

Research Article

Synthesis and comparative study of Novel cross linked Bio polyesters from corn oil

S. Begila David¹, K. Priya Rajini^{2*}

¹Department of chemistry Scott Christian College. Nagercoil, Kanyakumari District, Tamilnadu, India.

²Department of chemistry Sun College of Engineering and Technology. Nagercoil, Kanyakumari District, Tamilnadu, India

***Corresponding author**

K. Priya Rajini

E mail: kpriyasingh13@gmail.com

Abstract: Novel cross linked bio polyesters were synthesised from naturally available corn oil. Epoxidation of corn oil has been carried out by per acetic acid method. Further an acrylated epoxy resin (AECO) was synthesised from the epoxidized corn oil (ECO). The (AECO) was characterised by spectral and physicochemical properties (Specific gravity, viscosity, Saponification value, iodine value). The Novel cross linked bio polyesters were prepared by using AECO with Diethylene glycol trimethacrylate. The mechanical properties of cross linked biopolyester were improved by adding filler like wood flour. The environmental degradation was assessed by soil burial test and sem analysis. The outcome of the studies revealed that the newly prepared cross linked bio polyesters are potential biodegradable material for various consumer applications like package materials, sporting goods and floor mats.

Keywords: Biodegradation, Corn oil, Epoxidation, Tensile modulus, Thermal analysis

INTRODUCTION

The utilization of renewable resources can consistently provide raw materials for everyday products, effectively avoiding further contribution to green house effects, because of the minimization of CO₂ emissions [1]. Therefore, academic and industrial researchers are devoting increasing attention and efforts to the possible utilization of renewable resources as raw materials for the production of both chemicals and polymeric materials. The renewable raw materials most widely used are polysaccharides (mainly cellulose and starch), proteins, sugar, and natural rubber and plant oils [2, 3]. Among these, vegetable oils are the most widely used renewable resource for the chemical and polymer industries owing to their superb environmental credentials, including their inherent biodegradability, low toxicity, avoidance of volatile organic chemicals, easy availability and relatively low price [4]. The main components of the triglyceride vegetable oils are saturated and unsaturated fatty acids which in its pure form are also synthesis [5, 6]. Larock *et al* have developed a family of chemically modified plant oils which can be polymerised using free radical initiators, in to rigid composites rubbers and adhesives [7]. Cross linked biodegradable polymers have been prepared from edible oils with unsaturated anhydrides or acids have useful applications as adhesives, filler's and elastomers [8]. Depending on their specific application, polymers are often reinforced with fibres or

fillers to improve their dimensional stability, strength, toughness and environmental resistance, resulting in high performance polymer composites have found wide application in the automobile, aircraft, military, sporting goods and marine industries [9]. These renewable resources have proved to be useful basis for the synthesis of a variety of monomers as well as linear and cross linked polymers of different types (e.g. polyolefin, polyesters, polyurethane resins and others) [10]. The present study explore the potential utility of the edible corn oil for the preparation of novel cross linked bio polyesters as eco-friendly biodegradable material of various consumers application like packaging materials and sporting goods.

EXPERIMENTAL

Materials

Corn oil purchased from the supermarket, Acetic acid (glacial), hydrogen peroxide (Rankhem), Diethylene glycol trimethacrylate (Sigma Aldrich), Benzoyl peroxide (Merck) were purchased from respective dealers. All the materials were used without purification.

Synthesis of novel cross linked Bio polyesters

Epoxidation of oil using 30% hydrogen peroxide was carried out by per acetic acid method [11]. Corn oil, acetic acid and 30% hydrogen peroxide were heated at 10 hrs in a three necked flask. The

resulting product was separated and extracted with warm water then the extracted product was acrylated using acrylic acid, triethylamine was used as catalyst and benzene as the solvent. The reaction mixture was again refluxed for 15 minutes at 80°C. Reaction of the epoxy functionalized triglyceride with acrylic acid incorporates acrylates into the triglyceride [12]. Two bio polyesters were prepared by free radical polymerisation of AECO resin of corn oil with cross linking of co-monomer Diethylene glycol trimethacrylate, benzoyl peroxide as free radical initiator, dimethyl aniline as accelerator and wood flour as filler. The mixture was casted on clean silicon oil spreaded glass plate curved for 1hr at 100°C. All the cured material showed high toughness, elastomeric and good transparency.

