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Synthesis, Characterisation and Degradation of Glass Fibre Reinforced Polyester and Their Composites Based On Punnal Oil

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Abstract: ***Punnal oil is non-edible oil and is extracted from the seed oil of the Calophyllum inophyllum tree. Punnal oil is easily available, less toxic, inexpensive etc that can be used for the synthesis of polyesters. Punnal oil based polyester sheet was synthesised by treating punnal oil with peroxyacetic acid followed by the addition of hydrogen peroxide. The synthesised epoxidised punnal oil was heated with phthalic anhydride and cured in the presence of benzoyl peroxide and dimethyl aniline. The glass fibre reinforced polyester composites were synthesised using punnal oil based polyester resin with glass fibres of varying compositions. The spectral studies such as FTIR and ^{1}H NMR analysis, the mechanical properties, scanning electron microscope analysis, soil burial test and antimicrobial test were evaluated. It has been evaluated that the variation of composition of fibres influences the mechanical properties and degradation rate.***
Keywords: Polyester, Composites, phthalic anhydride, glass fibre, punnal oil

I. INTRODUCTION

Polymers are mainly used in chemical industry such as lubricants, plasticisers, stabilisers, coatings etc. The demand of these applications is increasing day by day. In earlier days, polymers and polymer composites are derived from petroleum feedstocks. As the demand of polymer and polymer composites increases, there is a need of renewable resources as an alternate petroleum feed stocks. Vegetable oils are a sustainable and renewable raw material. The polymers derived from vegetable oils have many advantages such as cheap, most abundant feedstock, low toxic, biodegradability etc than the petroleum based polymers [1]. Punnal oil is the naturally occurring vegetable oil and is extracted from the seed of the *Calophyllum inophyllum* tree. It contains 92% triglycerides. The major fatty acids present in punnal oil are palmitic acid, palmitoleic acid, stearic acid, oleic acid, linoleic acid and linolenic acid [2].The unsaturated bonds are the most important points in which different functional groups can be introduced into the oils to get chemical modifications [3]. Therefore, the double bonds in the punnal oil have to be converted to more reactive functional groups such as epoxide groups, acrylate groups, hydroxyl groups etc.

Glass fibre is a synthetic fibre and used as a reinforcing agent for many polymer products. The commonly used glass fibres are E-glass and S-glass [4]. E-glass is an alumino-borosilicate glass with less than 1% w/w alkali oxides, mainly used for glass-reinforced plastics [5]. The advantages of glass fibre are low cost, high tensile strength, high chemical resistance and excellent insulating properties [6]. The glass fibres are used for making composites with the newly synthesised polyester resin based on punnal oil.

The present work deals with the synthesis, spectral, mechanical and degradation of punnal oil based polyester and their composites with glass 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 dimethaacrylate (Sigma-Aldrich), benzoyl peroxide (Sigma-Aldrich) and dimethyl aniline (Sigma-Aldrich) were used without further purification. Glass fibre was procured from local sources.

B. Synthesis of glass fibre reinforced polyester and their composites

Punnal oil (1 M) was taken 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^{o}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^{o}C for 2 h to yield yellowish brown viscous polyester resin. The product was

cured with 1 ml of triethylene glycol dimethaacrylate (crosslinking agent) in the presence of benzoyl peroxide (initiator) and dimethyl aniline (accelerator) with glass 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^{o}C for 6 h. The obtained anhydride based polyester sheet was coded as POP. The 5%, 10% and 15% glass fibre reinforced composites were coded as POPGF5, POPGF10 and POPGF15.

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. ^{1}H NMR spectra of the synthesised resins were recorded using $CDCl_3$ with tetramethyl silane as an internal standard. The spectrum was recorded using Brucker Avance H 500 MHz spectrometer.

D. 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.

E. Soil burial degradation test

The polyesters and their 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 ability to adhere and degrade the polymer. At predetermined time, the samples were removed, washed with distilled water in order to ensure the stop of the degradation, dried at room temperature to a constant weight and stored in darkness [7].

F. Scanning electron microscope analysis

Scanning electron microscope analysis (SEM) was conducted (ESEM-Quanta 200, Fei) to study the degradation of the polyesters and their composites before and after soil burial test.

