



## SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOR OF THERMOSETTING POLYESTERS FROM BIO-DEGRADABLE PLANT OIL

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### Abstract

Thermal Analysis (TA) is an essential analytical technique in the polymer research. In polymer science Thermal Characterization of Polymers is an extreme analysis and brief assessment of the application of thermal analysis this technique is used for evaluation of comparative thermal stability of different polymers. The following materials were synthesized from Odal, Chennakai, Neem and Thennamarakudi oils. They were synthesized and characterized by UV-Visible and IR Spectra. NMR spectral studies carried out to identify the nature of the polymer formed. SEM analysis confirmed that the polymer was biodegradable in nature. The thermal degradation at different time intervals was analyzed by TG-DTA analysis. TGA analysis was conducted to identify the thermal degradation patterns and to determine product performance. The cross-linking ability of the resins was checked by DSC analysis.

**Keywords:** Polymer, Cross- linking, Biodegradability, Thermal analysis, Degradation,

### Introduction

Researchers are attracted towards polymeric materials due to economic and environmental concerns. The utilization of renewable resources for the production of polymeric materials can reduce the plastic pollution.<sup>i</sup> Vegetable oils are considered as good starting materials for polymer production. Due to ready availability, their low cost and versatile applications, vegetable oils are encouraging renewable resources for polymers. The plant oils are composed of triglycerides which can be modified using the reactivity of the functional groups in their structure.<sup>ii</sup> Synthesis of resins from plant oil involves chemical modifications of unsaturated oils to undergo crosslinking. This cross linking was responsible for good

mechanical and thermal properties of the resins.<sup>iii</sup>

Synthesis of polymers from renewable resources of plants is attractive because of increasing price of petroleum.<sup>iv</sup> Biodegradable and inexpensive polymers are obtained from low cost and readily available raw materials.<sup>v</sup> Plant oil is a biodegradable triglyceride with unsaturation.<sup>vi</sup> It has unsaturated double bonds which are easily reactive and induce functional groups including epoxy, hydroxyl and other more active double bonds. The chemical modification of the triglyceride of plant oil is preferred, enabling the synthesis of oligomeric triglyceride resin in the way to target polymeric materials. The chemical transformation of the non-edible oil triglyceride affords a wide variety of monomers for the synthesis cross linked structural polymers. The modification of triglycerides can be performed using the reactivity of the functional groups in their structure.

## **Experimental**

### **Materials**

Odal, Chennakai, Neem and Thennamarakudi oils were purchased from local market, Formic acid (97%) (Rankem), Hydrogen peroxide (30%) (Rankem) were used in the first step fractionalization. Maleic anhydride (Rankem) and Morpholine (Rankem). Benzoyl peroxide (Rankem) was used as a radical initiator and N, N-Dimethyl aniline (Rankem) was used as accelerator in the curing process. Styrene (Rankem) was used as a vinyl co-monomer.

### **Synthesis of plant oil polyol**

100 g of Odal / Chennakai / Neem / Thennamarakudi oil was taken in a three necked flask fitted with condenser and thermometer. 100 ml of 97% formic acid and 55 ml of 30% hydrogen peroxide was added and the reaction mixture was vigorously stirred over 16h. Ice water bath was used externally to keep the temperature below 40°C. The resulting emulsion was poured into a separating funnel and extracted with ether. The ether layer was dried over anhydrous sodium sulphate and the resulting product was polyol resin from Odal / Chennakai / Neem / Thennamarakudi oil.

### **Synthesis of polyesters**

The polyol resin was heated in a three necked flask and maleic anhydride was added in 1:2 ratio at 70°C. Morpholine was used as a catalyst. After 2 hours a golden yellow viscous liquid formed it indicates the formation of oligomerised Odal / Chennakai / Neem / Thennamarakudi oil fumarate resin.

### **Synthesis of polyester film from oligomerised Odal / Chennakai / Neem / Thennamarakudi oil fumarate resin and co-monomer styrene**

Synthesis of aliphatic polyester was carried out by free radical addition polymerization reaction by using the homopolymer (oligomerised Odal / Chennakai / Neem / Thennamarakudi oil fumarate resin) and styrene at different concentration using benzoylperoxide as catalyst and Dimethylaniline as accelerator. The viscous liquid is transferred in to glass mould coated with silicon oil at room temperature. The polyester thin films were synthesized from homopolymer and styrene. Finally the yellow colored polyesters sheets were removed from the mould.