Characterisation of Biopolyesters

The AECO resin were subjected to extensive analysis for the determination of specific gravity, iodine value, saponification value, as per the ISI standard 840-1964. The resins were analysed by UU, IR, and NMR spectral analysis. The FT-IR spectral analysis of the two bio polyesters was done by Magna-IR 550 Spectrophotometer. Tensile strength of the bio polyesters were determined using rectangular shaped polymer samples in the form of strips Test speed:10mm/min; Tested with 100N load cell; instron model 3345. The values represented are an average mean of about 5-6 samples. The thermal analysis of the bio polyesters was determined by TGA instruments.

The replicate pieces of the sample (5×3cm) were buried in the garden soil at the depth of 25cm from the ground surface for 3 months, inoculated with the sewage sludge having ability to adhere and degrade the polymer film. The test specimen was periodically removed from the soil and the specimen was then gently washed to remove attached soil and dust after being dried in vacuum oven. The extent of degradation was examined by weight loss and surface observation.

RESULTS AND DISCUSSION

Corn oil is a mixed glyceride of unsaturated components (oleic acid, linoleic acid and linolenic acid) and saturated compound (palmitic and stearic acid), since the concentration of unsaturated compounds are higher the mixed unsaturated triglyceride molecule offers a number of reactive sites, C=C bonds, the carbon alpha to the ester group for functionalisation [13, 14]. Under the present experimental conditions epoxidation takes place at the double bonds of the triglyceride units. The reaction of epoxidized corn oil with triethyl amine catalyst by acrylic acid leads to the formation of Acrylated epoxidized corn oil resin (AECO). The analytical data are given in Table 1. Finally the cross linking of AECO resins involves the reaction of unsaturated sites in the polymer chain with a Co-monomer which may of DEGMA to form bio polyester.

Table-1: Physical properties

Parameters	Corn oil	Epoxy resin	Acrylated epoxy resin
Specific gravity gm/cc at 30°C	0.915	0.879	0.965
Saponification value mg koH/gm	170.2	155.2	133.4
Iodine value	134.6	8.73	46.7
Viscosity at 30°C	68.6	218	96
Molecular weight/calculated	1096	1186	1498
Hydroxyl Number	-	-	4.01
Molecular weight/ Saponification value	987	1082	1259

Spectral analysis of AECO resin

UV spectral analysis

The UV spectra of corn oil, epoxidized and acrylated epoxidized resin are shown in Figure 1. The corn oil shows an absorption peak at 230nm (ester). Epoxy corn resin exhibited peak at 220 nm due to the

substitution of the unsaturated groups. In acrylated epoxy corn resin the peak again shifted to 246nm. The substantial red shift in electronic absorption exhibited in acrylated samples would indicate the presence of a double bond (k-band) in the fatty acid molecule [15].

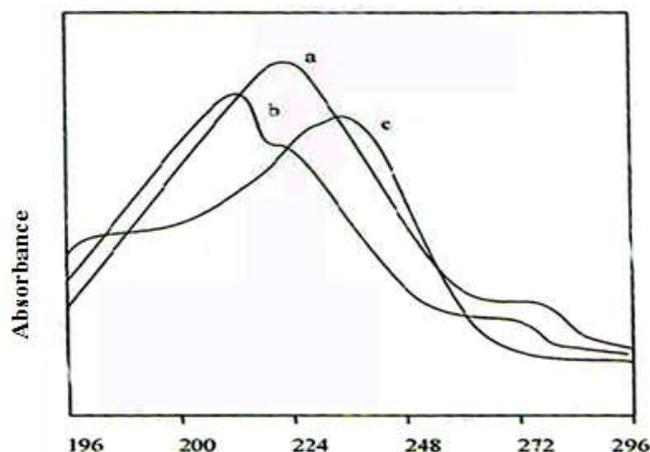


Fig-1: UV Spectra of a) Corn oil b) epoxidized corn oil c) Acrylated epoxidized corn oil

¹H-NMR Spectral analysis

The possible peaks ¹H-NMR for quantitating unsaturated fatty acids are peak at 0.75 ppm corresponds to the hydrogen ending methyl groups (CH₃-(CH₂)_n-). Peaks at 1.2-1.4 ppm originate from aliphatic methylene hydrogens (-CH₂-). The peak at 2.05 ppm corresponds to allyl hydrogens (-CH₂-CH=CH-).