G. Antimicrobial test

The performance of the polyesters and their composites under bacterial attack conditions were evaluated by investigating antimicrobial activity. Antibiotic susceptibility tests were determined by agar disc diffusion (Kirby–Bauer) method [8]. Bacterial strains were swabbed using sterile cotton swabs in nutrient agar plate. Disc of 6 mm were punched from Whatman No.1 filter paper. Up to 10 µl of each concentration of the extract were respectively introduced in the discs using sterile pipettes. The disc was then placed on the surface of medium and the compound was allowed to diffuse for 5 minutes and the plates were kept for incubation at 37°C for 24 h. At the end of incubation, inhibition zones were examined around the disc and measured with transparent ruler in millimeters. The bacterial strains used for the study were Gram positive such as Staphylococcus aureus and Bacillus subtilis and Gram negative such as Escherichia coli and Klebsiella pneumonia.

III. RESULTS AND DISCUSSION

A. 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 [9].

The FTIR spectrum of anhydride based polyester resin 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 polyester resin. 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 polyester resin and the polyester sheet.

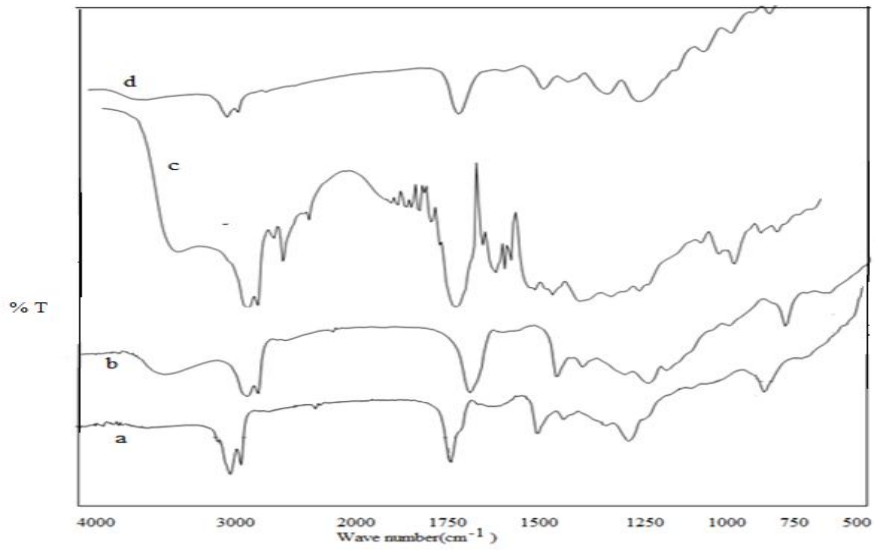


Fig 1 FTIR spectrum of punnal oil (a), epoxidised punnal oil (b), anhydride based polyester resin (c), polyester sheet (d)

B. ^1H NMR spectral analysis

The ^{1}H NMR spectral analysis of punnal oil is shown in Fig 2. It reveals that the peak at 0.75 δ corresponds to the hydrogen ending methyl groups (CH_3–$(CH_2)_n$–). Peak appeared at 1.2 – 1.4 δ indicate the aliphatic methylene hydrogens (– CH_2–) [10]. The peak at 2.05 δ attributes the allyl hydrogen (– CH_2–CH=CH–). The peak around 2.7 δ is originated from the hydrogen of two double bonds (–CH=CH–CH_2–CH=CH–). The peaks at 4.1 – 4.3 δ is due to the protons in the methylene groups of the triglyceride. The peak sited at 5.2 – 5.5 δ indicates the presence of olefinic protons of the punnal oil.

The ^{1}H 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 δ that mean the double bond is replaced by the epoxy group. The peak at 3.2 δ shows –CH– hydrogen between two epoxy groups. The allyl hydrogen of punnal oil at 2.05 δ is shifted to 1.45 δ in epoxidised punnal oil.

