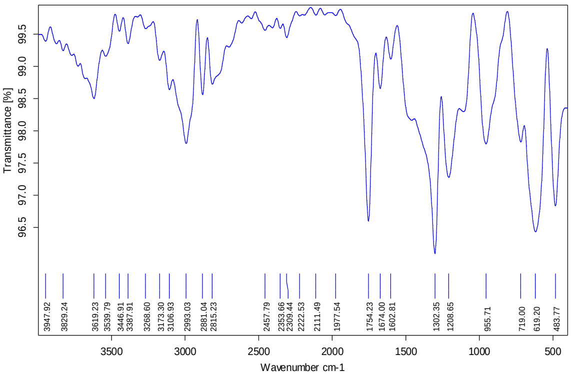

Figure 6.ATR Spectrum of sample without cross linker

SEM ANALYSIS

SEM micrographs show the strong bonding in composite without cross linker than in with cross linker. These results clearly provide strong interfacial adhesion and good wetting, as evidenced by the almost complete absence of holes around the matrix and paucity of breaking of bio-flour during tensile fracture.

WITH CROSS LINKER

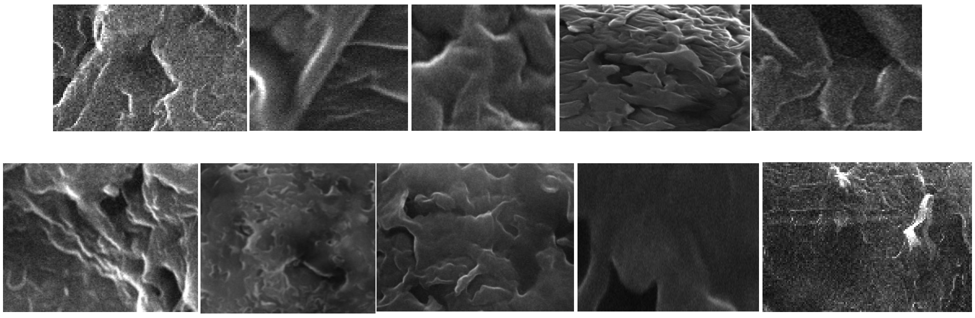

Figure 7.SEM Photographs of sample with crosslinker

WITHOUT CROSS LINKER

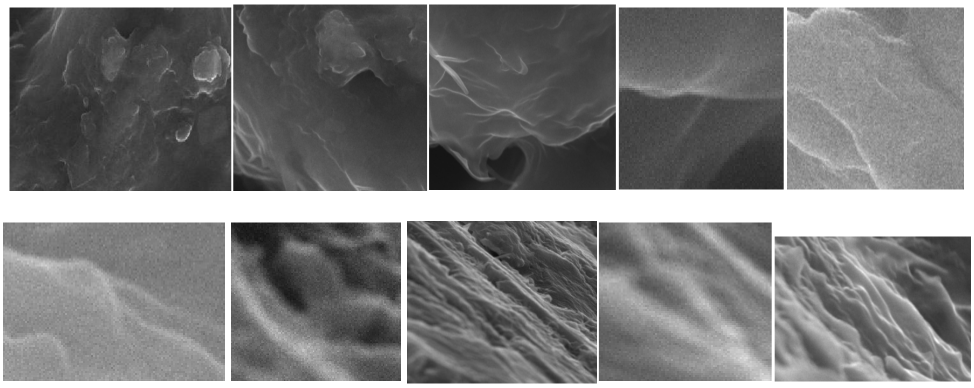

Figure 8.SEM Photographs of sample without cross linker

THERMAL ANALYSIS

Properties of polymer affected by the crosss linking degree, which correlated with the degree of functionality of the monomer.DSC can be used to check the curing results of the thermosetting resin .Both resins with cross linker and without cross linker were analysed by DSC.