Peak at 2.7 ppm originates from hydrogen between two double bonds. (-CH=CH-CH₂-CH=CH-). Methylene hydrogens from the glyceride moiety (CH-CH₂-O-) appear at 4.1-4.4 ppm. Finally vinyl hydrogens and methyne hydrogen from glyceride group (CH-O-CO) was detected at 5.2-5.5 ppm are shown in figure 2.

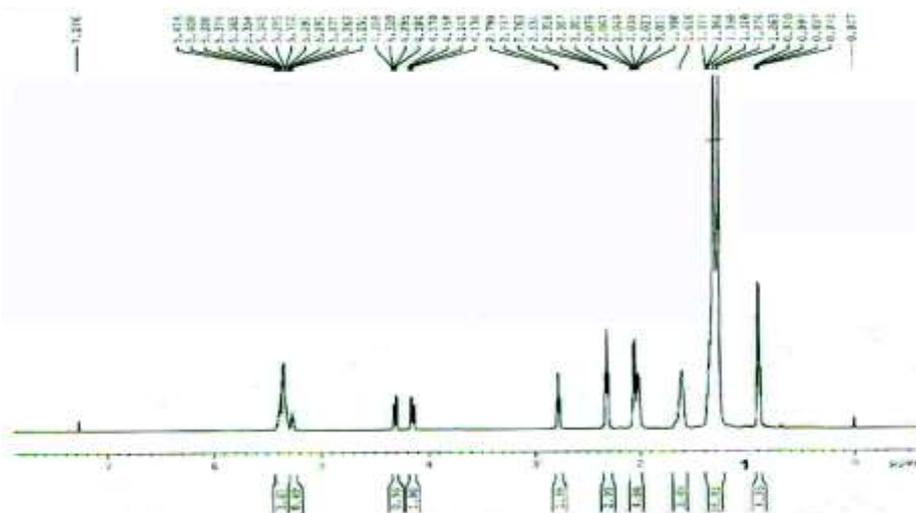


Fig-2: NMR Spectrum of corn oil

This peaks are disappeared in the epoxy resin showing that the double bond is replaced by the epoxy group were appeared at 2.9 ppm in ECO resin. The peak

at 3.1 ppm shows -CH- hydrogen's between two epoxy groups. The peaks at 1.45 ppm correspond to -CH - hydrogen adjacent to epoxy groups shown in figure 3.

