

## Synthesis & Characterization of a Novel Cross Linked Bio-based Polyurethane from the Egg Oil.

GINJU.M.L<sup>1</sup> and DR.BEGILA DAVID. S<sup>2</sup>

<sup>1</sup> Research Scholar, Department of Chemistry, Scott Christian College, Nagercoil, Tamilnadu.

<sup>2</sup> Assistant Professor in Chemistry, Scott Christian College, Nagercoil, Tamilnadu.

Corresponding Author: ginju.ml@gmail.com.

### Abstract

*In this study the novel bio-based polymer was synthesized by the free radical polymerization of egg oil followed by esterification. The polyol formed as a result of esterification forms polyurethane with monomer such as hexamethylene diisocyanate. The reactions were followed by FT-IR and <sup>1</sup>H NMR spectroscopy. The thermal stability of the polyurethanes were investigated. Thus the thermal stability of egg polymer was studied by TG-DTA Analysis. The studies explained the cured thermosetting polymer decomposes at 297.89 °C.*

Keywords: Thermosetting polymer, bio-based resin, thermal properties.

### Introduction

In recent years biodegradable polymers play a major role in emerging technologies like biotechnology and polymer science. Egg oil was manufactured naturally and the polymer produced from the egg oil has a wide range of advantages. To the best of our knowledge, plant oil might be the most popular renewable resources in the synthesis of bio-based thermosetting resins. The conversion of biomass to useful polymers has considerable economical and environmental value. Biopolyols can be obtained from agricultural products like vegetable oil, wood, carbohydrates (cellulose and starch) and Lignin. Oleochemical polyols are a great alternative for the polyurethane industry. The properties such as hydrophobicity, hardness, flexibility and chemical resistance are needed. The hydroxylation of double bonds through one of the main approaches. a) Epoxidation followed by the ring opening, almost secondary hydroxyl groups were generated. b) Formation of bio-polyurethane by the addition of a monomer such as hexamethylene diisocyanate [6]. Recently polyurethane has been developed as one of the most versatile resins. However the demand of bio-degradability stresses the use of renewable sources [13].

### Materials & Methods

Egg Oil, The Hexamethylene diisocyanate (99.9%), N,N<sup>1</sup>-Dimethylaniline (Sigma-Aldrich), glacial acetic acid (Rankem), 30% Hydrogen peroxide (Rankem), Malonic acid (Sigma-Aldrich), Ethylene glycol (99.9%) (Rankem).

About 100g of Egg oil was taken in a three necked flask fitted with condenser, dropping funnel and thermometer. To this solution add hydrogen peroxide drop wise continuously for about two hours. Then to this solution add glacial acetic acid & 1:1 sulphuric acid. The set up was held over rotamantle to about 10 hour at 60-80 °C. Then the formed epoxy resin should be taken carefully and wash it again with light warm water. Then the epoxy resin was kept for

about one hour below 100<sup>0</sup> C. To a small amount of epoxide add ethylene glycol and a pinch of malonic acid the epoxidised resins were carried out at temperature 200<sup>0</sup> C for 5 hour. At last a brown viscous liquid was formed and it shows the formation of polyol. Polyurethane resins & foams is the most significant group of products based on vegetable oils. Polyurethanes were prepared from polyols & isocyanates<sup>[12]</sup>. Two kinds of Polyurethanes were synthesized through addition reaction between Polyol and hexamethylene diisocyanate monomer in presence of N,N<sup>1</sup> diphenyl amine. The molar ratio of the –NCO group to the hydroxyl group as 1:2.

## Spectral Analysis:

### FT-IR Studies:

IR Spectroscopy allows us to collobrate the chemical nature of the products & also demonstrate that the reaction went from epoxidation to ring opening to form the hydroxyl group. The samples were coated on Potassium bromide pellets and the spectra were obtained over the range from 400 to 4000 cm<sup>-1</sup> [6]

For Egg oil the principal function is the ester group due to the large bonds of triglycerides that compounds it. Esters have two strong characteristic absorption bands arising from C=O and C-O stretching. In case of carbonyl group appears in the at 1159-1098 region as strong bond.