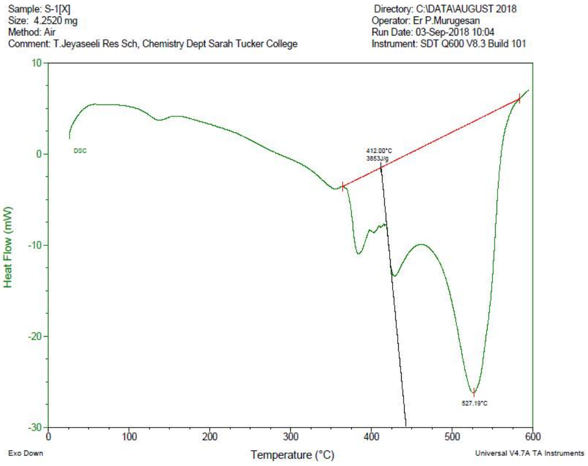

Figure 9.DSC thermogram of sample with cross linker

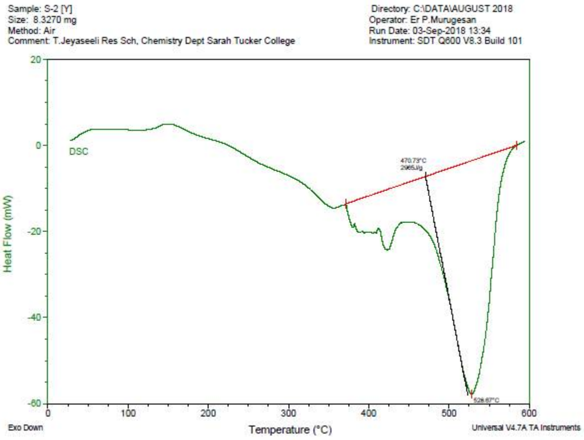

Figure 10.DSC thermogram of without cross linker

The peak for the sample with cross linker is 527.19^{o}c, indicating the fastest cure for this resin will occur at the temperature. The onset of the cure peak for this resinis 412.00^{o}c and the total heat of the reaction is 3853J/g.

The peak for the sample without cross linker is528.6 ^{o}c, indicating the fastest cure for this resin will occur at the temperature. The onset of the cure peak for this resin is 470.73^{o}c and the total heat of the reaction is 2965J/g. It can be seen that resins with cross linker released out more heat during the curing process, which indicate more double bonds inside the resins.

TGA for resins was conducted to indentify their degradation characteristics.

The resin with cross linker was stable up to 150^{o}c with no significant weight loss,the initial weight loss was observed at157.21^{o}c ,indicating the loss of volatiles and moistures. Significant weight loss began at306.36^{o}c due to the degradation of the resin.

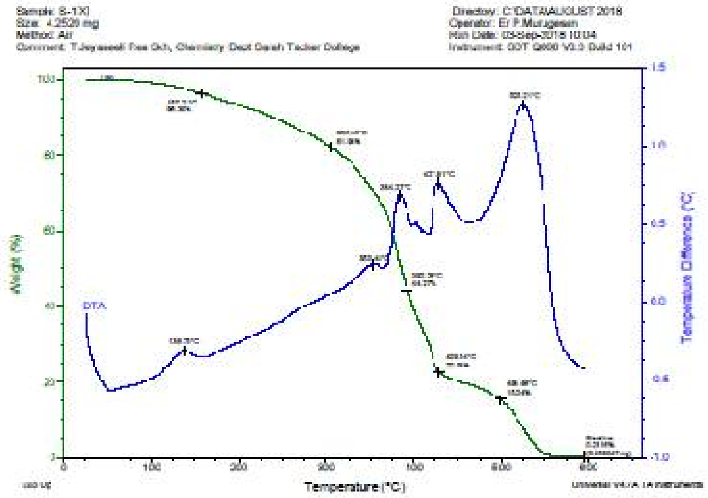

Figure 11.TGA, DTA thermogram of sample with cross linker

When the temperature reached 499.46°c, weight loss was recorded. The maximum rate of decomposition occurred at 525.21°c; the residual mass is around 0.009847 mg.

The resin without cross linker was stable up to130 °c with no significant weight loss, the initial weight loss was observed at135.91°c, indicating the loss of volatiles and moistures. Significant weight loss began at 320.35°c due to the degradation of the resin.When the temperature reached 510.45°c, weight loss was recorded. The maximum rate of decomposition occurred at 527.42°c; the residual mass is around 0.2557 mg.

From this, we see that for resins with cross linker are more resistive to temperature increasing, this is due to cross linker increased the cross linking network of the resins. The residue percentage is lower than resins without cross linker.

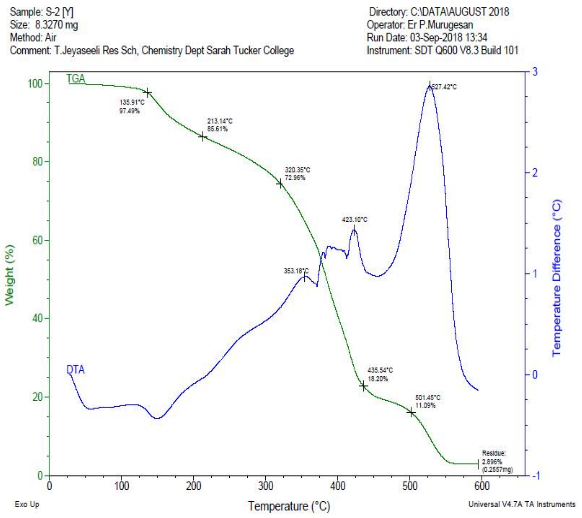

Figure 12.TGA, DTA thermogram of sample without cross linker

DNA BINDING ASSAY

A polymer binds to DNA through intercalation usually results in hypochromism and bathochromism, due to a strong stacking interaction between a polymer and the base pairs of DNA.