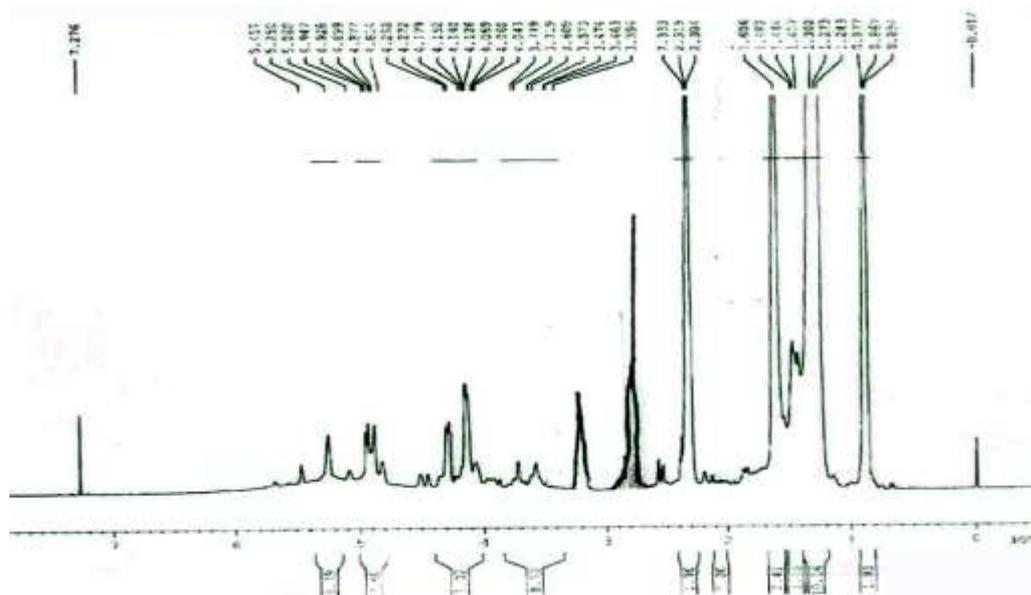


Fig-3: NMR Spectrum of Epoxidized corn resin

In AECO resins the peak at 3.1-3.2 ppm is due to the deshielding effects of hydroxyl and carboxylate ester linkages. The strong peak at 1.3 ppm is attributed

to the long chain (more than five methylene groups) [16]. The peaks at 0.95 to 2.3 ppm were due to the long aliphatic side chain shown in figure 4.

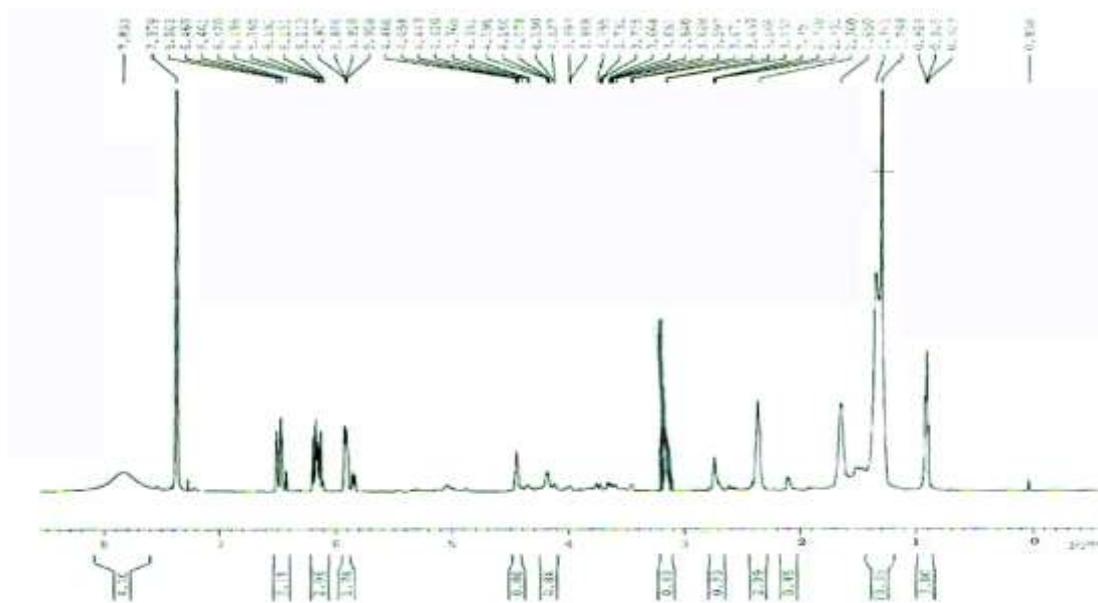


Fig-4: NMR Spectrum of Acrylated epoxidized corn resin

IR spectral analysis

The corn oil, epoxidized corn oil resin and AECO resins can also be monitored by Fourier transform infrared (FTIR) spectroscopy shown figures (5-7). The room temperature infrared data was

determined and reported previously by Obaleye and Orjiekwe [17, 18]. The corn oil showed a very strong and sharp band at 1740 cm^{-1} due to the ester carbonyl group.

