



# Developmental Studies on Novel Biodegradable Polyester Films from Maravetti Oil

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## ABSTRACT

A unique biodegradable polyester film was made from naturally accessible Maravetti crude (*Hydnocarpus wightianus*), formic acid and 30% hydrogen peroxide, using a step-wise polymerization technique. The polymer was created by reacting resin with styrene. UV, FTIR and NMR spectral studies were carried out to identify the structural characteristics of the polymer product. The biodegradability of the polyester film was investigated using Soil burial test. The thermal deterioration was investigated using TG-DTA analysis at various time intervals. The cross-linking potential of the polymers was determined using DSC analysis. Tensile and impact strengths and other mechanical parameters were assessed. The resultant polymers were found to have acceptable mechanical characteristics and cured quickly.

**Keywords:** Cross-linking; Degradation; Polymer Soil Burial; Styrene.

## 1. INTRODUCTION

Globally, over 6.3 billion plastics are generated, only 9% is recycled, 12% is incinerated and the remaining 79% gets accumulated in natural environment. In the production of plastics, monomers used which are derived from fossil hydrocarbons. Most of the plastics are slow to degrade (Roland *et al.* 2017). Because of increasing prize of petroleum and environmental awareness, researchers are interested in the synthesizing of polymers from renewable resources of plants. Plant oils are considered as building blocks of polymers due to their low cost, availability and eco-friendliness (Barnes *et al.* 2009). Active functional groups such as double bonds, ester groups and hydroxyl groups, on the triglyceride chain make the polymer to be chemically modified and to synthesis polymers with desirable properties (Wang *et al.* 2008). *Hydnocarpus* is a kind of *Hydnocarpus wightiana* seed oil, also known as chaulmoogra oil or Maravetti oil, comes from the seeds of the *Wightiana* plant. As a paste suspended in gum or as an emulsion, it has been used in medicine as an antibiotic for the treatment of many skin diseases and leprosy (Nortan, 1994). The oil is unusual in not being made up of straight chain fatty acids but acids with a cyclic group at the end of the chain.

## 2. EXPERIMENTAL METHODS

### 2.1 Materials and Methods

The thermal deterioration was investigated using TG-DTA analysis at various time intervals. The cross-linking potential of the polymers was determined using

DSC analysis. Tensile and impact strength were assessed, as well as other mechanical parameters. The resultant polymers have acceptable mechanical characteristics and cure quickly. In the curing procedure, benzoyl peroxide was used as a radical initiator and N, N-Dimethyl aniline was used as an accelerator.

### 2.2 Synthesis of *Hydnocarpus wightianus* Oil Polyol

Three-necked reagent flask with a water condenser was filled with 100 g of *Hydnocarpus wightianus* oil. 100 mL of formic acid (97%) and 55 mL of hydrogen peroxide (30%) were added to the flask, which were vigorously stirred for about 16 h. Externally, the temperature was maintained below 400 °C. The emulsion was then put into a separating funnel and removed using ether. The polyol resin from *Hydnocarpus wightianus* oil was obtained by drying the ether layer over anhydrous sodium sulphate.

### 2.3 Synthesis of Polyesters

The polyol resin product was heated in a three-necked reagent flask by adding maleic anhydride in 1:2 ratio at 70 °C. Morpholine was used as a catalyst. After 2 hours, a viscous liquid with golden yellow colour was formed, indicating the formation of oligomerized *Hydnocarpus wightianus* oil fumarate resin.

## 2.4 Synthesis of Polyester Film from Oligomerized *Hydnocarpus wightianus* Oil Fumarate Resin and Co-monomer Styrene

Utilizing the homopolymer (Oligomerized *Hydnocarpus wightianus* oil fumarate resin) and styrene at various concentrations, aliphatic polyester was synthesized using a free radical addition polymerization process with benzoyl peroxide as catalyst and dimethyl aniline as accelerator. At room temperature, the viscous liquid was poured into a glass mould covered with silicon oil. From homopolymer and styrene, polyester thin films of various concentrations such as 1:0.5, 1:1 and 1:2 were synthesized. Finally, the yellow polyester sheets were taken out of the mould.

## 2.5 Characterisation of Resins

The UV and FTIR analyses were carried out for *Hydnocarpus wightianus* oil, hydroxylated *Hydnocarpus wightianus* oil and also the resin. The  $^1\text{H-NMR}$  spectra

were obtained for epoxy resin, polyols and pre-polymers dissolved in  $\text{CDCl}_3$  by recording using BRUKER AVANCE III, 400 MHz FT NMR SPECTROPHOTOMETER. Cured samples were checked to see the degree of curing.