### **Characterization of polymer**

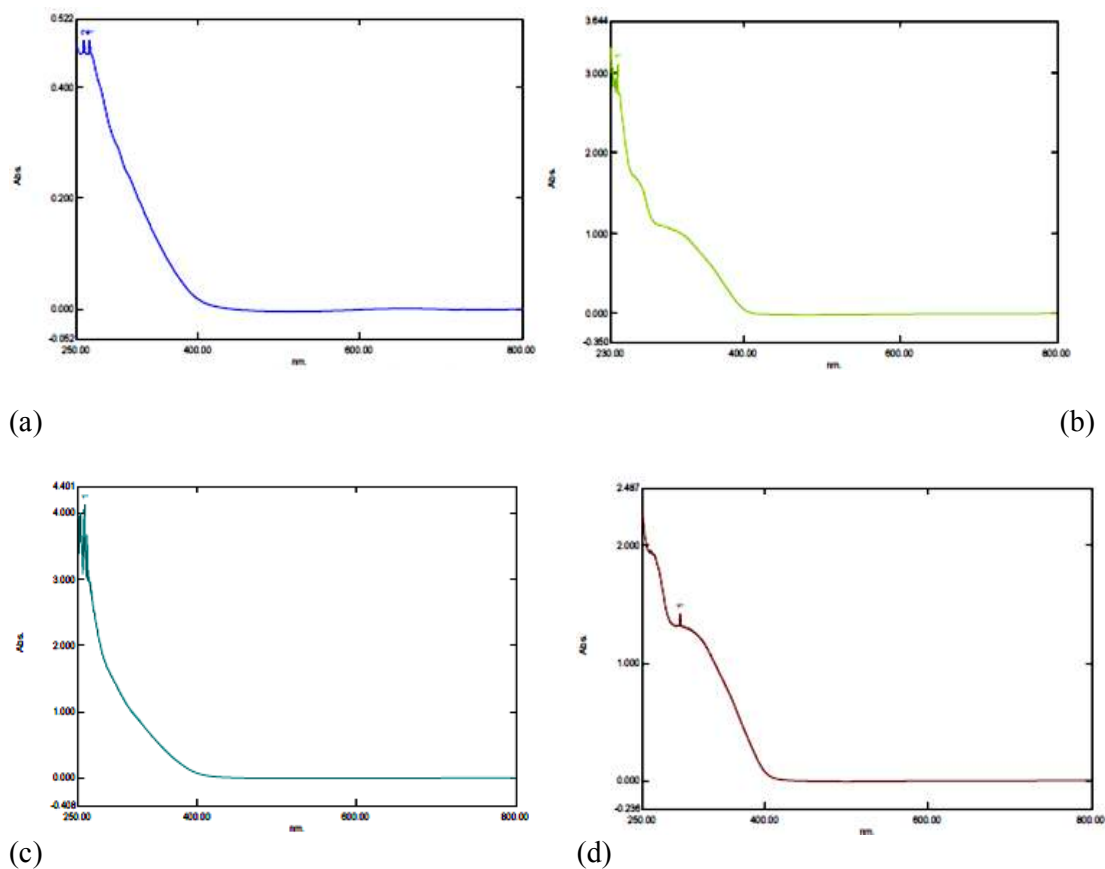
Double-beam UV/visible spectrometer is used to verify the characteristic absorption of the polymer composites. Fourier transform infrared (FTIR) spectra of polymers were obtained using Shimadzu FT-IR spectrophotometer using KBr pellet at wave-lengths between 4000  $\text{cm}^{-1}$  and 400  $\text{cm}^{-1}$  at 27°C. ATR spectra were obtained using BRUKER Optic GmbH FTIR SPECTROMETER with KBR crystal in the range of 4000  $\text{cm}^{-1}$  – 400  $\text{cm}^{-1}$ . The <sup>1</sup>H-NMR spectra for epoxy resin, polyols and pre-polymers were dissolved in CDCl<sub>3</sub> and recorded using BRUKER AVANCE III, 400 MHz FT NMR SPECTROPHOTOMETER. The

