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STUDIES ON NOVEL COMPOSITES BASED ON CORN OIL AND BANANA FIBRE

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Abstract

Over the past few decades, there has been an increasing demand for bio-based resins and polymers in industrial applications, due to their low cost and environmental impact. Fibre reinforced epoxy composites have been synthesised from anhydride based polyester corn oil resin, benzoyl peroxide, dimethyl aniline, and triethylene glycol dimethaacrylate and banana fibre. The physicochemical properties and spectral properties of the synthesised resin have been studied. The polyester and their composites were characterised with FT-IR, thermal properties, swelling coefficient, solvent absorptivity percentage, mechanical properties, soil burial test, and antimicrobial studies. These studies reveal the high performance of banana fibre reinforced composites with respect to the neat polyester.

Keywords: Anhydride based resin, Swelling coefficient, Solvent absorptivity percentage, Fibre reinforced composites.

1. Introduction

The utilize of materials from renewable resources is of rising significance as the world's top industries and manufacturers search to replace decreasing petrochemical-based feedstock with farming based materials. Corn oil is obtained from seeds (kernels) that have only 3 - 5% of oil. Obtaining oil openly from the kernels is technically possible, but corn oil would be expensive to produce, due to the squat levels of oil in the kernels. Corn oil has become an imperative vegetable oil in the mix of goods pretend from America's most imperative crop, and it is the co-product of starch.

The current growth and development of corn refinement, characterised by sophisticated equipment and range of industries it served demonstrates to the corn kernel similar to rough petroleum has happen to a significant resource of chemical feed stocks. Corn oil contains higher unsaturation of long hydrocarbon chain make the crosslinking easy on polymerisation contributes to improve the flexibility and strength. From the triglyceride structure of corn oil, it is possible to functionalize the triglyceride with polymerisable chemical groups [1].

Unsaturated polyester resin show excellent physical properties as well as good weatherability [2]. The resin is relatively despicable in comparison to other types of resin. Furthermore, polyester has the ability to accept a broad range of fillers which makes them applicable to a wide range of projects [3]. The polyester composites will display a wide range of chemical, mechanical, physical and thermal properties, depending on the compounds of the unsaturated polyester.

The natural fibres enclose lignin, cellulose, waxes, pectin and water soluble substances [4]. The compensation of natural fibres are light weight, squat density, inexpensive, easy accessibility, enhanced energy recovery and biodegradability, elevated toughness, high definite force, safer handling etc [5].

On the other hand, natural fibres contain a small number of disadvantages such as elevated moisture absorption, puffiness, inadequate compatibility with some thermoplastic matrices, squat processing temperature, low thermal constancy, unfortunate mechanical properties, elevated biodegradability when viewing to environment and small dimensional stability [6].

Natural fibres are used in different fields such as construction materials, unit boards, wadding boards, animal feed, cosmetics and fine chemicals [7]. The uses of natural fibres for polymer composites are in shipping, low price construction and other construction industries [8]. The automobile engineering is effectively applying composites reinforced with a variety of natural fibre to restore components such as heart panels and glass mat polymer-matrix composites [9].

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2. Experimental

2.1 Materials

The refined corn oil was commercially available in local markets. Hydrogen peroxide (99.9%), glacial acetic acid (100%), were purchased from Sigma- Aldrich and used as such. Triethylamine and phthalic anhydride were supplied by Sigma- Aldrich and used as such. The raw materials used for the synthesis of polyesters and their composites were triethylene glycol dimethaacrylate (TEGMA), Benzoyl peroxide, dimethyl aniline. These chemicals were obtained from Sigma-Aldrich. Banana fibre was procured from local sources.

2.2 Methods

Anhydride based polyester corn oil resin was subjected to extensive analyses such as saponification value, specific gravity, viscosity, iodine value, acid value and moisture content as per IS: 840-1964 standard. Fourier Transform Infrared spectral analysis (FT-IR) of synthesised resin and composites were analysed by KBr pellet method via Shimadzu FTIR-8400S spectrometer. ^{1}HNMR spectra of the synthesised resin were reported by $CDCl_3$ with tetramethylsilane though internal standard. The graph was recorded via Brucker Avance H 500 MHz spectrometer. Thermal properties of new polyesters and composites were determined using differential thermal analysis (DTA) and thermo gravimetric analysis (TGA).