## 3. RESULTS AND DISCUSSION

### 3.1 FTIR Analysis

The FTIR spectra of *Hydnocarpus wightianus* oil, hydroxylated *Hydnocarpus wightianus* oil and the resins were recorded between  $500$  to  $4000\text{ cm}^{-1}$  (Rohan *et al.* 2018). In hydroxylated MVO, the FTIR spectra showed a strong absorption band at  $3522.74\text{ cm}^{-1}$ , due to the presence of free-OH group in the molecule, which is absent in MVO. A strong absorbance band in  $1734.85\text{ cm}^{-1}$  was due to the presence of  $\text{C}=\text{O}$  in esters. A strong band in  $2927.68\text{ cm}^{-1}$  was due to the symmetrical  $-\text{C}-\text{H}$  bond in  $-\text{CH}_2-$ group of the side chain.

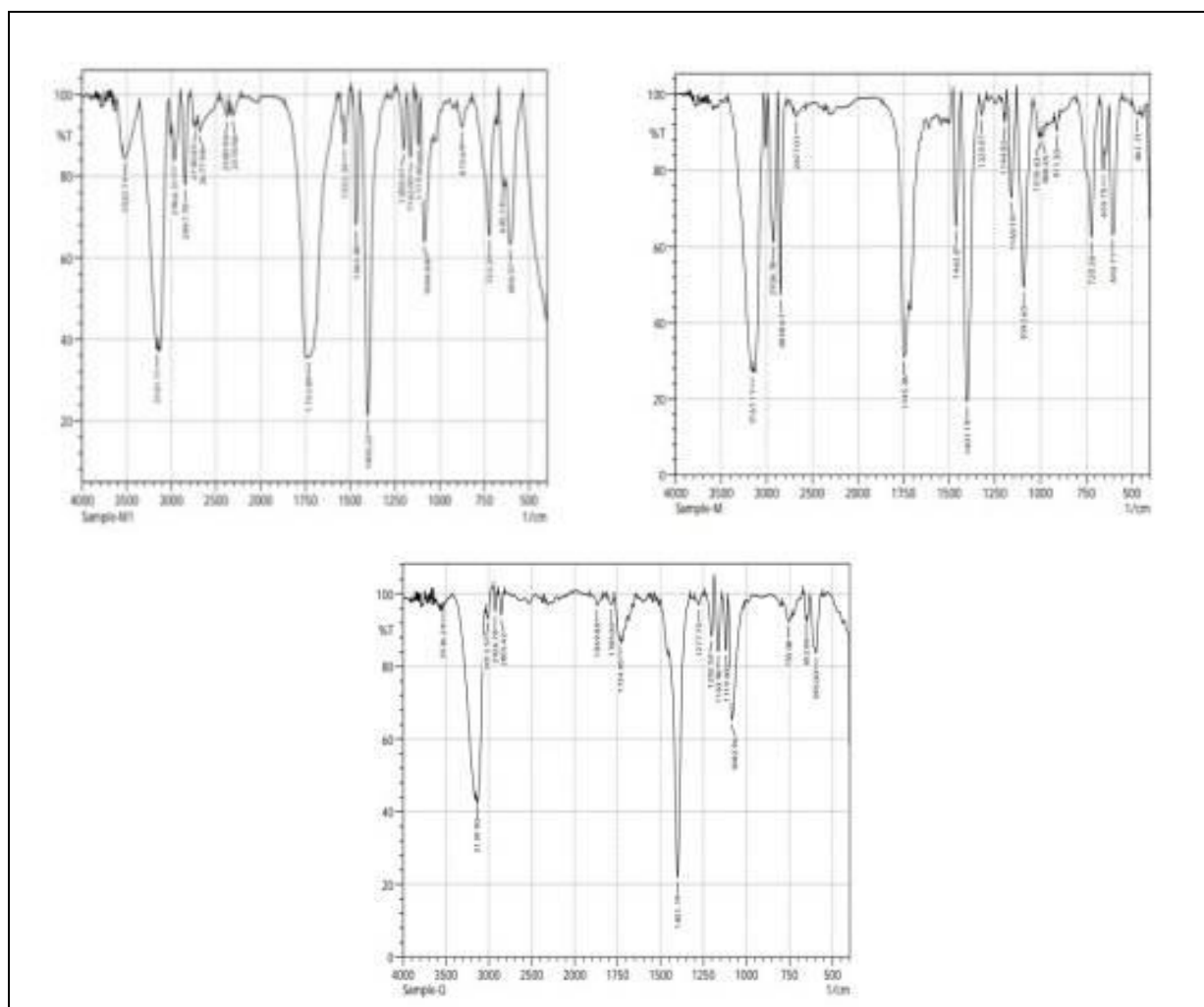


Fig. 1: FTIR spectra of MVO, Hydroxylated MVO and MVO Resin

**Table 1. FT-IR - Probable assignments**

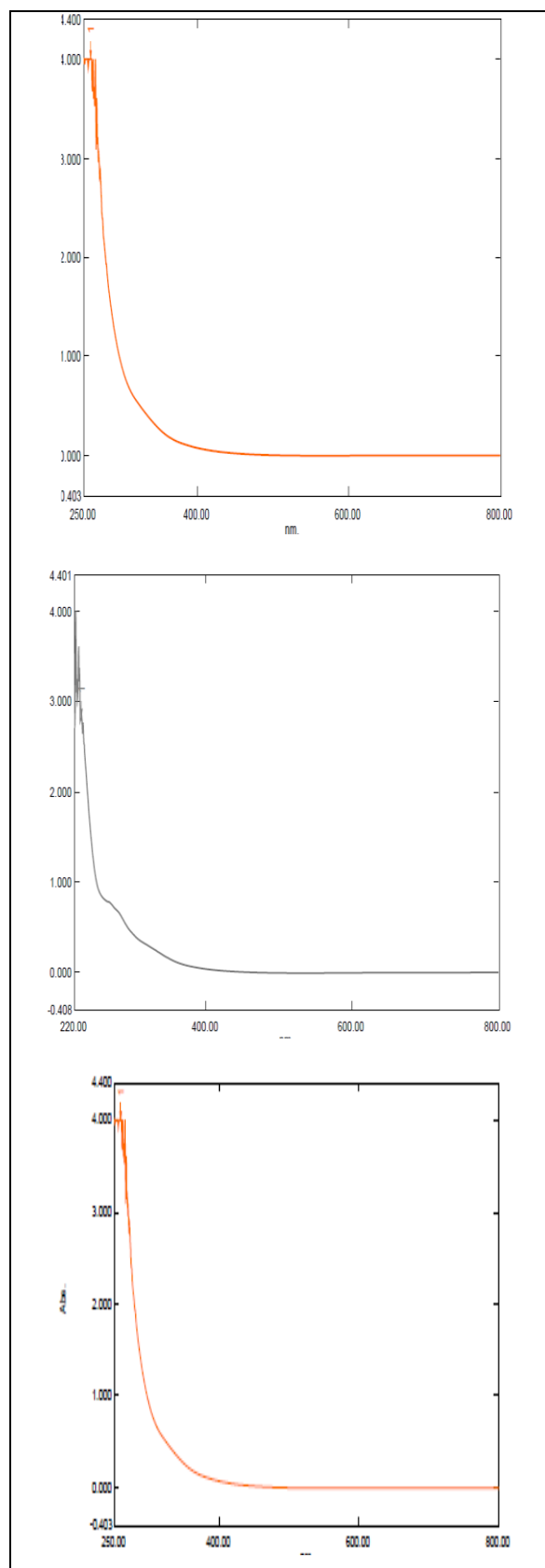
Probable assignment	MVO (cm <sup>-1</sup> )	Hydroxylated MVO (cm <sup>-1</sup> )	MVO Resin (cm <sup>-1</sup> )
-CH <sub>2</sub> Group	2927.68	2966.31	2926.78
-C- O Group in GM	2848.67	2847.7	-
C=O in esters	1745.46	1733.89	1734.85
Terminal CH <sub>3</sub> Groups	1 194.82	1200.61	1202.53
Carboxyl Group of acids	1160.10	1163	1163.96
-CH-CH- Stretching	1092.60	1084.88	1082.96
CH <sub>2</sub> -sequences of the aliphatic chains	720.36	722.29	755.08
-OH Group	3161.11	3522.74	3536.24

### 3.2 UV Analysis

The ultraviolet spectra of the resin, hydroxylated triglyceride oil and resins were studied (220 nm - 800 nm). The electronic absorption band in the resin sample was at 239 nm. When compared to the original oil, the hydroxylated resin has shown a blue shift, which was due to the hydroxyl group being substituted at the unsaturated moiety. The replacement of the hydroxyl group at the olefinic double bond, as well as geometric distortion, caused a drop in absorbance as compared to parent oil. The substitution of the fumarate group caused a significant red shift in electronic absorption in the resin, as well as a distortion in the molecule's shape owing to the insertion of the fumarate group (Priya *et al.* 2015).