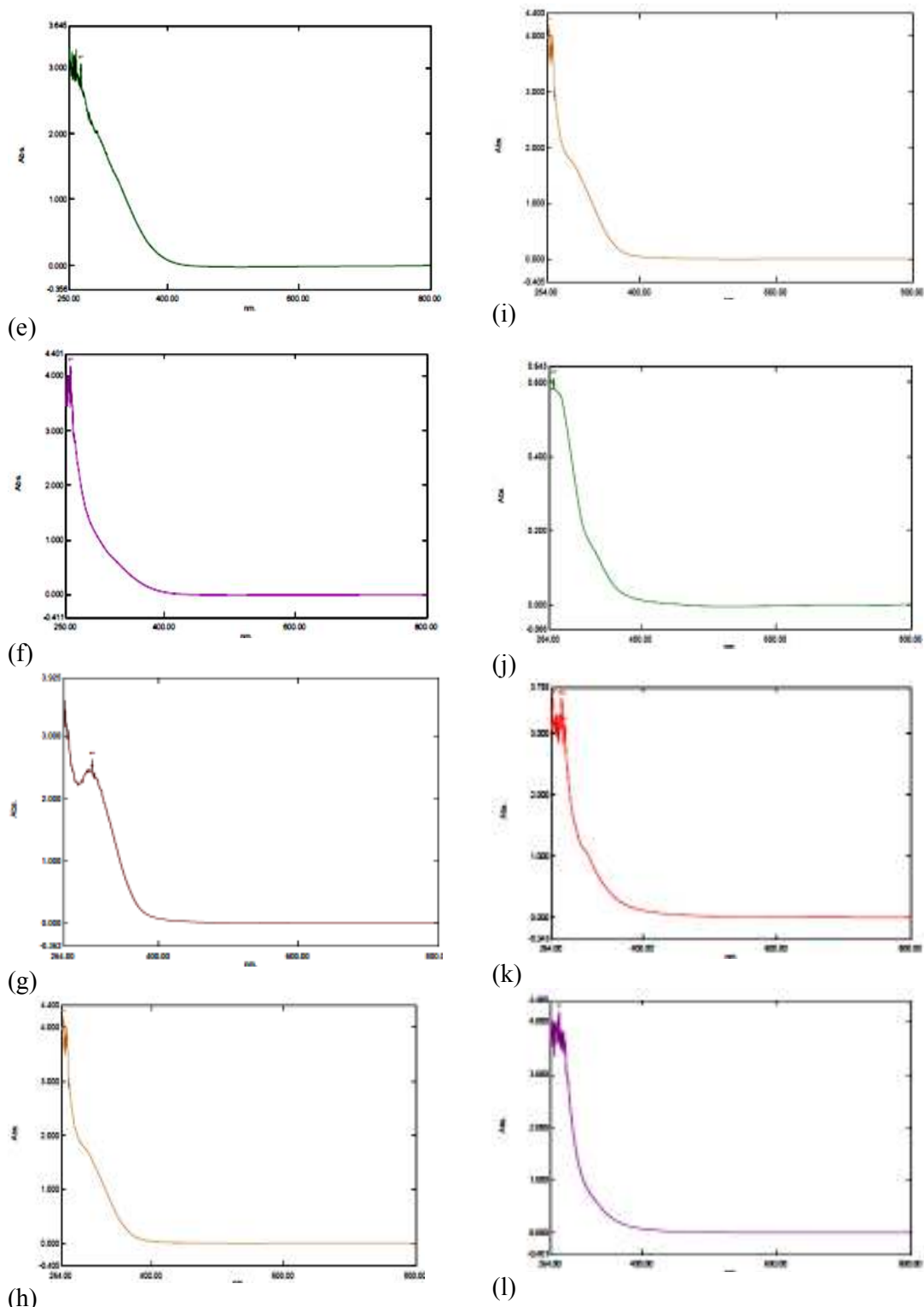
chemical shift in ppm for  $^1\text{H}$  NMR Spectra were obtained relative to TMS as internal reference. TG/DTA thermo grams of the post-polymers were obtained at a scanning speed of  $10^\circ\text{C min}^{-1}$  in the range of  $40^\circ\text{C}$ -  $700^\circ\text{C}$  under the flow of nitrogen gas using PERKIN ELMER, DIAMOND TG/DTA. The SEM analysis of the polymers was obtained using VEGA3TESCAN.

## Result and discussion

### UV Analysis

Figure 1 shows the UV spectra of Odal/ Chennakai/ Neem / Thennamarakudi oil, hydroxylated triglyceride oil resins and O-PTF resins. They have been investigated (230 nm - 800 nm). The oil samples (Odal, Chennakai, Neem and Thennamarakudi) showed an electronic absorption band around 238,295.50,262 and 270.50 nm respectively. The hydroxylated resins exhibited a blue shift when compared with the corresponding parent oil which is attributed to the substitution of hydroxyl group at the unsaturated moiety.<sup>vii</sup>

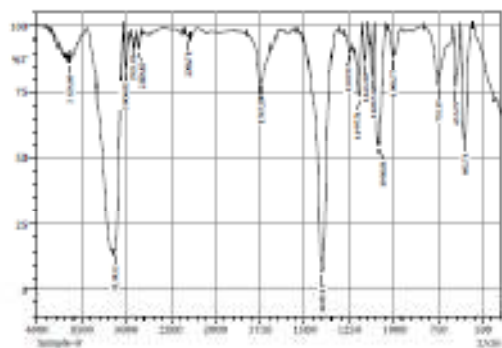




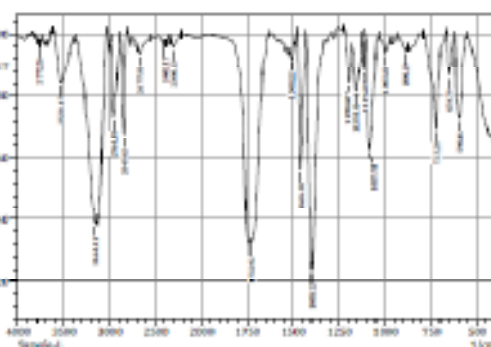
**Figure 1.** UV Spectrum of (a) Odal oil (b) Hydroxylated Odal oil (c) Odal Resin (d) chennakai oil (e) Hydroxylated Chennakai oil (f) Chennakai Resin (g) Neem oil (h) Hydroxylated Neem oil (i)Neem Resin (j) Thennamarakudi oil (k)HydroxylatedThennamarakudi oil (l) Thennamarakudi Resin

**FTIR spectral analysis**

Figure 2 shows the IR spectra of Odal/ Chennakai/ Neem / Thennamarakudi oil, hydroxylated triglyceride oil and resins. They have been investigated between  $500\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ . In hydroxylated triglyceride resins, FT-IR spectra showed a strong absorption band at  $3772.5$ ,  $3770.58$ ,  $3565.17$  and  $3172.68\text{ cm}^{-1}$  respectively, due to the presence of free –OH group in the molecule. The corresponding peaks are completely reduced in the resins indicates the entire OH group get substituted.<sup>viii</sup>