2.2.1 Determination of swelling coefficient

The polyester sheet and its composites were subjected to swelling experiments. The density of the polyester sheets and corresponding composites were analysed using ASTM D 792 standard.

The swelling coefficient 'Q' was evaluated using the formula,

$$\text{Swelling coefficient (Q)} = \frac{\text{Weight of the solvent in swelled polymer}}{\text{Weight of the swelled polymer}} \times \frac{\text{Density of polymer}}{\text{Density of solvent}}$$

2.2.2 Determination of solvent absorptivity percentage (SA %)

Swelling behaviour of polyesters and their composites was also studied. Each polyester sheet was put in 3ml of different solvents for 24 hrs. After 24 hrs, the excess solvent on the outside of polyester sheet was detached by using filter paper. Then it was weighed and the solvent absorptivity percentage was evaluated using the following equation,

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

Where,

W_1 = Weight of the polyester composites, W_2 = Weight of the polyester composites after absorption of the solvent.

2.2.3 Evaluation of mechanical properties

Tensile strength of the newly prepared polyesters and its composites were evaluated in Universal Testing Machine at across head speed of 100 mm for minute using rectangle shaped samples (10 x 1 cm) punched out from polyesters and composites sheets as for ASTM D6100. The gauge length was set at 3cm in each test. The Young's modulus, tensile strength and elongation at break were evaluated using standard methods. Shore A hardness of polyesters and its composites were evaluated as per ASTM D2240. Polyesters and their composite sheets of 5mm thickness were used for hardness measurements.

2.2.4 Soil burial degradation test

The polyester neat sheet banana fibre reinforced composites (5 x 3 cm) were buried in the soil at a depth of 30 cm from the ground surface for 60 days, inoculated with compost having the capacity to hold and

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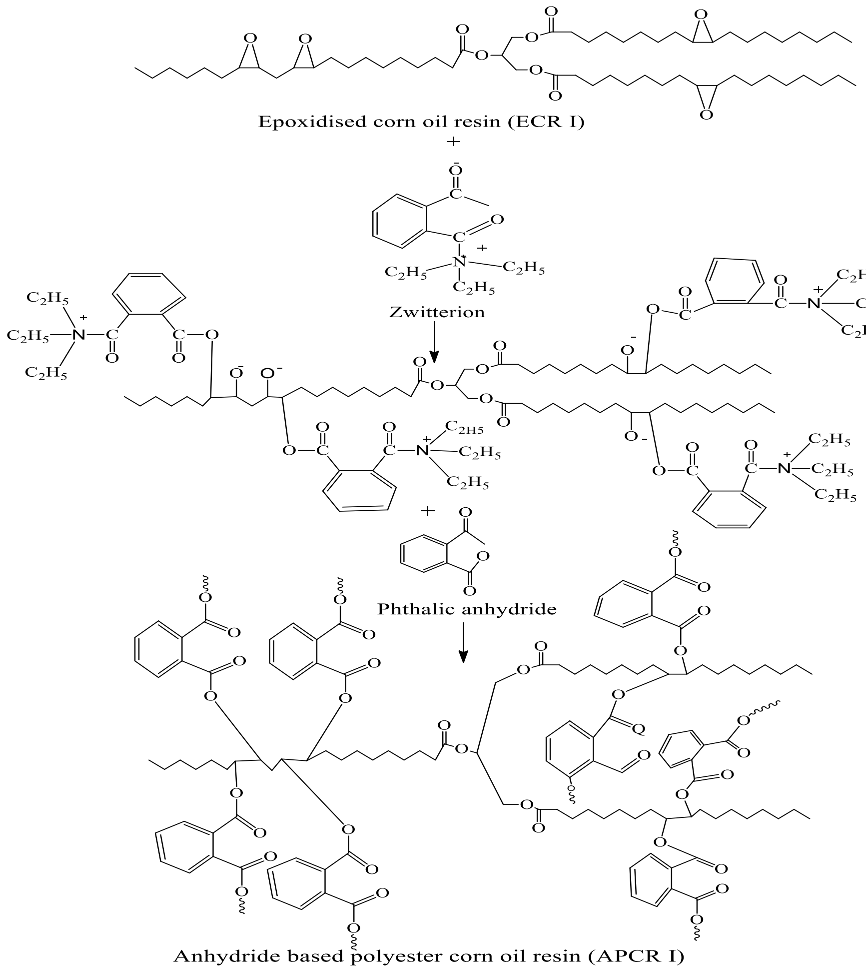
degrade the polymer .At fixed time, the samples were detached, washed with distilled water in order to ensure the stop of the degradation, dried out at room temperature to a constant weight and stored in dusk