### 3.3 H<sup>1</sup>NMR spectral studies

The H<sup>1</sup>NMR spectra recorded from the chosen resin are shown in Fig. 3. The peaks in H<sup>1</sup>NMR for quantitating unsaturated fatty acids are those of the terminal methyl protons (0.85-0.89 ppm), olefinic protons (5.4-5.6 ppm), methylene -CH<sub>2</sub>- (1.1-1.6 ppm), protons attached to allylic carbon (2.01-2.05 ppm) and protons attached to bis-allylic carbons (2.2 - 2.7 ppm). The corresponding olefinic protons peak in the hydrolysis products have almost disappeared, revealing that the double bonds in resin were replaced by the hydroxyl group. This peak was shifted to 8.1 ppm in the chosen resin due to the de-shielding effect of hydroxyl and carboxylate ester linkages (Shakina *et al.* 2012).



**Fig. 2: UV spectra of MVO, Hydroxylated MVO and MVO Resin**

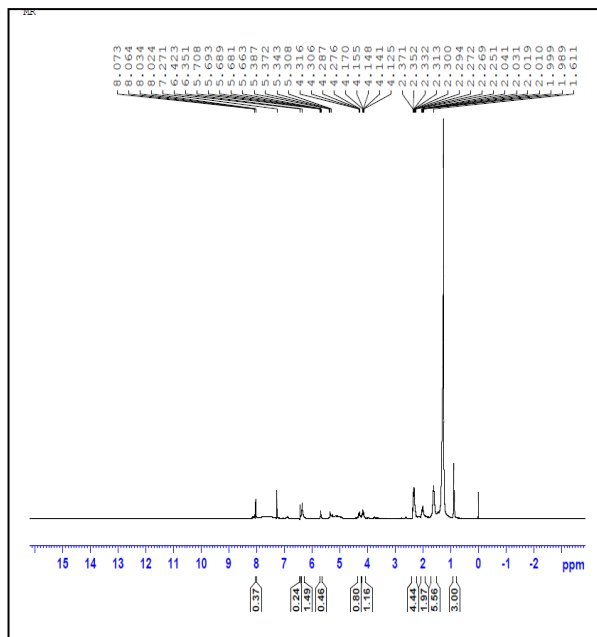


Fig. 3: NMR Spectrum of MVO Resin

### 3.4 XRD Pattern of Polymer Composite

From XRD analysis, average crystallite size was found to be 7.02 nm. The peak was narrow; hence, the polymer composite was found to be crystalline (Birendra Pratap Singh *et al.* 2012).

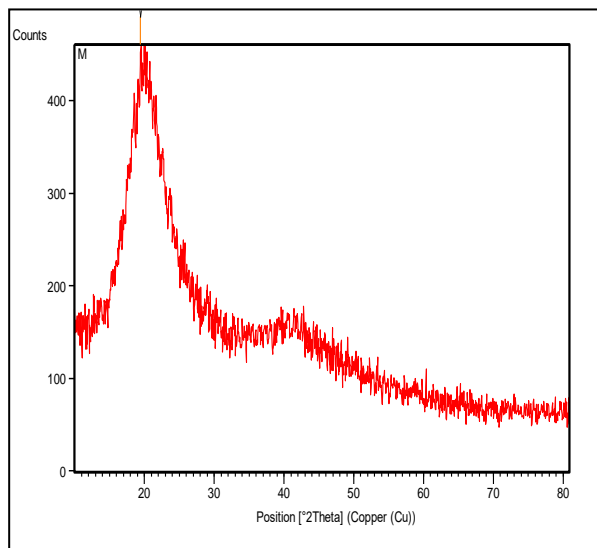


Fig. 4: XRD pattern of MV Polymer

### 3.5 Thermal Analysis

The degree of cross-linking influenced the properties of the polymer, which was associated with the monomer's functionality. The thermosetting resin's curing outcomes may be checked using DSC. The peak temperature for the sample with cross-linker was 527.19 °C, indicating that this resin will cure the fastest at this temperature. For this

resin, the start of the cure peak was 412 °C, and the total heat of the reaction was 3853 J/g (Li *et al.* 2017).