(a)

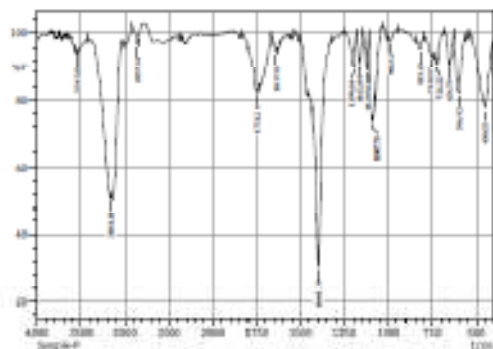


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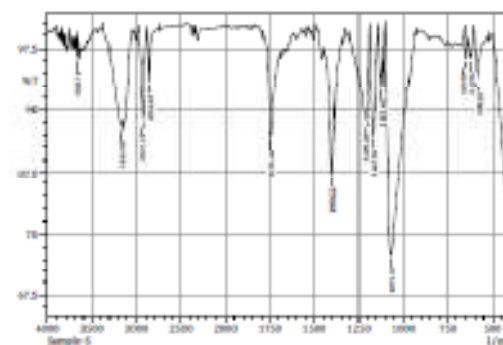
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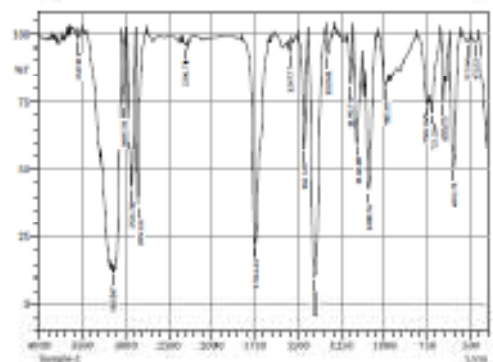
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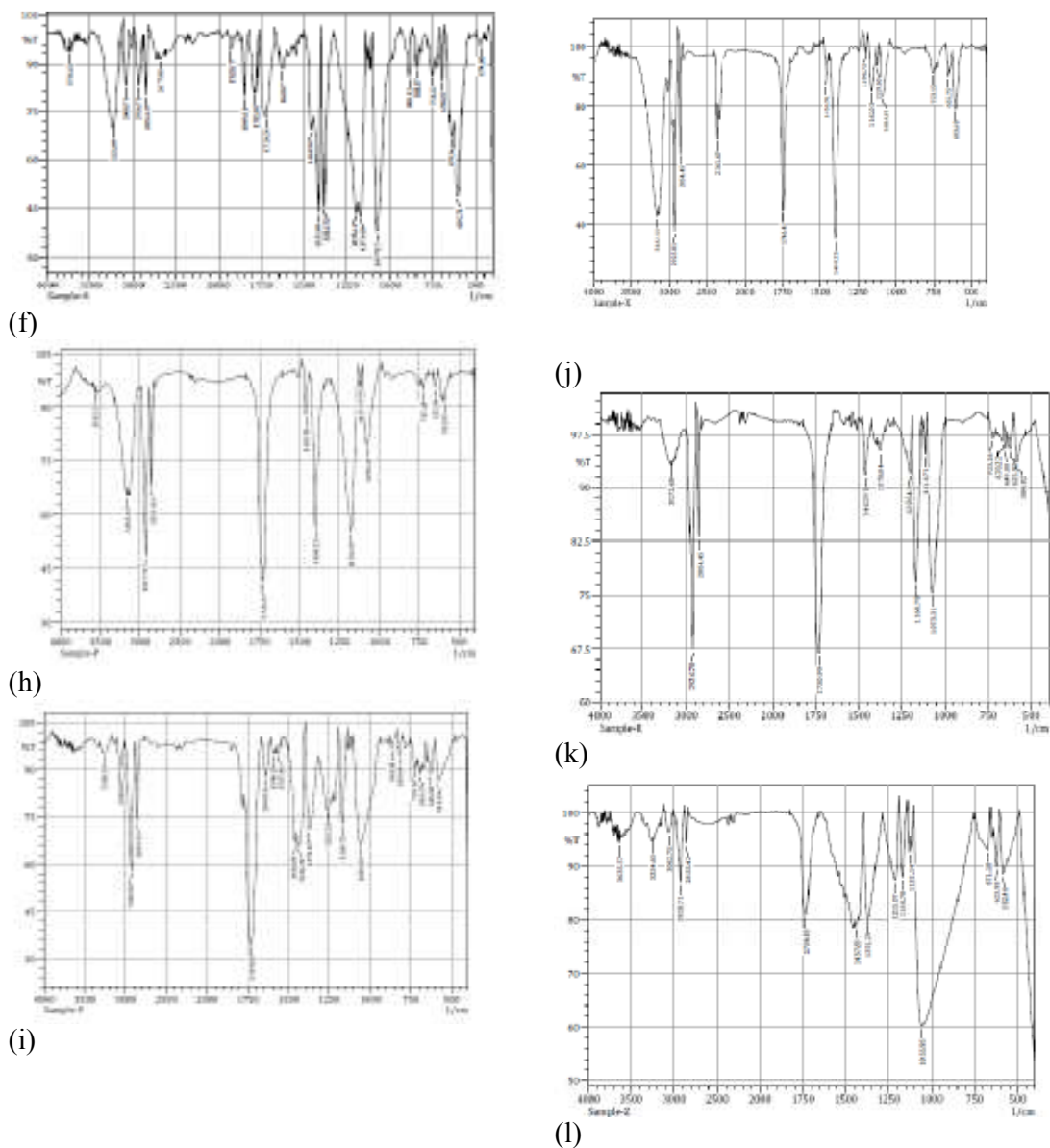
(d)