The ^{1}H NMR spectra of anhydride based polyester resin is shown in Fig 4. It reveals that the new peak at 7.54 – 7.71 δ correspond to the aromatic proton of phthalic anhydride. The disappearance of epoxy band at 2.8 δ shows that phthalic anhydride is added to the epoxy ring. The peak at 1.4 δ corresponds to the long chain methylene groups and the peak at 0.95 – 2.3 δ is attributed by aliphatic side chain.

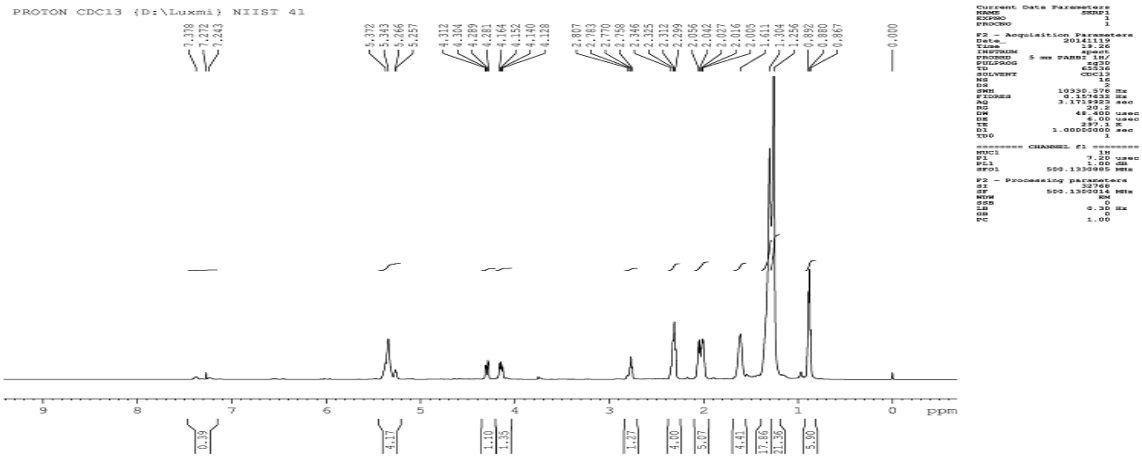


Fig 2 ^{1}H NMR spectra of punnal oil

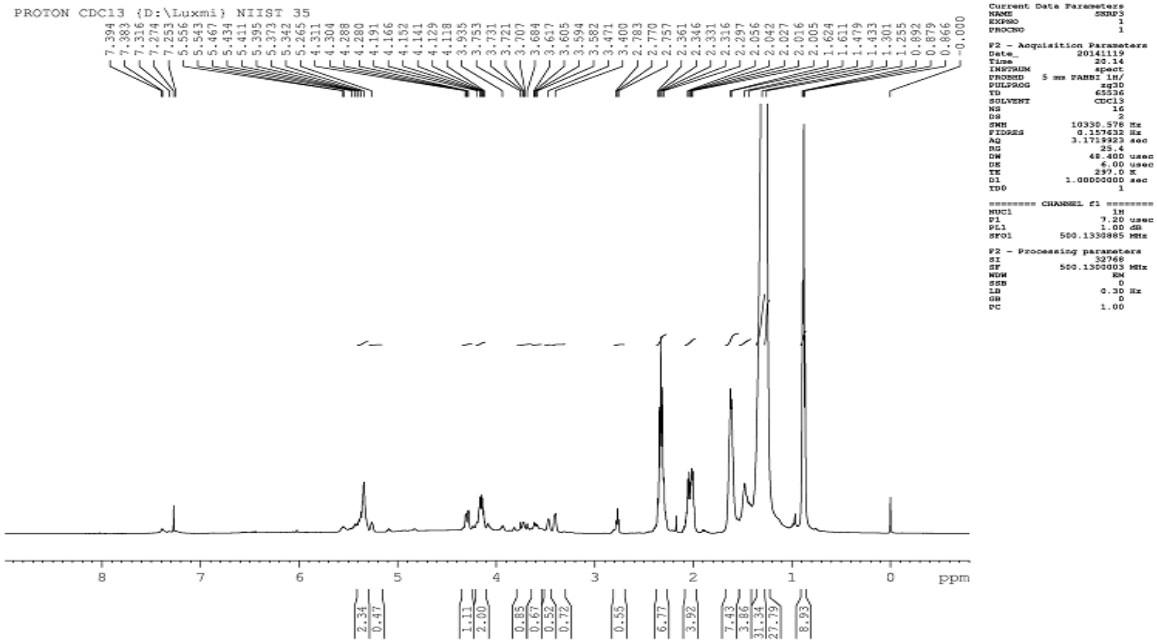


Fig 3 ^{1}H NMR spectra of epoxidised punnal oil

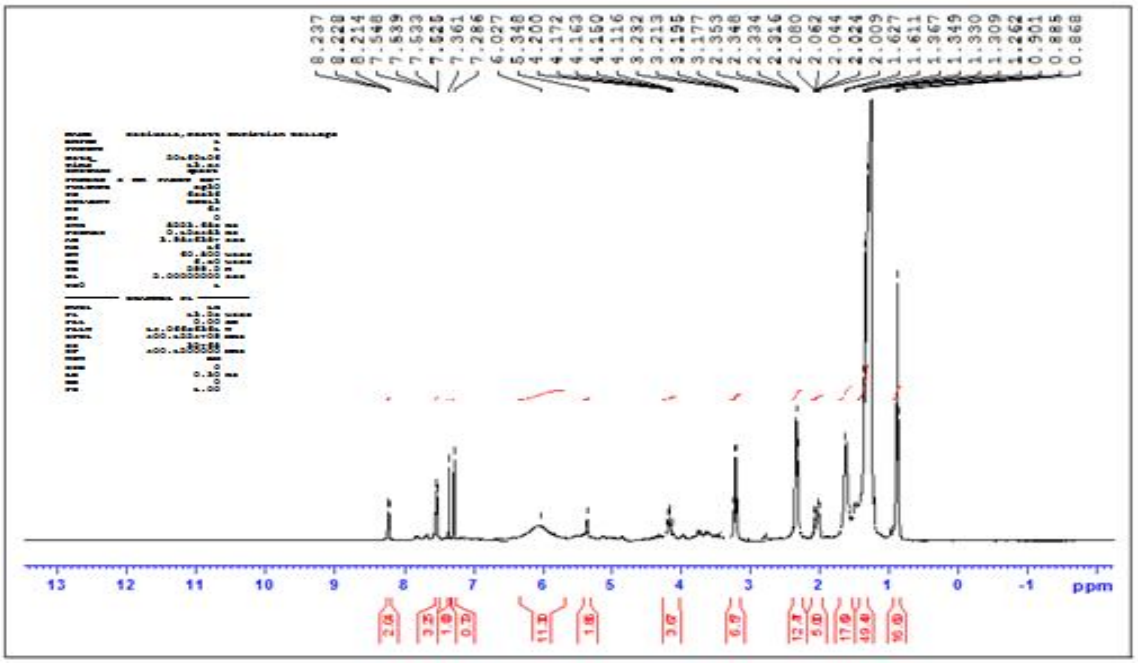


Fig 4 ^{1}H NMR spectra of anhydride based polyester resin

C. Mechanical properties

The glass fibre reinforced anhydride based polyester composites shows higher tensile strength and Young's modulus than the neat anhydride based polyester sheet due to its high crosslink density. As the content of glass fibres are increased, more fibres shared the tensile stress to improve the tensile strength and Young's modulus greatly. When compared, the glass fibre reinforced polyester composites having higher percentage fibre possess higher tensile strength and Young's modulus than the neat polyester sheet due to improved mechanical properties of glass fibre. But the elongation at break decreases. The hardness of glass fibre reinforced polyester composites increases with the increase in the percentage of glass fibres due to high crosslink density than the neat polyester sheet.