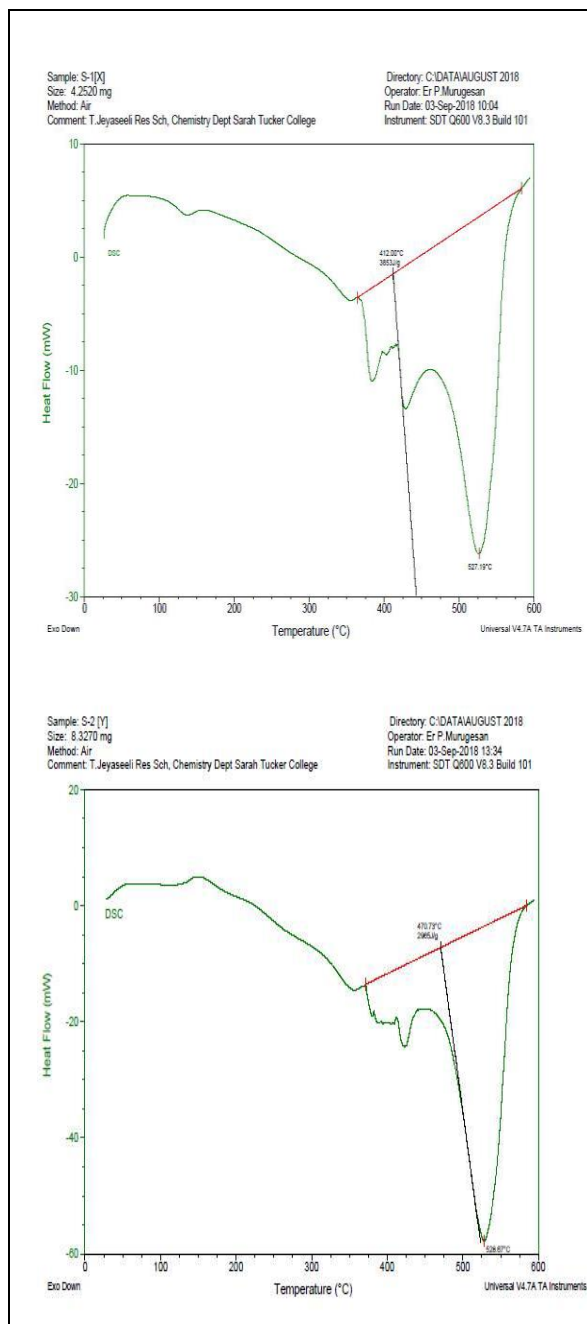


Fig. 5: DSC Thermograms of Polymer composite with and without cross-linker

The peak for the chosen material without cross linker is 527.8 °C, indicating that the fastest cure for the resin will occur at this temperature. The onset of the cure peak for this resin was 471.64 °C and the total heat of the reaction was 2964 J/g. It can be seen that resins with cross-linker released more heat during the curing process, which indicate more double bonds inside the resin. TGA for resins was conducted to identify their degradation characteristics.