(g)



(e)



**Figure 2.** IR Spectrum of (a) Odal oil (b) Hydroxylated Odal oil (c) Odal Resin (d) Chennakai oil (e) Hydroxylated Chennakai oil (f) Chennakai Resin (g) Neem oil (h) Hydroxylated Neem oil (i) Neem Resin (j) Thennamarakudi oil (k) Hydroxylated Thennamarakudi oil (l) Thennamarakudi Resin

**Table1:** FT-IR probable assignment of Odal and Chennakai oil

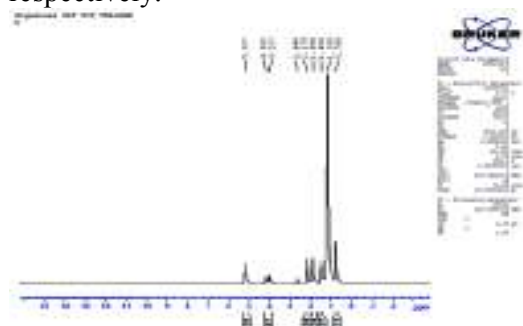
Probable assignment	Odal oil (cm <sup>-1</sup> )	Hydroxylated Odal oil (cm <sup>-1</sup> )	Odal Resin (cm <sup>-1</sup> )	Chennakai oil (cm <sup>-1</sup> )	Hydroxylated Chennakai oil (cm <sup>-1</sup> )	Chennakai Resin (cm <sup>-1</sup> )
-CH <sub>2</sub> Group	2925.81	2961.49	2961.49	2926.78	2960.53	2926.78
-C- O Group in GM	2306.71	2308.71	2854.34	2852.52	2347.21	2853.49
C=O in esters	1747.39	1732.92	1751.24	1746.42	1746.42	1783.07
Terminal CH <sub>3</sub> Groups	1197.71	1119.6	1199.64	1195.78	1464.83	1199.64
Carboxyl Group of acids	1163	1159.14	1401.19	1160.1	1164.92	1171.68
-CH-CH- Stretching	1086.81	1087.78	1087.78	1088.74	1085.85	1077.17
CH <sub>2</sub> -sequences of the aliphatic chains	752.19	723.26	748.33	750.26	723.26	751.22
-OH Group	3634.6	3772.5	3545.88	3547.81	3770.58	3736.82

**Table2:** FT-IR probable assignment of Neem and Thennamarakudi oil

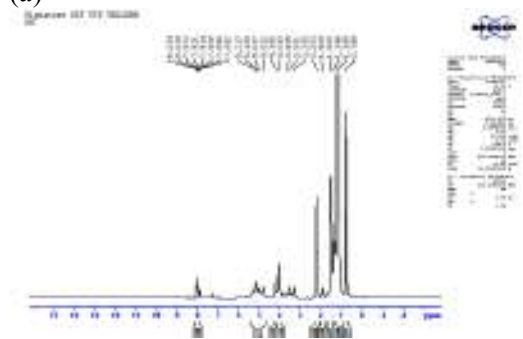
Probable assignment	Neem oil (cm <sup>-1</sup> )	Hydroxylated Neem oil (cm <sup>-1</sup> )	Neem Resin (cm <sup>-1</sup> )	Thennamarakudi oil (cm <sup>-1</sup> )	Hydroxylated Thennamarakudi oil (cm <sup>-1</sup> )	Thennamarakudi Resin (cm <sup>-1</sup> )
-CH <sub>2</sub> Group	2927.74	2927.74	2929.67	2925.81	2926.78	2928.71
-C- O Group in GM	2854.45	2855.45	2855.42	2854.4	2854.45	2855.42
C=O in esters	1745.46	1726.17	1729.06	1746.42	1730.99	1734.85
Terminal CH <sub>3</sub> Groups	1209.28	1400.22	1460.01	1196.75	1116.71	1168.78
Carboxyl Group of acids	1167.82	1178.43	1374.19	1162.03	1145.75	1132.14
-CH-CH- Stretching	1072.35	1076.21	1058.85	1086.81	1073.31	1055.95
CH <sub>2</sub> -sequences of the aliphatic chains	649	725.18	723.26	753.15	723.26	671.18
-OH Group	3658.71	3565.17	3268.15	3161.11	3172.68	3635.57