In figure 1, epoxidation reaction is evident due to the disappearance of the bands for the alkene group (3009 cm<sup>-1</sup>) along with a new bond that shows up in 861 for the spectrum this spectrum expected in 861 to 882 cm<sup>-1</sup> as a split signal. A main bands of the spectrum called fingerprint region are located between 1500- 500. The superposition of this region between both spectrum allow us to understand about the formation of the Polyol.

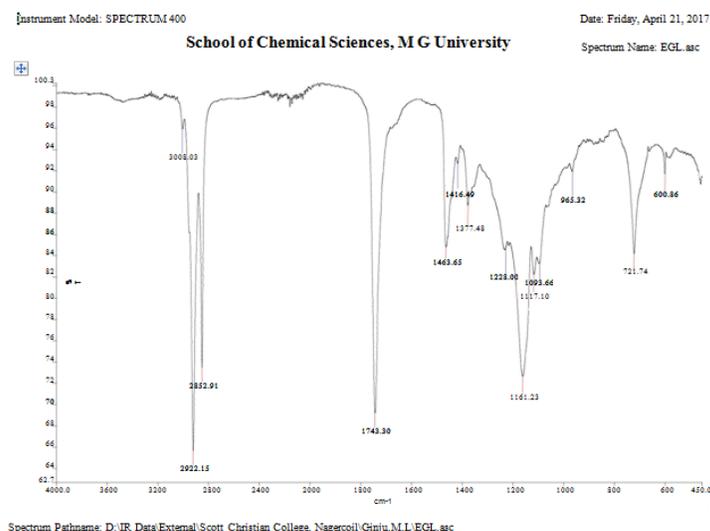


Fig.1 FTIR Spectrum of Egg Oil

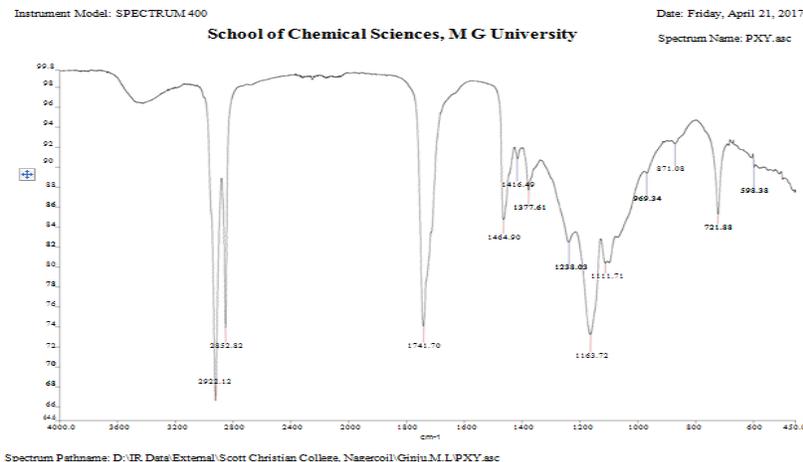


Fig.2. FTIR Spectrum of Egg Polyol.

**NMR Studies:**

The  $H^1$  Nmr spectra was recorded on an 400MHz (Bruker.co.Germany)operated at 400MHZ using Tetramethyl silane(TMS) as an internal standard and  $CDCl_3$  Solvent<sup>[5]</sup>. In the NMR spectrum of both Polyols the peak at 0.8 to 1.6 corresponds to the terminal methyl protons, the peak at 1.6 to 2.3 corresponds to  $CH_2$  and  $CH$  protons, the peak at 2.1 to 2.3 corresponds to the protons in allylic and bis allylic carbons. The peak at 4.2 to 4.5 corresponds for protons in the ester group and the peak at 5.2 corresponds to the olefinic protons. The peak at 7.3 is due to the presence of aromatic hydrogen.