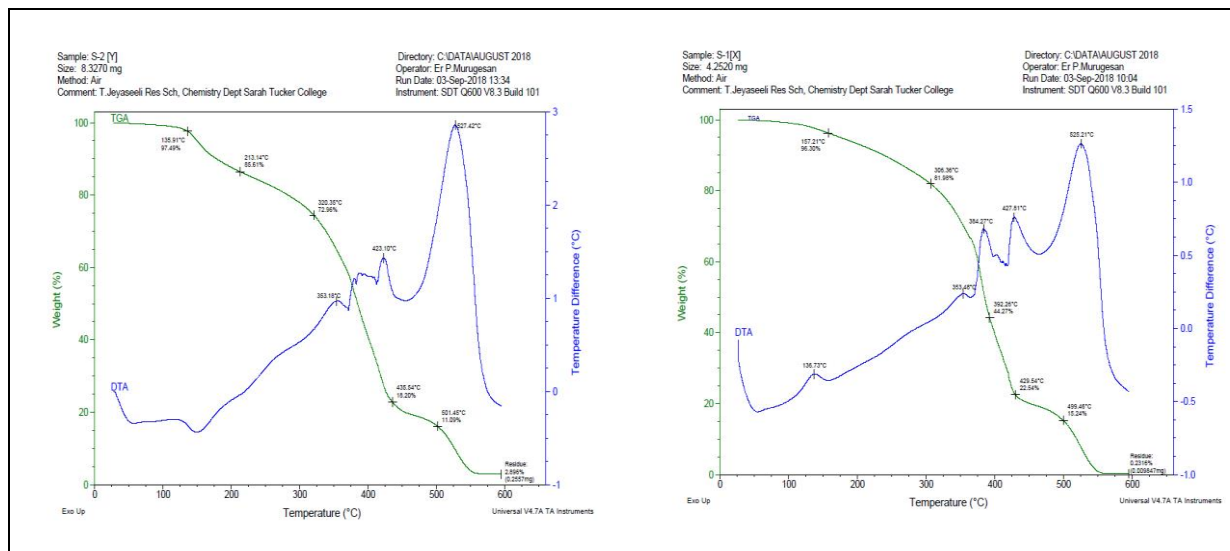


Fig. 6: TGA, DTA Thermograms of the sample with and without cross-linker

The resin with cross-linker was stable up to 150 °C with no significant weight loss. The initial weight loss was observed at 157.21 °C, indicating the loss of volatiles and moistures. Significant weight loss began at 306.36 °C due to the degradation of the resin. When the temperature reached 499.46 °C, the weight loss was recorded. The maximum rate of decomposition occurred at 525.21 °C. The residual mass was around 0.009847 mg. The resin without cross-linker was stable upto 130 °C with no significant weight loss; the initial weight loss was observed at 135.91 °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 511.25 °C, weight reduction was found. The maximum rate of decomposition was recorded at 528.22 °C; the residual mass was around 0.256 mg. It was clear that resins with cross-linkages were more resistive to temperature; this was due to the fact that the cross-

linkages increased the cross-linking network of the oil. The percentage of residue was somewhat lower than resins without cross linkage (Sathishkumar *et al.* 2013).

### 3.6 FTIR-ATR Analysis

The samples were analysed over the range of 400-4000  $\text{cm}^{-1}$  with a spectrum resolution of 4  $\text{cm}^{-1}$ . All spectra were averaged over 64 scans. The cross-linking was confirmed through the ATIR spectral studies.

The strong peaks observed at 1737.76  $\text{cm}^{-1}$  and 1754.23  $\text{cm}^{-1}$  indicated that the surfaces of the sample with and without cross-linker were comprised predominantly with ester linkages, respectively (Shakina *et al.* 2014).