2.2.5 Evaluation of performance under bacterial exposure

Solid media ager-plate tests were conducted to evaluate the biodegradation of polyester neat sheet and its banana fibre reinforced composites by specific strains of microorganisms such as *Pseudomonas aerogenis*a and *Bacillus subtilis* for 168 hrs.

2.2.6 Synthesis of anhydride based polyester corn oil resin

Anhydride based polyester resin (Scheme.1) was synthesised from epoxidised corn oil resin phthalic anhydride and triethylamine in the mole ratios 1:1.5. The intended amount of epoxidised corn oil resin and phthalic anhydride was taken in a three necked flask situate with Liebeg condenser, mechanical stirrer and thermometer. Triethylamine was added to the reaction mixture through dropping funnel. The reaction was continued at a temperature 100^0C for 3hrs. The yellowish brown viscous liquid was obtained.



Scheme 1. Formation of anhydride based polyester corn oil resin

2.2.7 Synthesis of anhydride based polyester neat sheet and composites

The anhydride based polyester neat sheet (Scheme. 2) and its composites were synthesised by treating anhydride based polyester corn oil resin with 2ml of Triethylene glycol dimethacrylate (TEGMA) (crosslinking agent), benzoyl peroxide (initiator) and dimethyl aniline (accelerator). The neat sheet was coded as CPS. The treated banana fibre with varying compositions (5, 10 and 15 wt. %) added to the above mixture. The mixture was poured into the clean silicon oil spreaded glass mould. The mixture poured glass mould was dried in vacuum air oven at 60^0C for 24 hrs. The 5%, 10%, and 15% banana fibre reinforced composites were coded as CPB5, CPB10 and CPB15.

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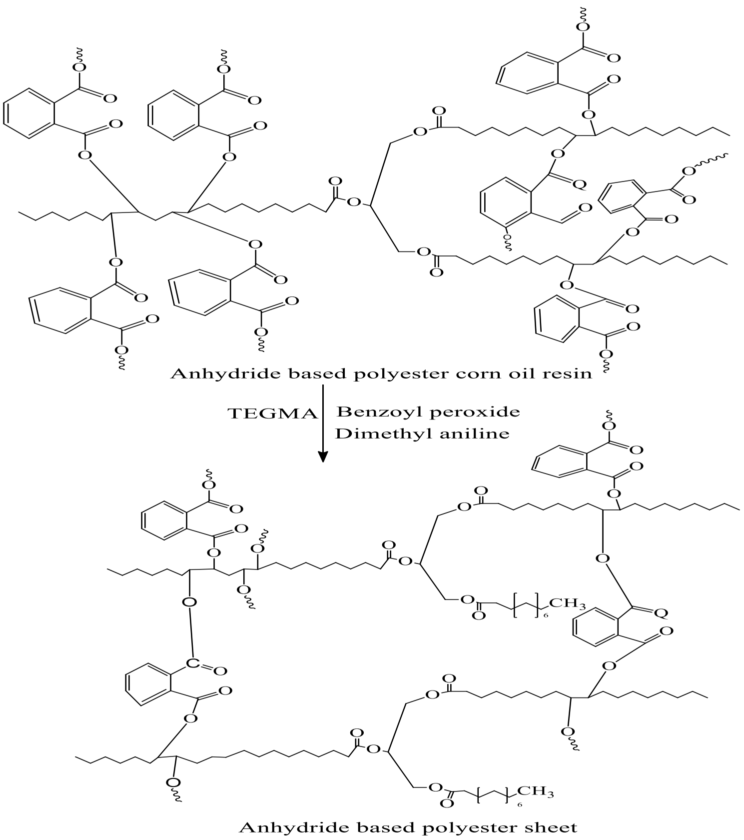

Scheme 2. Formation of anhydride based polyester sheet

3. Results and discussion

3.1 Charaterisation of anhydride based polyester resin

3.1.1 FT-IR analysis

FT-IR spectrum of anhydride based polyester corn oil resin is shown in Figure 1.