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

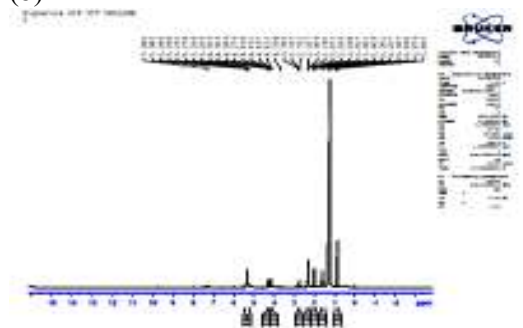
In this study, the NMR spectrum of plant oils, the peak at 4.0-5.2 ppm shows the presence of methylene protons. The peak at 2.6-2.1 ppm indicate the presence of hydrogen in ethylenic bond. The peak at 5.2 ppm shows the olefin proton present in plant oils.<sup>ix</sup> The chemical shift associated at 4.1 ppm shows methylene protons of ester associated with triglyceride molecule. In the <sup>1</sup>H-NMR spectrum of polyol of plant oils show the presence of hydroxyl group at 8.0 ppm. Thus the formation of polyol confirmed from these studies. The chemical shift at lower region from 5.2-0.7 ppm supports oleic and saturated fatty acids respectively.



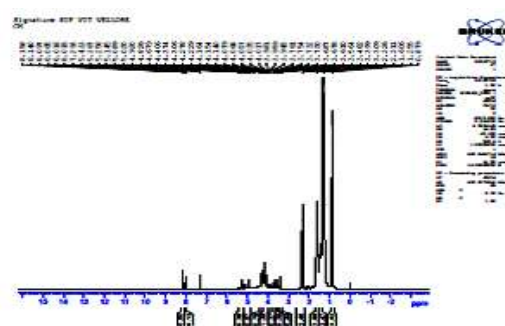
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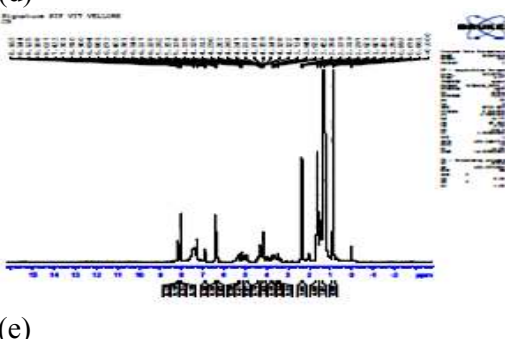
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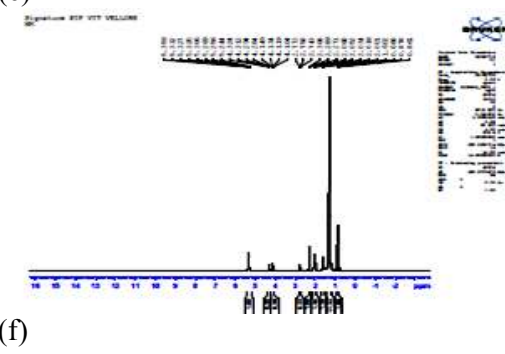
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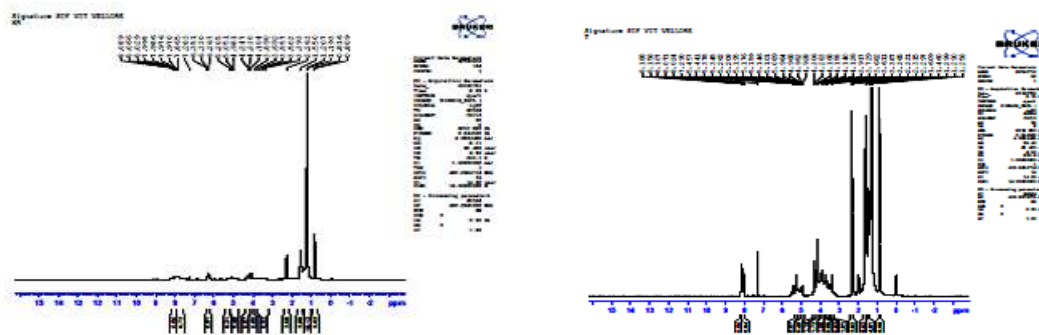


(e)



(f)

