

Synthesis and Comparative study of Glass Fibre Reinforced Polyester and their Composites based on Punnal oil

T. J. Sasikala¹, A. Malar Retna^{*2}

Department of Chemistry, Scott Christian College (Autonomous), Nagercoil-3, Tamilnadu, India
malarscott@gmail.com

ABSTRACT

Punnal oil is obtained from the seed of the *Calophyllum inophyllum* tree. The advantages of this oil are low cost, readily available, less toxic etc that can be used for the synthesis of polyesters. Punnal oil based biopolyester resin was synthesised by reacting punnal oil with peroxyacetic acid and hydrogen peroxide followed by acrylation with acrylic acid. The obtained polyester resin was cured with styrene in the presence of benzoyl peroxide. The glass fibre reinforced polyester composites were synthesised using punnal oil based biopolyester resin with glass fibre of varying compositions. The spectral studies such as FTIR and ¹H 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. The evaluation of ageing performance reveals that the glass fibre reinforced polyester composites showed lower degradation rate than the polyester sheet because glass fibres are non-biodegradable.

Keywords: Polyester, Composites, acrylic acid, glass fibre, punnal oil

I. INTRODUCTION

Polyesters 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 their composites are derived from petroleum feedstocks. As the demand of polymers increases, there is a need of renewable resources as alternate petroleum feedstocks. Vegetable oils are a renewable raw material. The polymers synthesised from vegetable oils are 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, stearic acid, oleic acid, linoleic acid and linolenic acid [2]. The unsaturation present in punnal oil are responsible for the 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 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 polyesters based on punnal oil.

The present work deals with the synthesis and comparative study 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), acrylic acid (Sigma-Aldrich), triethyl amine (Sigma-

Aldrich), triethylene glycol dimethacrylate (Sigma-Aldrich), benzoyl peroxide (Sigma-Aldrich) and dimethyl aniline (Sigma-Aldrich) were used without further purification. Glass fibres were procured from local sources

B. Synthesis of glass fibre reinforced polyester and their composites

Punnal oil (1 M) was placed in a 500 ml three neck flask equipped with reflux condenser containing the required amount of acetic acid (0.5 M). Then 30% hydrogen peroxide 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 then washed with warm water and then extracted with ether. The synthesised epoxidised punnal oil was acrylated with acrylic acid and triethyl amine. The mixture was heated to 80°C for 1 h to yield acrylated epoxidised punnal oil (AEPO). The polyester and their composites were prepared by reacting acrylated epoxidised punnal oil, triethylene glycol dimethacrylate, styrene (monomer), benzoyl peroxide (initiator) and dimethyl aniline (accelerator) with glass fibre of varying compositions (5, 10 and 15wt. %). The cast was cured in vacuum oven at 80°C for 6 h. The obtained polyester sheet was coded as POAC. The 5%, 10% and 15% glass fibre composites were coded as POAGF5, POAGF10 and POAGF15.

C. Physico-chemical properties

The physico-chemical properties such as saponification value, acid value, iodine value, viscosity and specific gravity were determined using standard methods. Fourier transform infrared spectral analyses (FTIR) were carried out by KBr pellet method using Shimadzu FTIR-8400S spectrophotometer. ¹H NMR spectra were recorded using CDCl₃ with tetramethyl silane 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 [7],

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

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 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.

F. Scanning electron microscope analysis

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

G. Soil burial degradation test

The polyester 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 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 [8].

H. 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 [9].

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 μ l 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. 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,

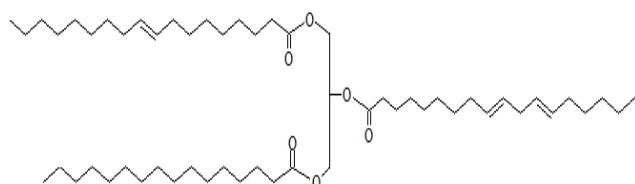


Fig. 1 Triglyceride structure of punnal oil

In the present study, the reduction in iodine value indicates the oxidation of double bonds during epoxidation [10]. 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 [11]. This may also be caused due to the change in molecular weight, polarity and intermolecular forces [12]. The decrease in iodine value in acrylated epoxidised punnal oil reveals the consumption of epoxy groups as a result of the acrylation process. On the other hand, the addition of acrylate groups to the epoxy chain results

in high molecular weight and high viscosity compared to that of the punnal oil.