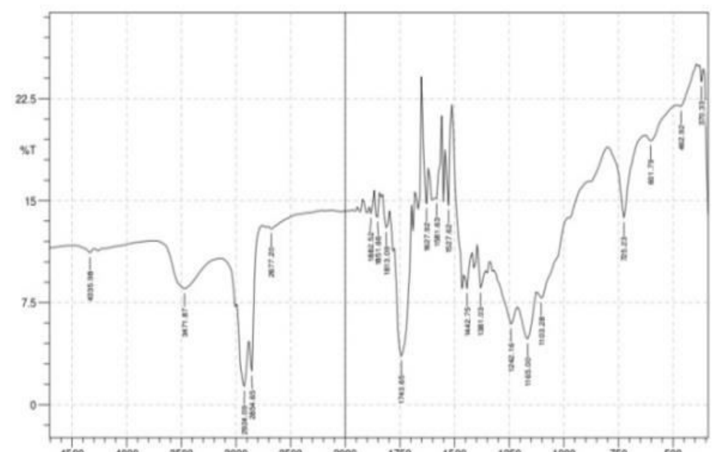

Fig. 1. FT -IR spectrum of anhydride based polyester corn oil resin

In the FT-IR spectrum of corn oil (Fig. 1) showed maximum absorption at 3471.8 cm^{-1} corresponds to the higher proportion of linoleic acid groups. The broadening of the peak at1743.65 cm^{-1} indicates the presence of ester carbonyl group. The FT-IR spectrum of anhydride based polyester resin the

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epoxy peak in the epoxidised resin 840.96 cm^{-1} is disappeared in anhydride based polyester resin corresponds to the phthalic anhydride substituted in the epoxy ring.

3.1.2 ^{1}HNMR analysis

^{1}HNMR spectrum of corn oil and anhydride based polyester corn oil resin are shown in Figure 2. The ^{1}HNMR spectra of anhydride based polyester corn oil resins the loss of peak at 2.8 ppm showed that the phthalic anhydride substituted to the epoxy group.

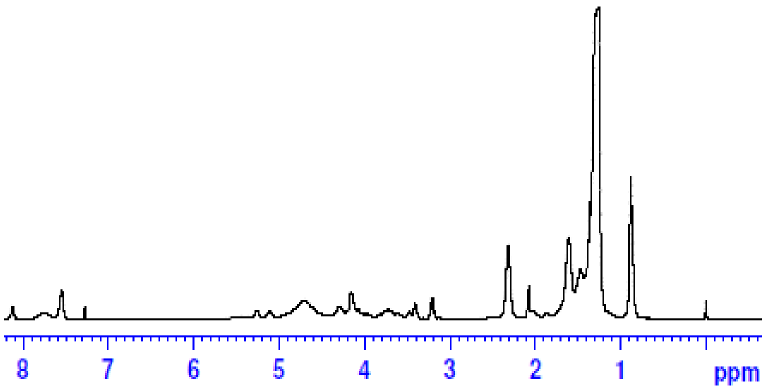

Fig. 2. 1HNMR spectrum of anhydride based polyester corn oil resin

3.2 Characterisation of polyesters and its composites
3.2.1 FT-IR analysis

FT-IR spectrums of polyester neat sheet and banana fibre reinforced composites are given in Figure 3 - 6. The FT-IR spectrum of anhydride based polyester neat sheet CPS is almost same as that of anhydride based polyester corn oil resin but the absence of peak at 1666.50cm^{-1} indicates the absence of double bonds. The FT-IR spectrum of banana fibre reinforced anhydride based polyester composites show that the irregular bands present in the spectrum. The new bands are not formed in the spectrum due to the formation of fibre reinforced composites.