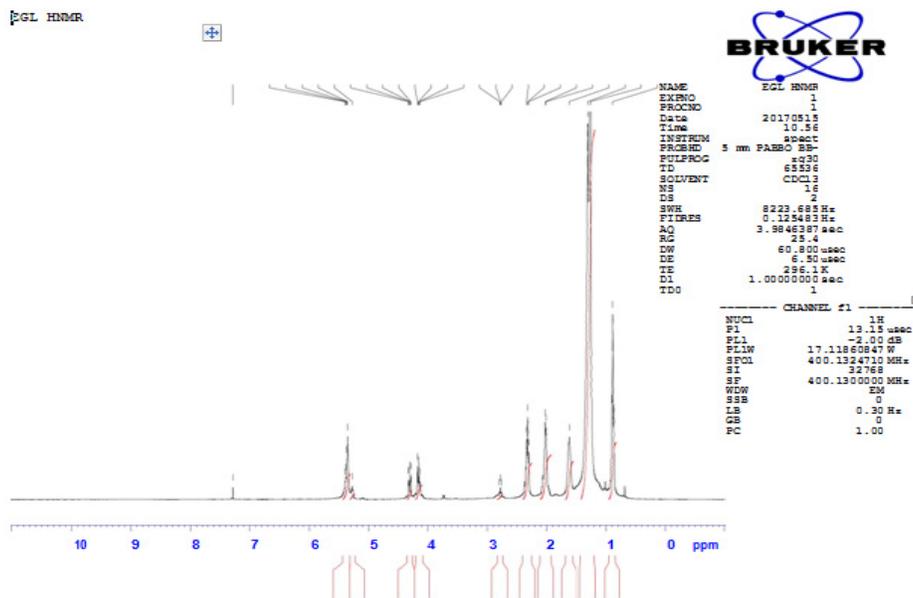


Fig.3  $H^1$  Nmr Spectrum of Egg Oil

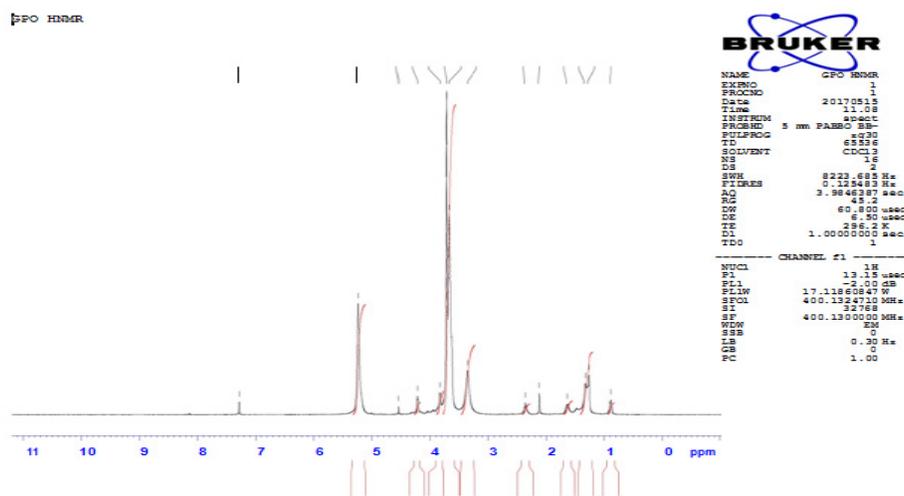


Fig.4. <sup>1</sup>H Nmr Spectrum of Egg Polyol

**Thermal Stability of Polyurethane film:**

TG Analysis was performed on Perkin-elmer diamond TG/DTA with high purity nitrogen as a pure gas at scan rate of 10<sup>0</sup>C/min<sup>[3]</sup>. The process involves change in weight attributed to moisture uptake & thermal stability of the polymer [8]. This analysis enabled to determine a value of moisture loss of the polymers in addition to that obtained by conventional methods.<sup>[10]</sup>

Differential thermal analysis and thermo gravimetric analysis allow to determine thermal effects during physical or chemical changes. During examination of samples it was possible to determine the DTA curve and notice peaks of characteristic endothermic (or) exothermic changes. The thermo gravimetric analysis was carried out the rate sample mass change in the function of time and set temperature. Temperature rise rate during examination was 20<sup>0</sup>C /min and the final temperature was 750<sup>0</sup>C.<sup>[7]</sup>