TABLE 1 MECHANICAL PROPERTIES of POLYESTER and THEIR COMPOSITES

Polyester and their composites	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Shore-A hardness
POP	2.5	115	2.17	35
POPGF5	6.2	107	5.79	52
POPGF10	9.9	106	9.33	57
POPGF15	14	102	13.7	60

D. Soil burial test

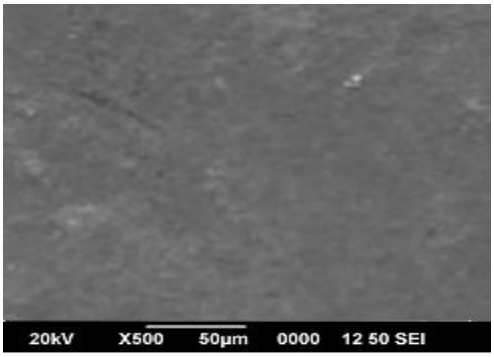
Soil burial test was used to find out the environmental resistance of the composites. As the percentage of fibre content increases, the degradation of composites decreases. It is concluded that the glass fibre reinforced polyester composites with higher percentage of fibres posses lower degradation than the neat polyester sheet because glass fibres are non- biodegradable.

TABLE 2 WEIGHT LOSS of POLYESTER and THEIR COMPOSITES UNDER SOIL BURIAL TEST

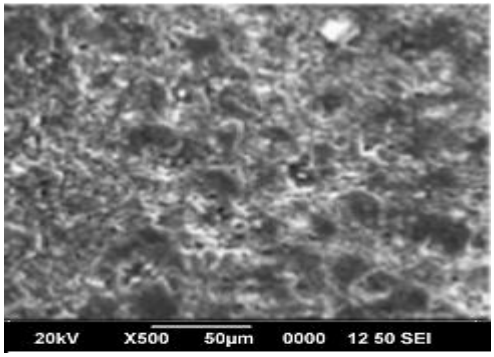
Polyester and their composites	Weight loss (%)
POP	32
POPGF5	38.09
POPGF10	27.31
POPGF15	24

E. Scanning electron microscope analysis of polyester and their composites

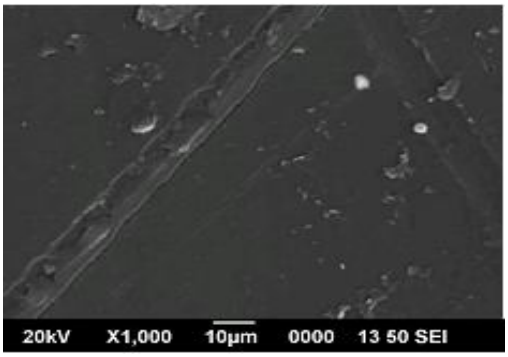
The scanning electron microphotograph of neat polyester sheets exhibits a relatively smooth surface. The 5% glass fibre reinforced polyester composites exhibit rough surface than the neat polyester sheets. With the increase of fibre content, the roughness increases slightly due to its high crosslink density. Increasing the fibre content increases the adhesion between fibres and polymer which improves the mechanical properties of the composites. After 60 days in the soil, a small holes, cavities and pinholes are observed in polymer sheets indicated that the polyester surface is attacked by the microorganism under soil environment.



POP (before)

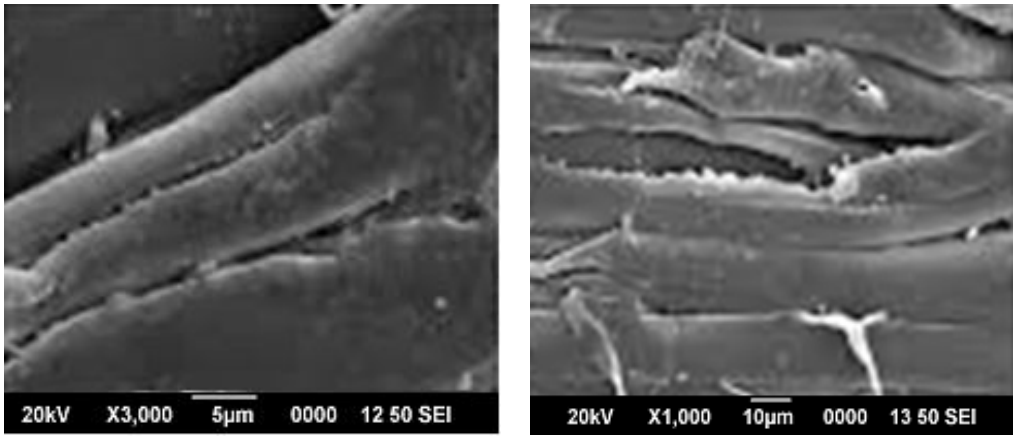


POP (after)