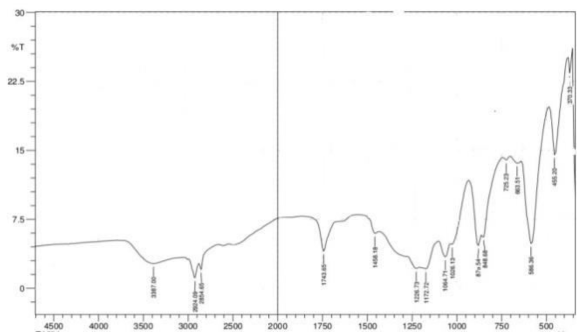

Fig. 3. FT-IR spectrum of CPS

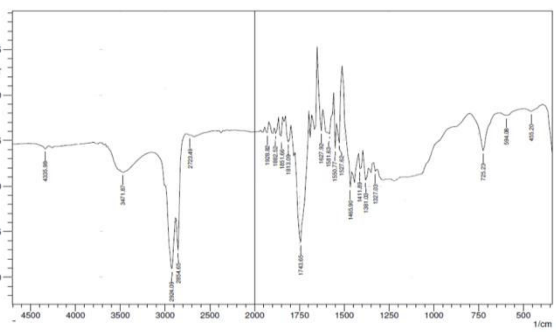

Fig. 4. FT-IR spectrum of CPB5

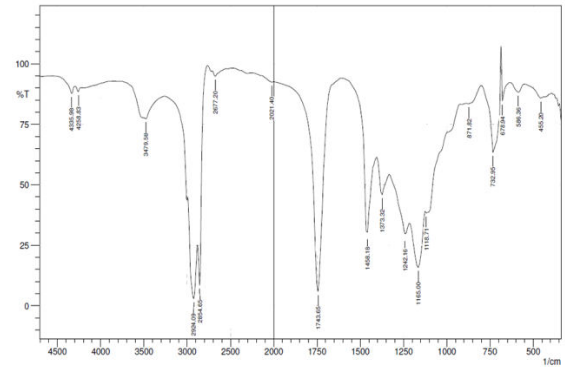

Fig. 5. FT-IR spectrum of CPB10

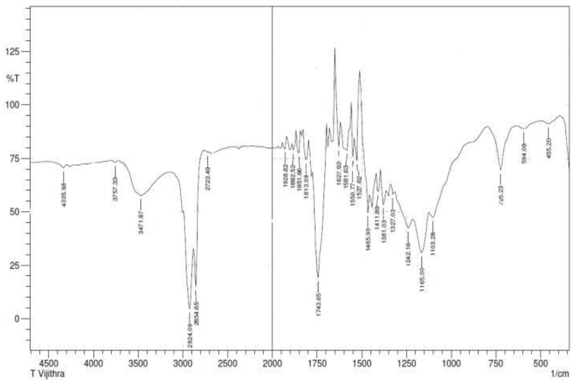

Fig 6. FT-IR spectrum of CPB15

3.2.2 Thermal properties

In the present study, the TGA and DTA thermograms of polyester and its composites are given in Fig 7 – Fig 10. Thermogravimetric analysis reveals that all the composites have higher starting degradation temperature (T_{start}) and weight losses. The decomposition of composites shows more than one stages. The third stage of decomposition is about 98% in the temperature range 430^{0}C to 500^{0}C due to the complete decomposition of the polyester moiety of the composites results the char residue. The DTA thermogram of CPS, CPB5, CPB10 and CPB15 shows an endothermic peak at 350^{0}C to 380^{0}C. The second endothermic peak around 360 to 450^{0}C it is due to the degradation of crosslinking composites fragments.