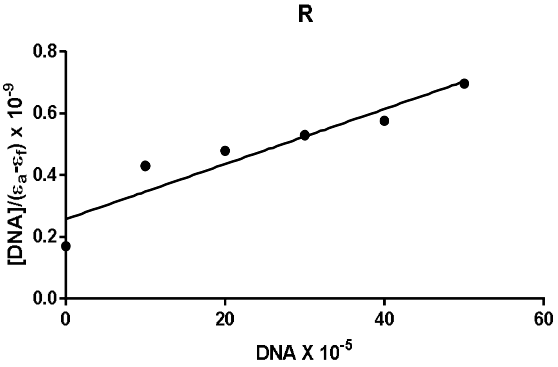

Figure 13.Plots Plotsof [DNA]/ (εa-εf) *versus* [DNA]

Table 2.OD values of the Drug Treated

Drug Treated	Concentration	OD Value
50 µg/ml of the R	0	0.17
10 µM CT DNA +50 µg/ml of the R	10	0.43
20 µM CT DNA +50 µg/ml of the R	20	0.479
30 µM CT DNA +50 µg/ml of the R	30	0.53
40 µM CT DNA +50 µg/ml of the R	40	0.576
50 µM CT DNA +50 µg/ml of the R	50	0.697

The intrinsic binding constant K_b of the polymer with CT-DNA was -3.717x 10^{-4}

MICROBIAL STUDIES

Antibacterials present in the sample were detected by Agar well diffusion method using bacterial strains Actinomycetes Israelii and Aeromonas hydrophilla. The antibacterial activity was assayed by measuring the diameter of the inhibition zone.

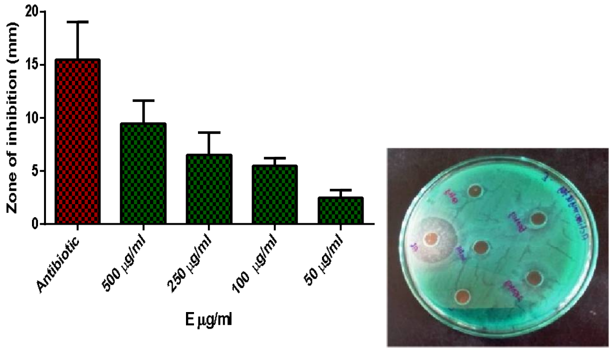

Figure 14.Effect of sample againstActinomycetes Israelii

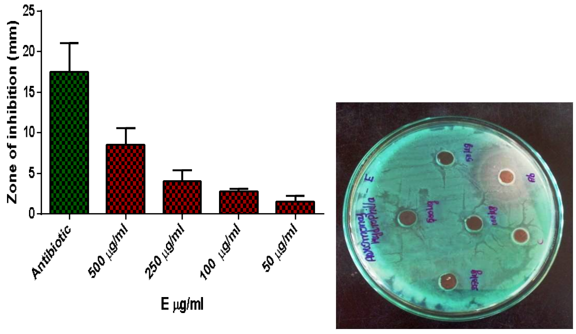

Figure 15.Effect of sample against Aeromonas Hydrophilla

Table 3.Means of zone of inhibition obtained by sample against, Actinomycetes israelii and Aeromonas hydrophila

S. No	Name of the test sample	Name of the test organism	Zone of inhibition (mm)				
			500 µg/ml	250 µg/ml	100 µg/ml	50µg/ml	AB
1.	E	*Actinomycetes israelii*	9.5	6.5	5.5	2.5	15.5
2.	E	*Aeromonas hydrophilla*	6.5	5.5	2.5	1.5	12.5

The newly prepared biopolyesters have been studied against bacterial strain Actinomycetes Israelii and Aeromonas hydrophilla .The polymers showed potential antibacterial activity against micro organisms.

Antifungal present in the sample was detected by Agar well diffusion method using fungal strain Aspergillus Niger. The antifungal activity was assayed by measuring the diameter of the inhibition zone.

RESULTS

EFFECT OF COMPOUND EON *ASPERGILLUS NIGER*

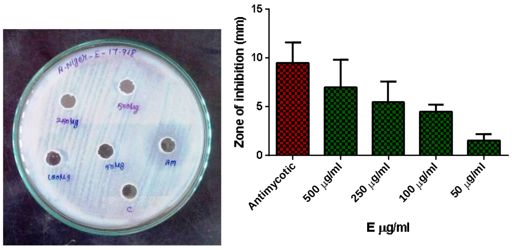

Figure 16.Effect of compound E on Aspergillus Niger

Table 4.Means of zone of inhibition obtained by sample E against*Aspergillus Niger*

S. No	Name of the test sample	Name of the test organism	Zone of inhibition(mm)				
			500 µg/ml	250 µg/ml	100 µg/ml	50 µg/ml	AM
1.	E	*Aspergillus Niger*	7	5.5	4.5	1.5	9.5

The newly prepared biopolyesters have been studied against fungal strain Aspergillus Niger. The polymer showed potential antifungal activity against micro organisms.

CONCLUSION

We have synthesized Bio-basedthermoset resin from Hydnocarpus wightiana seed oil fatty acid.It was hydroxylated by hydrogen peroxide and formic acid; the resulted resin was modified by maleic anhydride. The obtained resins were used in the preparation of the biobased composites.

The composites were characterised by different mechanical analysis and showed relatively good flexural and impact strength which is comparable with the glass fiber reinforced composites.

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