POPGF5 (before)

POPGF5 (after)



POPGF10 (before) POPGF10 (after)

Fig 5 SEM images for the polyester and their composites with glass fibres before and after soil burial test

F. Antimicrobial activity of polyester and their composites

The antibacterial activity of polyester and their composites are investigated using Gram positive bacteria such as Staphylococcus aureus and Bacillus subtilis and Gram negative bacteria such as Escherichia coli and Klebsiella pneumonia. The zone of inhibition of the polyesters and their composites with chloroform solution are demonstrated in relation to amikacin. The glass fibre reinforced polyester composites show slight zone of inhibition against all the bacteria. Hence all the polyester and their composites posses lower degradation. This may be attributed to the steric hindrance of the anhydride group present in the polyester composites.

TABLE 3INHIBITION ZONE (MM) of POLYESTER and THEIR COMPOSITES

Polyesters and their composites	Microorganisms			
	Escherichia coli	Staphylococcus aureus	Klebsiella pneumoniae	Bacillus subtilis
POP	8	8	8	8
POPGF5	7	8	8	8
POPGF10	7	8	8	7
POPGF15	8	8	8	8

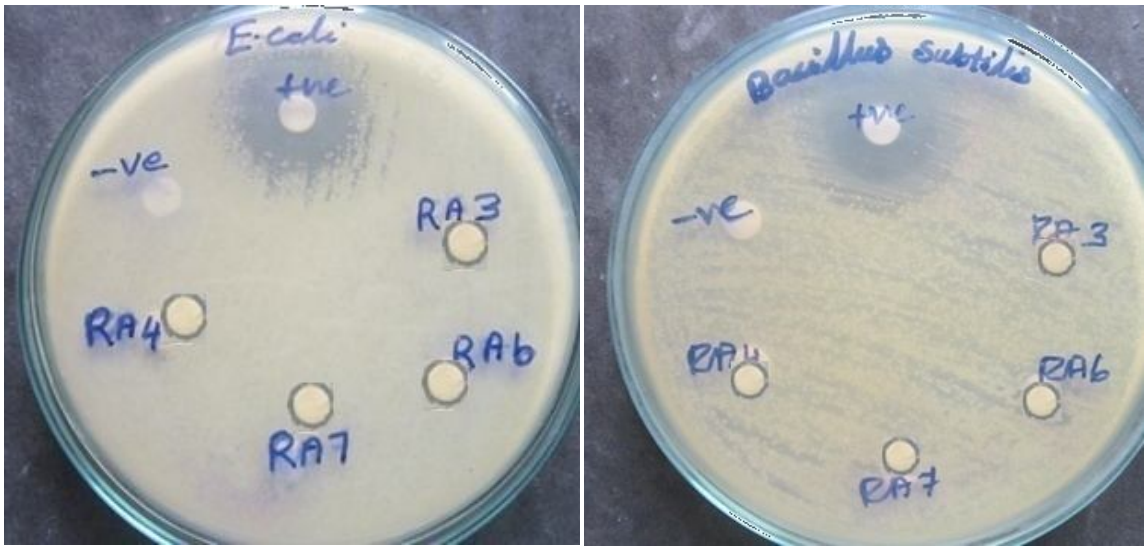


Fig 6 Culture plates of polyester and their composites with glass fibres using Staphylococcus aureus, Bacillus subtilis, Escherichia coli and Klebsiella pneumonia.

IV. CONCLUSION

Punnal oil is a mixture of triglycerides consisting of unsaturated fatty acids and saturated fatty acids. The unsaturated fatty acids present in the oil are oleic acid and linoleic acid. Punnal oil was epoxidised successfully by peroxy acetic acid with hydrogen peroxide at about 60^{o}C.The anhydride based epoxidised punnal oil were synthesised from epoxidised punnal oil. The synthesised resins were confirmed by FTIR and ^{1}H NMR spectral analysis. From the mechanical properties, it is concluded that the composition of glass fibre increases, the tensile strength and Young's modulus also increases along with it. But, the elongation at break decreases. Similarly, the hardness also increases with the increase in composition of the polyester and their composites due to its high crosslink density. In scanning electron microscope analysis, the increase of fibre content increases the roughness slightly due to its high crosslink density.