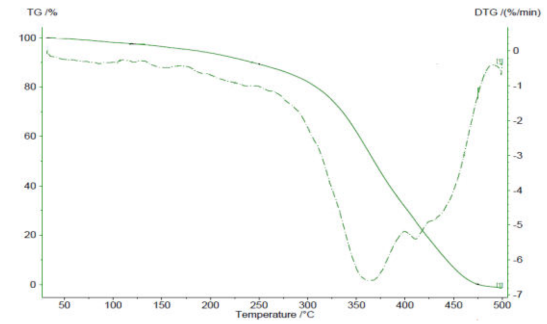

Fig. 7. TGA/DTA curve of CPS

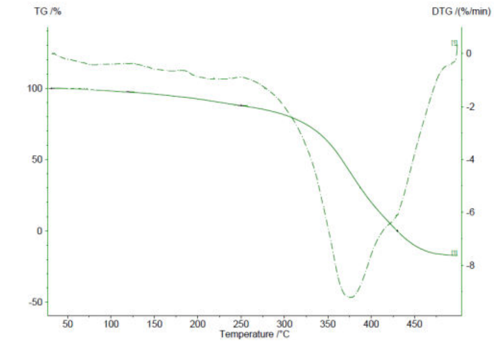

Fig. 8. TGA/DTA curve of CPB5

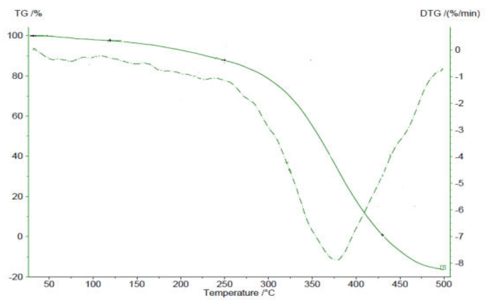

Fig. 9. TGA/DTA curve of CPB10

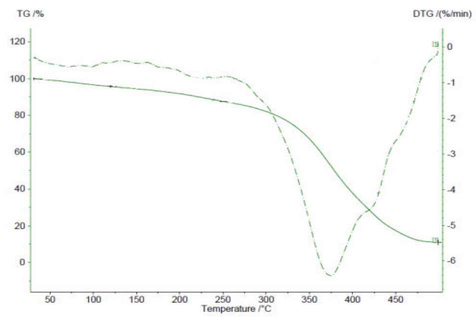

Fig. 10. TGA/DTA curve of CPB15

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3.2.3 Swelling coefficient

The swelling coefficient of the present polyesters and their corresponding composites are high in dimethyl acetamide. This reveals that the present polyesters and their composites are crosslinked. These crosslinked polymeric materials will only swell and not liquefy in a non-reactive solvent. The amount of swelling in a non-reactive solvent is used to evaluate the quantity of crosslinking and the molecular weight (Mc) between crosslinks. Molecular weight (Mc) between crosslinks higher the crosslink densities lower.

Table 1. Swelling coefficient of neat polyesters and banana fibre reinforced composites

Polyester and their composites	Swelling coefficient 'Q'							
	EMK	Toluene	Chloroform	Acetone	DMA	DMF	Ethylene glycol	Glycerol
CPS	0.27	0.25	0.31	0.40	1.15	0.71	0.11	0.06
CPB5	0.27	0.27	0.32	0.44	1.21	0.65	0.18	0.09
CPB10	0.28	0.28	0.33	0.45	1.20	0.67	0.19	0.08
CPB15	0.30	0.30	0.34	0.45	1.19	0.80	0.22	0.06

3.2.4 Solvent absorptivity percentage (%)

The solvent absorptivity percentage of the newly prepared polyester and their corresponding composites are given in Table 2. The solvent absorptivity is carried out in different solvents such as ethyl methyl ketone (EMK), toluene, chloroform, acetone, dimethyl formamide (DMF), ethylene glycol, dimethyl acetamide (DMA) and glycerol. This indicates that the newly prepared polyesters and their composites are hydrophobic in nature. In the present study, the newly prepared polyesters and their composites, the solvent absorptivity percentage is observed in the order CPB15 > CPB10 > CPB5 > CPS. Fibre reinforced composites have higher solvent absorptivity percentage in comparison with that of neat polyester.

Table 2. Solvent absorptivity percentage of neat polyester sheet and banana fibre reinforced composites

Polyester and their composites	Solvent absorptivity (%)							
	EMK	Toluene	Chloroform	Acetone	DMA	DMF	Ethylene glycol	Glycerol
CPS	15.19	17.07	25.50	20.58	80.00	55.97	4.36	8.41
CPB5	15.21	17.18	26.40	20.96	80.10	58.76	8.11	8.56
CPB10	15.22	17.33	26.56	21.13	83.83	59.03	8.90	8.91
CPB15	15.25	17.57	26.93	21.78	83.68	59.46	8.98	9.22

3.2.5 Mechanical properties

In the present study, the data of mechanical properties such as Young's modulus, tensile strength, elongation at break and shore A hardness of newly prepared composites are given in Table 3. It is observed that the fibre reinforced composites possesses greater mechanical properties than neat polyesters due to the presence of alkali treated banana fibres.