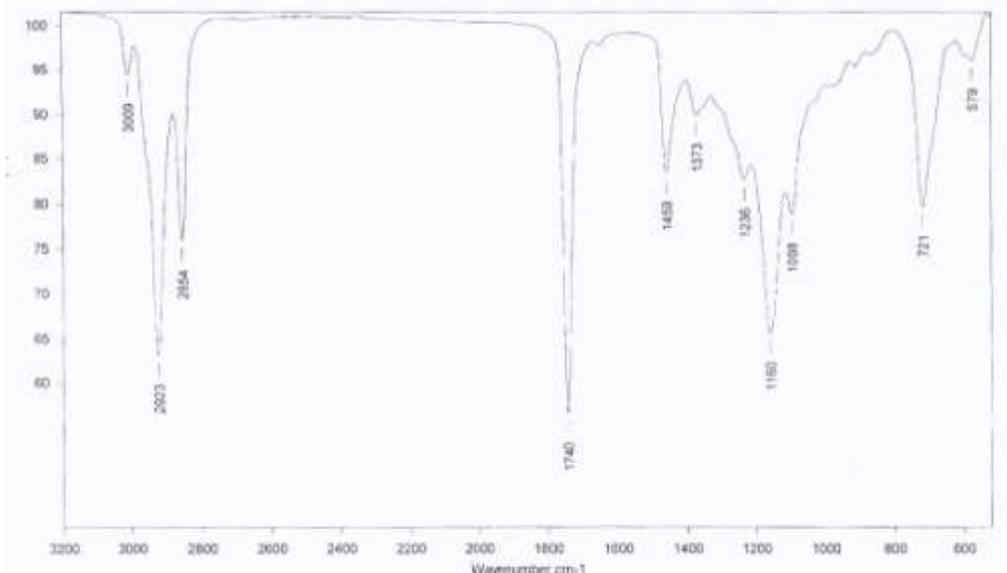


Fig-5: IR Spectrum of corn oil

In ECO resin epoxy groups showed three characteristic absorption bands appears at 1250cm⁻¹, 965cm⁻¹ and 850cm⁻¹. The epoxy band between 950cm-

¹ and 810cm⁻¹ was also reported by karunanayake and Fernando [19]

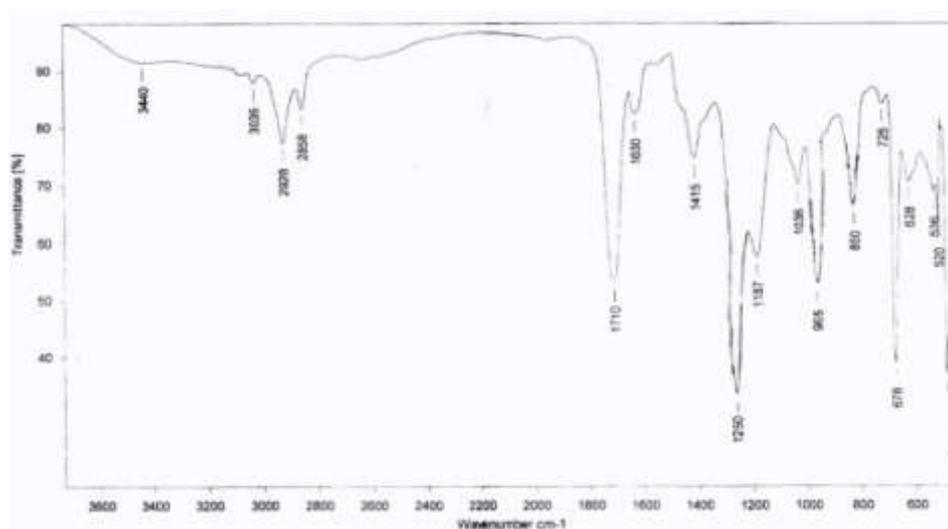


Fig-6: IR Spectrum of epoxidized corn resin

In AECO- resin shows that the epoxy group is successfully converted to the acrylated functionality through condensation esterification. This is indicated from the presence of hydroxyl functionality of resin absorption band at 3412cm⁻¹ associated with hydrogen bond of -OH groups. Strong absorption band for the

carbonyl group C=O of the acrylated compound appears at 1737cm⁻¹. The presence of vinyl functionality of the acrylated polymer is also supported by the absorption peak at 986 cm⁻¹ as this indicates the presence of vinyl group [CH₂=CH(CO)-O].