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

Properties	Punnal oil	Epoxidised punnal oil	Acrylated epoxidised punnal oil
Colour	Dark green	Pale yellow	Yellowish brown
Specific gravity	0.91	1.19	0.99
Acid value	35	-	-
Saponification value	182	-	-
Iodine value	71	48	44
Viscosity	0.03	0.04	0.05
Molecular weight	860	900	1108

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 $-\text{CH}_2$ 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 $-\text{C}-\text{H}$ bending of unsaturated methylene groups and the peak at 1115 cm^{-1} is for $-\text{C}-\text{O}$ stretching of ester group. A band at 725 cm^{-1} is due to the stretching vibration of $-\text{CH}-\text{CH}-$ groups.

The disappearance of 3006 cm^{-1} band in epoxidised punnal oil shows $-\text{C}=\text{C}-$ 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 [13].

The FTIR spectrum of acrylated epoxidised punnal oil indicates that the peak visible at 3500 cm^{-1} is attributed to hydroxyl group which indicate the opening of epoxide. The peak at 1735 cm^{-1} corresponds to the ester carbonyl peak of the acrylated compound. The peak at 1630 cm^{-1} is attributed to the stretching vibration of $-\text{C}=\text{C}-$. The signal at 985 cm^{-1} attributes to the $-\text{CH}=\text{CH}_2$ group.

The FTIR spectra of acrylated polyester sheet is almost same as that of the acrylated epoxidised punnal oil but the absence of peak at 1630 cm^{-1} indicates the absence of double bond. The absence of double bond is due to the addition of styrene. The ester carbonyl group appeared at 1743 cm^{-1} present in punnal oil is shifted to 1735 cm^{-1} in acrylated epoxidised punnal oil and 1728 cm^{-1} in acrylated polyester sheet. The -OH stretch of carbonyl group in the acrylated epoxidised punnal oil at 3500 cm^{-1} is shifted to 2924 cm^{-1} indicates the extra hydrogen bonding interaction with the hydroxyl group present in the acrylated polyester sheet. The following figure shows the FTIR spectrum of punnal oil, epoxidised punnal oil, acrylated epoxidised punnal oil and the polyester sheet.

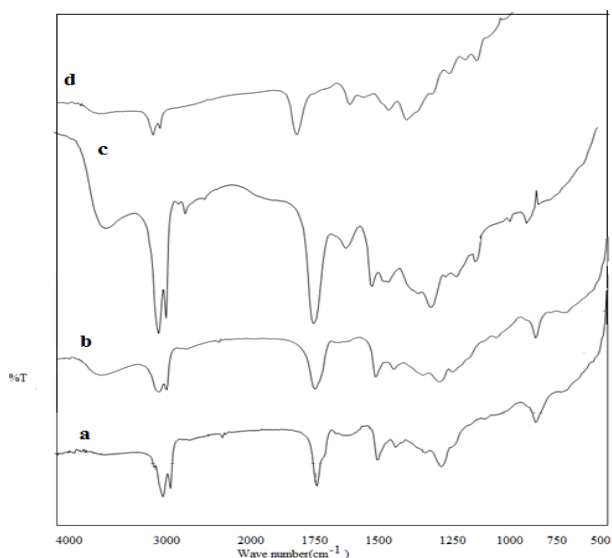


Fig. 2 FTIR spectrum of punnal oil (a), epoxidised punnal oil (b), acrylated epoxidised punnal oil (c), polyester sheet (d)

C. ^1H NMR spectral analysis

The ^1H NMR spectral analysis of punnal oil is shown in Fig. 3. 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 ($\text{-CH}_2\text{-}$) [10]. 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. 4. 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 acrylated epoxidised punnal oil shows the epoxy groups signal around $3\ \delta$ and also the peak at $5.3 - 5.6\ \delta$ which indicates an incomplete acrylation. Peak after acrylation at $5.8 - 6.7\ \delta$ indicate the three protons of the acrylate esters. The peak at $0.95 - 2.3\ \delta$ is attributed by aliphatic side chain.