The mechanical property shows that the 15% and 10% fibre reinforced composites possess higher Young's modulus and tensile strength than the 5% and neat polyester sheet. Samples like CPB15 and CPB10 composites having higher tensile strength and Young's modulus than other polyester composites. The banana, fibre increases, these fibres shared the tensile stress to improve the tensile strength and Young's modulus significantly. It concluded that the 15% fibre reinforced composites possesses high tensile strength and Young's modulus than other composites.

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In the present study, the shore A hardness of samples like CPB15 and CPB10 are greater than other prepared composites, due to the presence of higher percentage of banana fibre. It is concluded that as fibre content increases shore A hardness also increases.

Table 3. Mechanical properties of corn oil based polyesters and their composites

Polyesters and their composites	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Shore A hardness
CPS	9.2	114	8.17	32
CPB5	10.7	110	9.36	36
CPB10	11.3	106	10.98	49
CPB15	16.5	102	13.14	52

3.2.6 Soil burial test

Soil burial test was used to detect the environmental resistance of the polyester and banana fibre reinforced composites. The weight loss percentage of newly prepared polyester and their composites in soil burial test is depicted in Table 4. As the percentage of fibre content increase the degradation rate also increase. It concluded that the banana fibre reinforced composites possesses higher degradation than neat polyester sheet. The 10% and 15% fibre reinforced composites have higher degradation rate due to the rate of increased fibre content.

Table 4. Weight loss of neat polyester and its composites under soil burial test

Polyester and their composites	Weight loss (%)
CPS I	27.921
CPB5	36.588
CPB10	43.258
CPB15	62.789

3.2.7 Biodegradation of neat polyester sheet and banana fibre reinforced composites

The microbial activity images (Fig 11) indicate the degradation of neat polyesters and banana fibre reinforced composites in the presence of microorganisms such as gram-negative *Pseudomonas aerogenis*a and gram-positive *Bacillus subtilis* for 168 hrs. The results were presented in Table 5. The CPB15 and CPB10 composites shows maximum zone of growth against *Pseudomonas aerogenis*a and *Bacillus subtilis* when compared to neat polyester sheet.

Table 5. Growing zone rate (mm) for neat polyester sheet and banana fibre reinforced composites

Polyester and its composites	Microorganisms	
	Pseudomonas aerogenisa	Bacillus subtilis
CPS	14	14
CPB5	14	14
CPB10	15	15
CPB15	17	17

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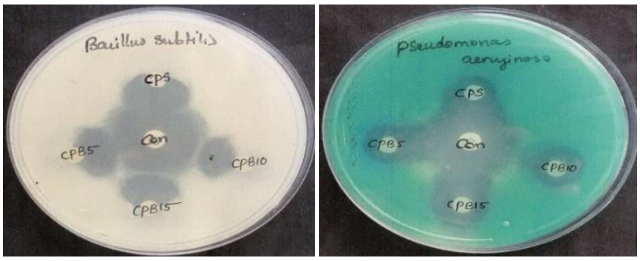

Fig. 11. Microbial activity of polyester and banana fibre reinforced composites based on corn oil

4. Conclusions

Corn oil is a combination of triglycerides it contain unsaturated and saturated fatty acids. The specific gravity and viscosity of anhydride based polyester corn oil resin is higher than the corn oil. The anhydride based polyester resin is used to fabricate high molecular weight polyester neat sheets and fibre reinforced composites. The DTA data of banana fibre reinforced composites shows that the fibre increases, the rate of decomposition also increases. The swelling coefficient of the present polyesters and their corresponding composites are high in dimethyl acetamide. This reveals that the present polyesters and their composites are crosslinked. The percentage of fibre content increases Young's modulus, tensile strength and shore A hardness also increases but elongation at break decreases. The banana fibre reinforced composites are highly biodegradable than neat polyester.

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