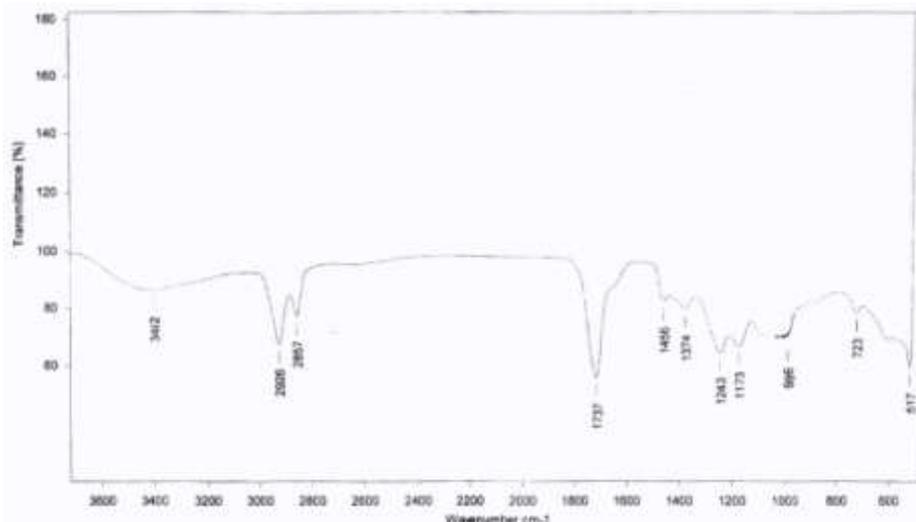


Fig-7: IR Spectrum of Acrylated epoxidized Corn resin

The spectra of cured sample were almost same and the absence of peak around 1637cm^{-1} indicates the absence of double bonds. The carbonyl band of triglyceride ester group at 1740cm^{-1} is shifted to 1737cm^{-1} in acrylated epoxy resin and 1728cm^{-1} in AECODEGMA. The maximum shift is obtained in brittle polymer and minimum shift in ductile polymer.

This is due to the tightness of the polymer network and reduced molecular mobility in brittle polymers. The –OH stretch of carboxylic group in the acrylated epoxy resin at 3412cm^{-1} is shifted to 2947cm^{-1} indicates extra hydrogen bonding interaction with the hydroxyl group present in the cured samples.

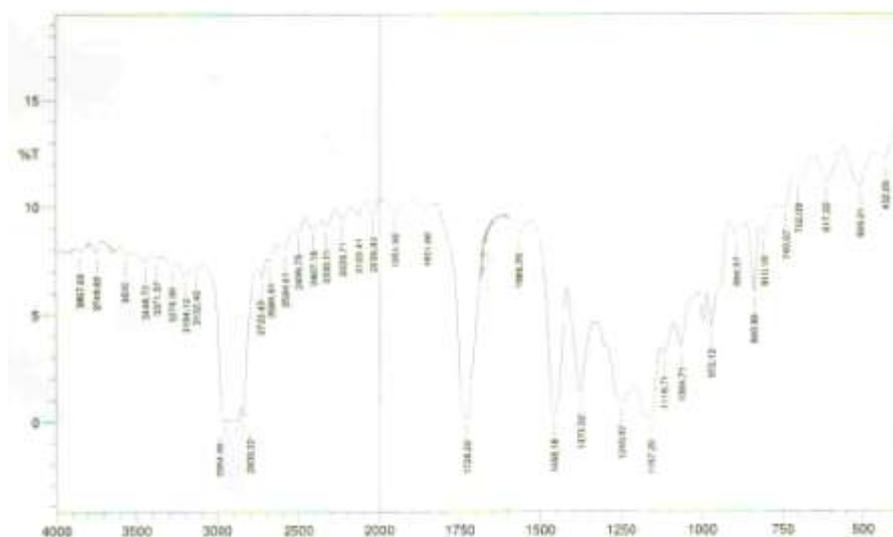


Fig-8: IR spectrum of AECO resin-Co-Diethylene glycol trimethacrylate polyester

Mechanical properties

The data of mechanical properties of all cured samples are shown in the Table 2. The higher tensile strength and modulus are observed in bio polyester [AECODEGMAWF] made by AECO resin, wood flour and DEGMA than polyester [AECODEGMA] made by AECO resin and DEGMA. Polymer nano composites

are a class of reinforced polymers with low quantities of nanometer- sized filler particles, which give them improved barrier properties, fire resistance and strength. Such properties have made these materials valuable in components such as panels and as barrier and coating materials in automobile, civil and electrical engineering as well as packaging [20].