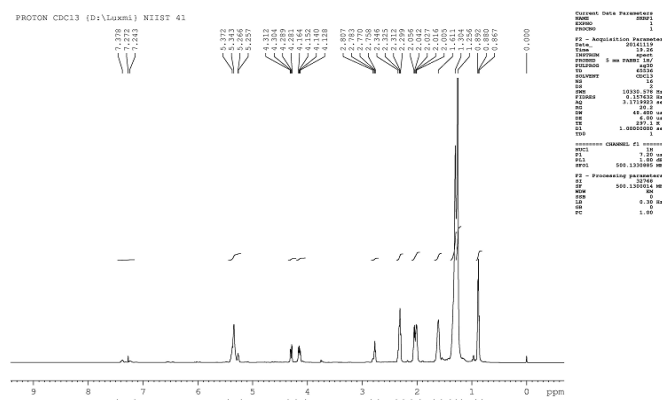


Fig. 3 ^1H NMR spectra of punnal oil

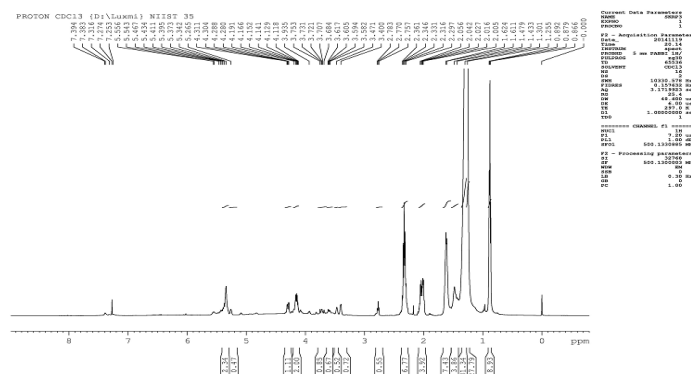


Fig. 4 ^1H NMR spectra of epoxidised punnal oil

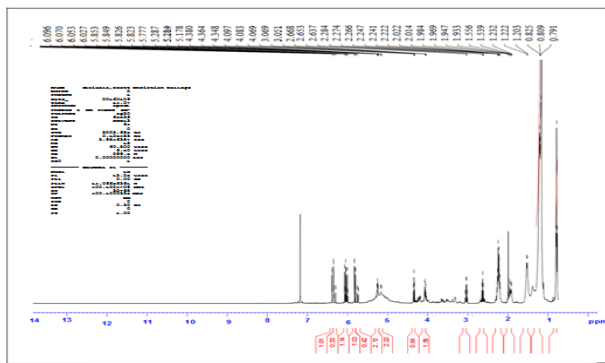


Fig. 5 ¹H NMR spectra of acrylated epoxidised punnal oil

D. Crosslink density

In the present study, the swelling coefficient is maximum in neat polyester sheet. It reveals that the 15% glass 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. 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 acrylate 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 ($\times 10^{-3}$)	Molecular weight between crosslinks (mole^{-1})
POAC	1.28	1.1	1.46	684.93
POAGF5	1.29	1.07	1.49	671.14
POAGF10	1.3	1.05	1.49	671.14
POAGF15	1.31	1.03	1.53	653.59

E. Mechanical properties

The glass fibre reinforced polyester composites shows higher tensile strength and Young's modulus than the neat acrylated 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 3 Mechanical properties of polyester and their composites

Polyester and their composites	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Shore-A hardness
POAC	10.5	148	7.09	37
POAGF5	14.2	139	10.22	52
POAGF10	17.8	135	13.19	58
POAGF15	19.3	134	14.4	59

F. 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 possess lower degradation than the neat polyester sheet because glass fibres are non-biodegradable.

Table 4 Weight loss of polyester and their composites under soil burial test

Polyester and their composites	Weight loss (%)
POAC	35.59
POAGF5	34.29
POAGF10	33.24
POAGF15	38

G. Scanning electron microscope analysis

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 pin holes are observed in polymer sheets indicated that the polyester surface is attacked by the microorganism under soil environment.