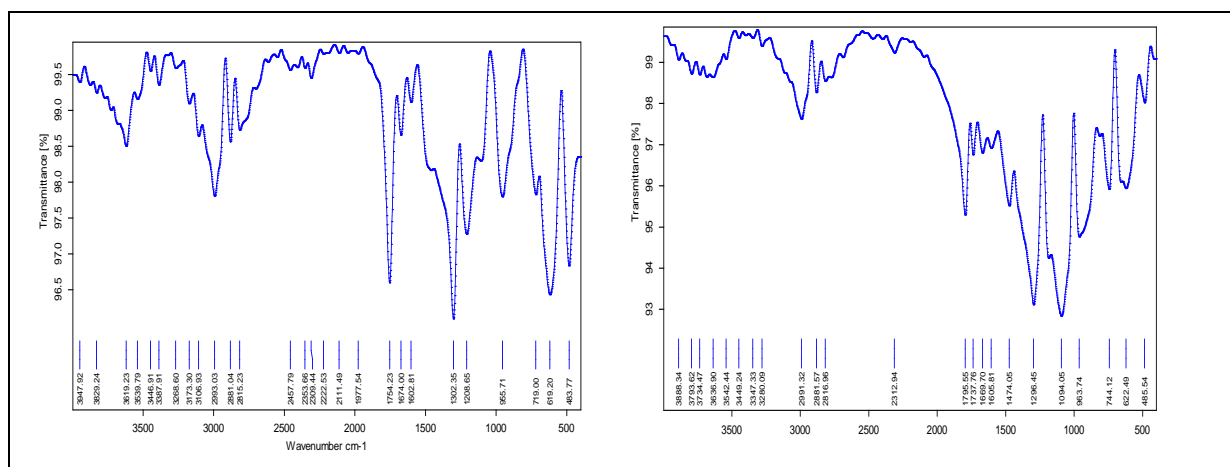
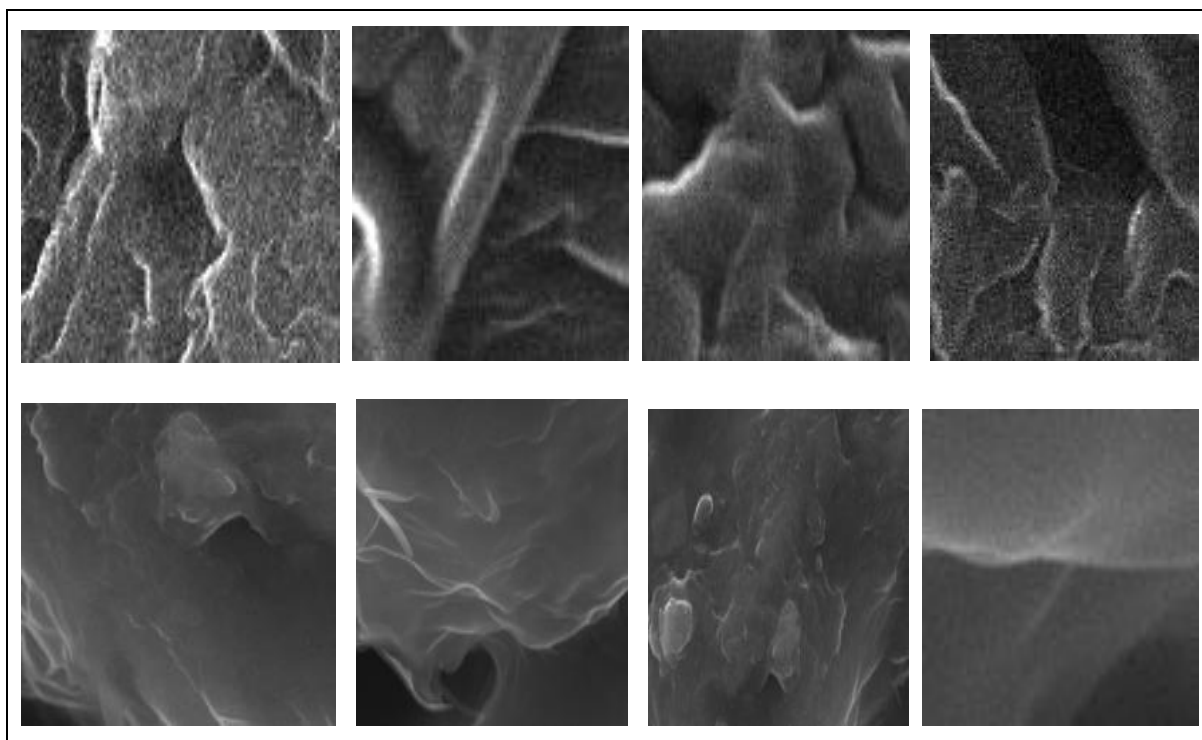


Fig. 7: ATR spectra of Polymer composite with and without cross-linker



**Fig. 8: SEM Photographs of Polymer composite with and without cross linker**

### 3.7 SEM Analysis

SEM micrographs have revealed that the composite without cross-linker has stronger bonding than the composite with cross-linker. Obviously, the virtually total absence of holes surrounding the matrix and the lack of bio-flour breaking during tensile fracture, offered strong interfacial adhesion and excellent wetting (Prabha *et al.* 2015).

### 3.8 Microbial Studies

Antibacterial activities were found in the sample by Agar well-diffusion method using bacterial strains *Actinomyces israelii* and *Aeromonas hydrophilla*. As prepared bio-polyesters showed potential anti-bacterial characteristics against micro-organisms. Anti-fungals present in the sample were detected by Agar well-diffusion method using fungal strain *Aspergillus niger*. The newly prepared bio-polyesters has shown potential antifungal activity against micro-organisms (Shakina *et al.* 2012).

## 4. CONCLUSION

A biodegradable polyester film was made from *Hydnocarpus wightianus*, formic acid and 30% hydrogen peroxide, using a step-wise polymerization technique. UV, FTIR and NMR spectral studies were carried out to identify the structural characteristics of the polymer product. The biodegradability of the polyester film was investigated using Soil burial test and the thermal deterioration was investigated using TG-DTA analysis. The cross-linking potential of the polymers was determined using DSC analysis. Tensile and impact strengths and other mechanical parameters

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## CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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