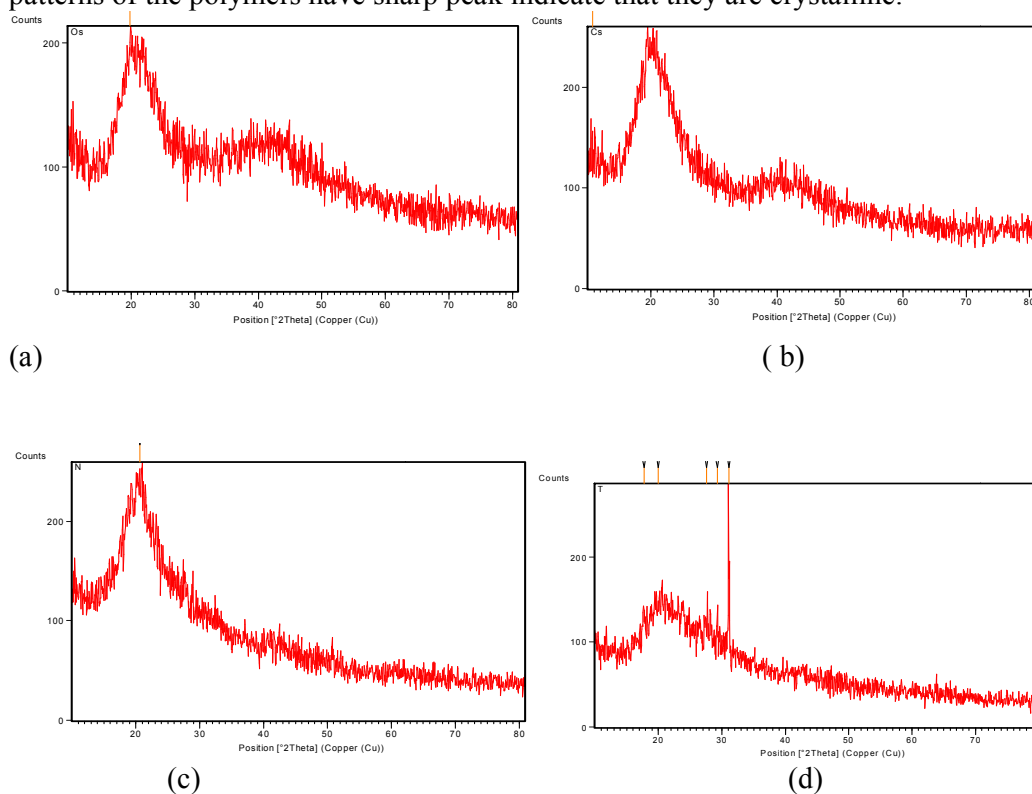




(g) (h)  
**Figure3.** NMR Spectrum of (a) Odal oil (b) HydroxylatedOdal oil (c) Chennakai oil (d) HydroxylatedChennakai oil (e) Chennakai Resin (f) HydroxylatedNeem oil (g) Neem Resin (h) Thennamarakudi oil

### XRD pattern

XRD is primary techniques to determine the degree of crystallinity in polymers.<sup>x</sup> The size of crystallites can be determined from XRD patterns using Scherer's equation. XRD patterns of the polymers have sharp peak indicate that they are crystalline.

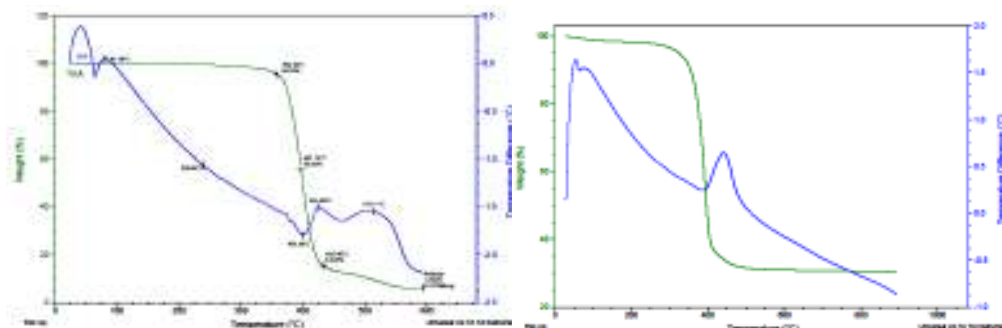


**Figure4.** XRD patterns of (a) Odal oil (b) Chennakai oil(c) Neem oil (d) Thennamarakudi oil

### Thermal analysis:

The Odal polymer was stable up to 80 °c with no significant weight loss; the initial weight loss was observed at 359.39°c, indicating the loss of volatiles and moistures.<sup>xi</sup> Significant

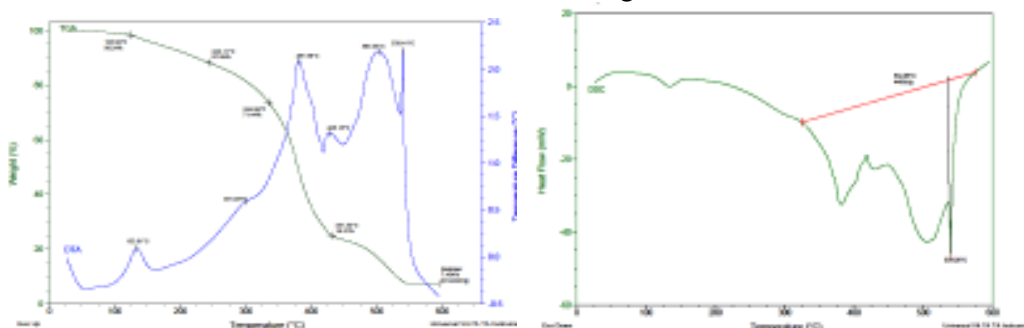
weight loss began at 397.15<sup>0</sup>c due to the degradation of the resin. When the temperature reached 432.48<sup>0</sup>c, weight loss was recorded. The residual mass is around 0.07298 mg .From this we see that polymers are more resistive to temperature increasing. The residue percentage is 1.200%.