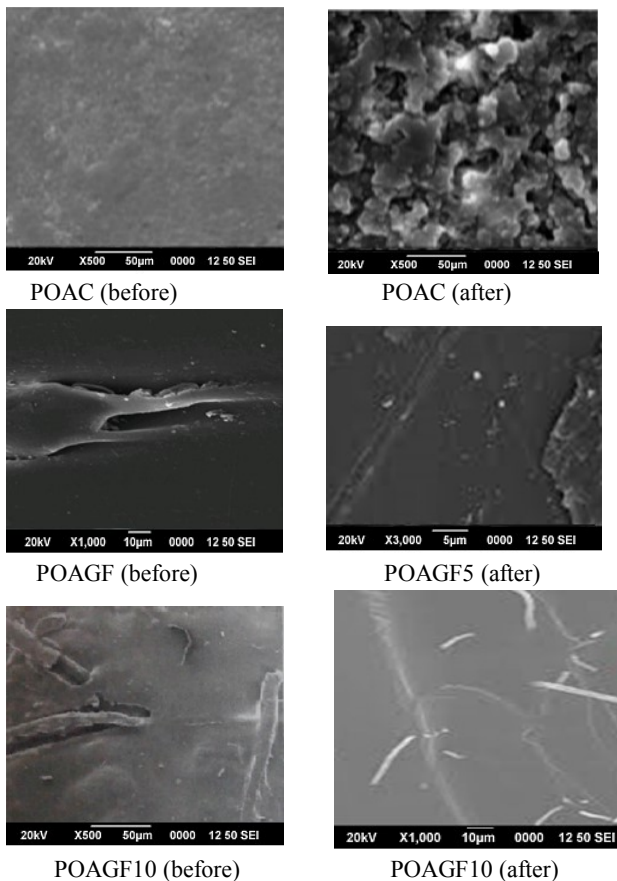


Fig. 6 SEM images for the acrylated polyester composites with glass fibres before and after soil burial test

H. 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 polyester 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 possess lower degradation. This may be attributed to the steric hindrance of the acrylate group present in the polyester composites.

Table 5 Inhibition zone (mm) of polyester and their composites

Polyesters and their composites	Microorganisms			
	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>	<i>Klebsiella pneumoniae</i>	<i>Bacillus subtilis</i>
POAC	8	8	8	8

POAGF5	8	8	8	8
POAGF10	8	8	9	8
POAGF15	8	8	8	8

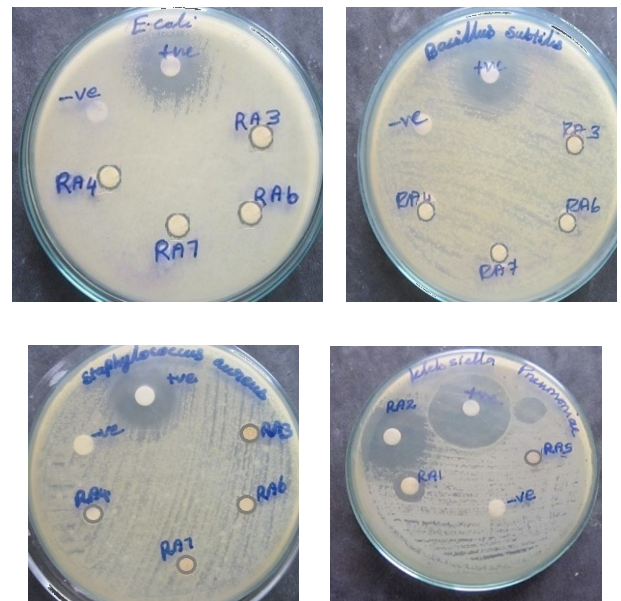


Fig. 7 Culture plates of polyester and their composites with glass fibres using *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Klebsiella pneumonia*.

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°C. The acrylated epoxidised punnal oil were synthesised from epoxidised punnal oil. The synthesised resins were confirmed by FTIR and ¹H NMR spectral analysis. 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.

V. REFERENCES

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