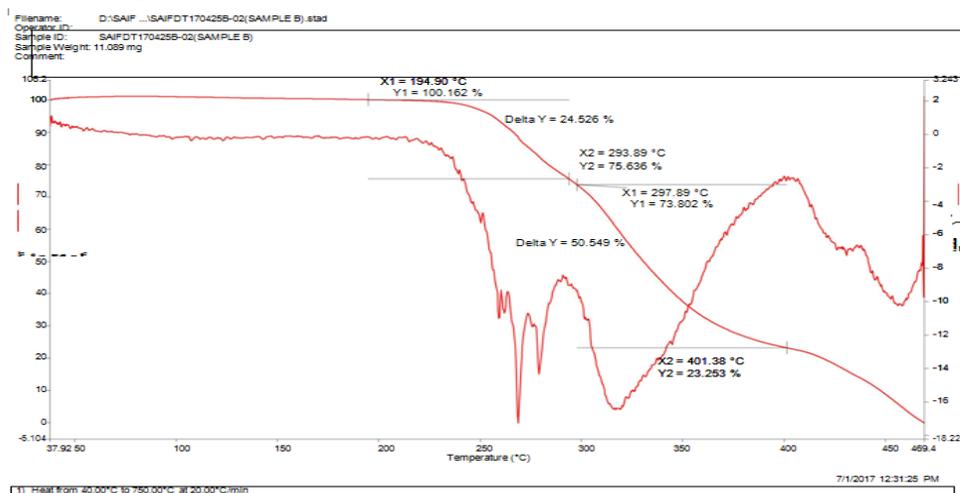


Fig.5. TG-DTA Analysis of Eggpolymer

The TG and DTA Curves of Polyurethane films are shown in figure, respectively. Two distinct temperature regions are observed where the samples experienced significant weight loss (99-206 °C ) and (100-194 °C). It is clear from the figure, that most of the unreacted free oil disappears at the temperature between (99-206°C) that is the region corresponds to the evaporation of the unreacted free oil. On the otherhand the insoluble substances were found to be highly cross linked thermo sets that decompose at temperature greater than 300 °C.

### Conclusion:

Bio-polyurethanes are successfully synthesized & the oligomers possess relatively narrow molecular mass distribution. A variety of novel bio-degradable polymers have been synthesized by the free radical Copolymerization of Egg Oil with Isocyanate as comonomer. Two distinct decomposition stages were found upon thermo gravimetric analysis, which corresponds to evaporation of the unreacted free oil present in the bulk polymer. The thermal stability of the polymer is mainly determined by the amount of unreacted free oil present in the bulk polymer.

### References:

- [1] Chaoqun zhang et al, Soya castor oil based polyols prepared using a solvent free and catalyst free method and polyurethanes. Green Chemistry ,2013
- [2] J.Shakinaetal, Synthesis and characterization of novel cross linked bio-polyesters from olive Oil as eco-friendly biodegradable materials. E-Journal of Chemistry, 2012, 9 (1), 181-192.
- [3] X.Q.Liu et al, Preparation of bio-based epoxy with comparable properties to those of petroleum-based counter parts. eXPRESS polymer letters Vol 6, No 4 (2012).
- [4] Sylvain et al, Synthesis of new polyester polyols from Epoxidised vegetable oils and bio-based acids. Eur.J.Lipidsci.technol.2012,114, 447-1459.
- [5] LIAO Feng etal, Synthesis and properties of UV curable polyurethane acrylates based on two different hydroxyethyl acrylates. J.cent.south univ (2012) 19: 911-917.
- [6] A.A.Beltran etal, Preparation of oleochemical polyols derived from Soyabeanoil.appl.res. vol.41.no.1 2011
- [7] M.Jesitotr et al, Thermal analysis of selected polymer materials for precision casting models, Archives of foundry engineering .Vol.3, 2/2013.
- [8] Ritu tomar etal, Experimental studies on PVP / KI Ion conductive polymer composite, International journal of scientific research engineering & technology, Vol 2 issue 5 pp 296-299. 8/2013.
- [9] M.K.Kulkarni etal, Effect of methyl methacrylate-acrylonitrile-butadiene-styrene (MABS) on the mechanical & thermal properties of PMMA Journal of minerals and materials,vol-11-No-4.
- [10] Yogesh Kumar etal, ion transport and ion polymer interaction in PEO based polymer, Elsevier journal, 22 August 2011.