**Figure 5.** TGA, DTA thermograms of Odal polymer and Chennakai polymer

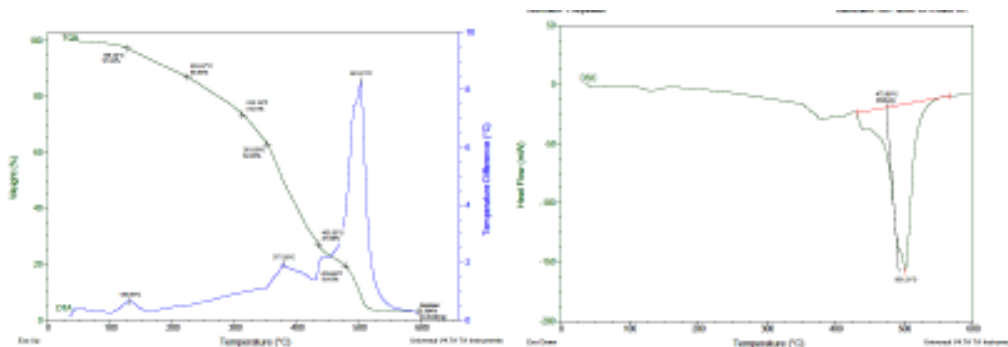
The Chennakai polymer was stable up to 100 °c with no significant weight loss; the initial weight loss was observed at 355.209<sup>0</sup>c, indicating the loss of volatiles and moistures. Significant weight loss began at 400.03<sup>0</sup>c due to the degradation of the resin. When the temperature reached 452.76<sup>0</sup>c, weight loss was recorded. The residual percentage 1.454%.

The Neem polymer was stable up to 120 °c with no significant weight loss; the initial weight loss was observed at 243.11<sup>0</sup>c, indicating the loss of volatiles and moistures. Significant weight loss began at 334.99<sup>0</sup>c due to the degradation of the resin. When the temperature reached 431.54<sup>0</sup>c, weight loss was recorded. The residual mass is around 0.5444 mg. The residue percentage is 7.434%. Thermal analysis indicates that both the polymers are semi crystalline in nature. The peak for the Neem polymer is 539.26<sup>0</sup>c, indicating the fastest cure for this resin will occur at the temperature. The onset of the cure peak for this resin is 534.98<sup>0</sup>c and the total heat of the reaction is 4469J/g



**Figure 6.** TGA, DTA thermograms of Neem polymer

The Thennamarakudi polymer was stable up to 120 °c with no significant weight loss; the initial weight loss was observed at 243.11<sup>0</sup>c, indicating the loss of volatiles and moistures. Significant weight loss began at 334.99<sup>0</sup>c due to the degradation of the resin. When the temperature reached 431.54<sup>0</sup>c, weight loss was recorded. The residual mass is around 0.5444 mg. The residue percentage is 7.434. The peak for the sample is 501.21<sup>0</sup>c, indicating the fastest cure for this resin will occur at the temperature. The onset of the cure peak for this resin is 473.09<sup>0</sup>c and the total heat of the reaction is 3508J/g

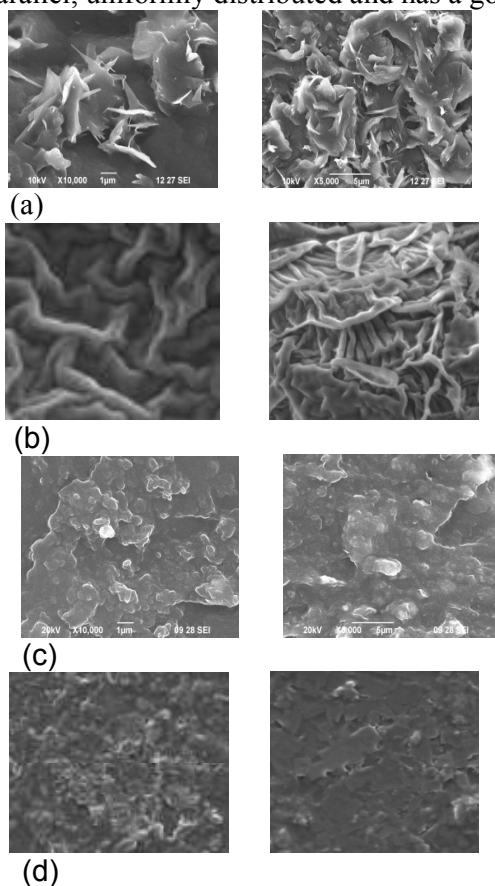


**Figure7.** TGA, DTA thermograms of Thennamarakudi polymer

Thermal analysis indicates that the polymers are semi crystalline in nature.

**SEM analysis**

Scanning electron micrographs of Odal, Chennakai, Neem and Thennamarakudi oil polymers are shown in figure8. Surface SEM images of the polyesters have symmetric chain units in parallel, uniformly distributed and has a good network pattern.<sup>xii</sup>



**Figure8.** SEM photographs of (a) Odal oil polymer (b) Chennakai polymer (c) Neem polymer (d) Thennamarakudi polymer

## Conclusion

We have synthesized plant oil polymers from Odal, Chennakai, Neem and Thennamarakudi oils were synthesised. The reaction mechanism was determined by FTIR and  $H^1$  NMR spectroscopy. XRD patterns show that they are crystalline. SEM analysis shows that they have good network pattern. Thermal analysis confirms the thermal stability of the polymers. In this experimental investigation, it is possible to develop low cost polyesters from naturally available non-edible oil for consumer applications.

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