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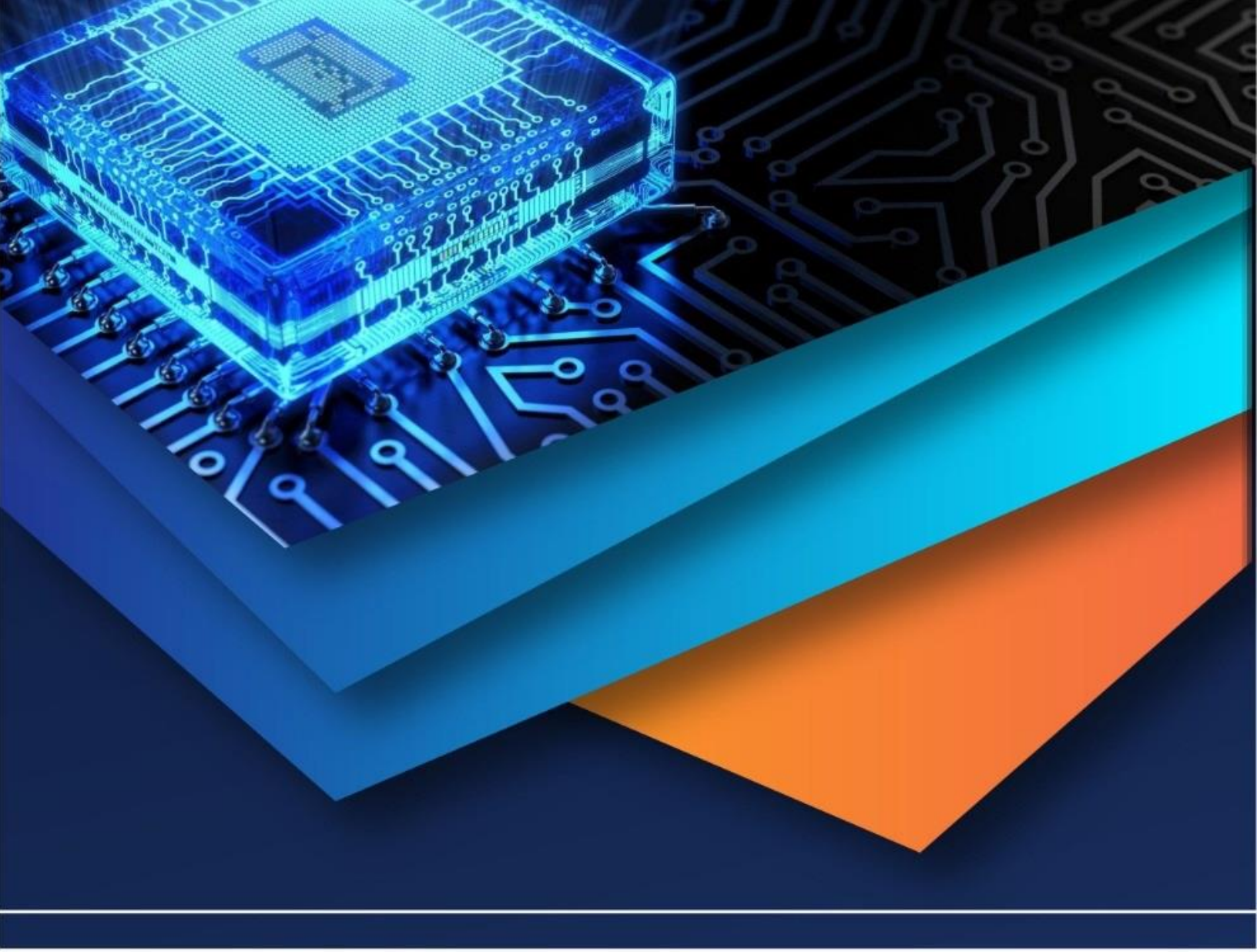

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