Table-2: Mechanical properties of Polyesters

Sample code	Tensile strength/Mpa	Strain@break %	Modulus/Mpa
AECODEGMA	2.53 ± 0.17	9.63 ± 3.90	135 ± 35
ECODEGMAWF	10.22 ± 0.47	4.37 ± 0.51	419 ± 60

Fig 9 shows the stress and strain behaviour of the bio polyesters. Higher stress strain behaviour obtained in bio polyester made by using wood flour (AECODEGMAWF) than bio polyester made by pure monomer (AECODEGMA). Increase in Tensile

strength and modulus significantly increase with the wood flour content as a result of hydrogen bonding between the wood flour and the resin which restricts the mobility and deformability of the resulting bio polyesters.

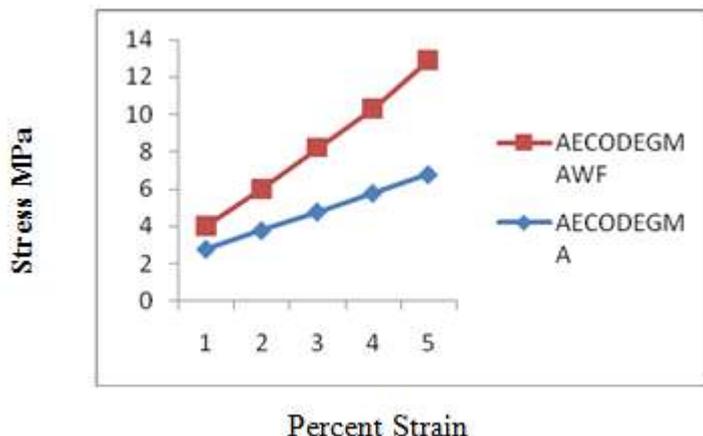


Fig-9: Stress and strain behaviour of the bio polyesters

Thermal properties

All the samples were subjected to thermogravimetric analysis. The biopolyester AECODEGMAWF shows improved thermogram than AECODEGMA. The initial decomposition temperature of AECODEGMAWF was observed at 310°C but AECODEGMA at 200°C. In the first step of thermal degradation (200°C-460°C) weight loss up to 27% is observed in both samples this may be caused by thermal

degradation of small fragments like CH₃ and OH on the side chain. The biopolyester AECODEGMA was more stable up to 430°C after the addition of wood flour AECODEGMAWF was more stable up to 550°C. The weight loss around 80% in the second stage of thermal degradation (470°C-660°C) may be due to the depolymerisation and cleavage of the biopolyesters in oxydegradative manner.

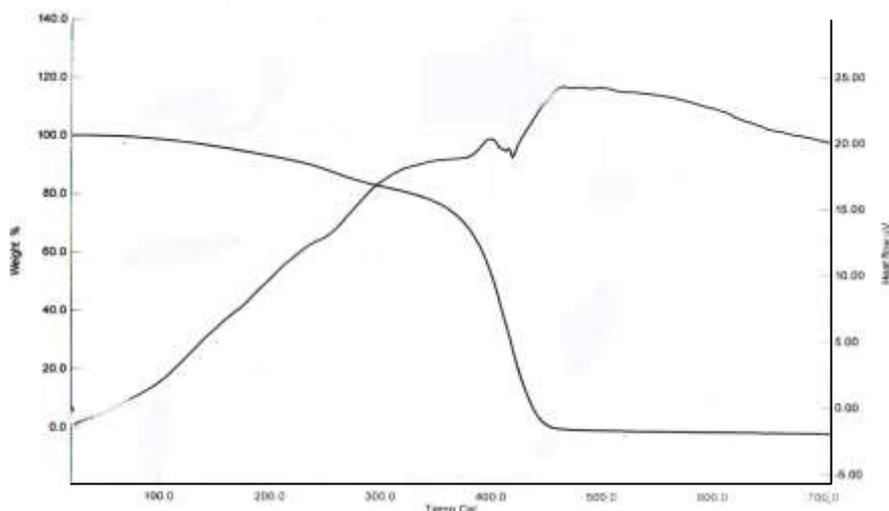


Fig-10: TGA-DTA curve of AECODEGMA

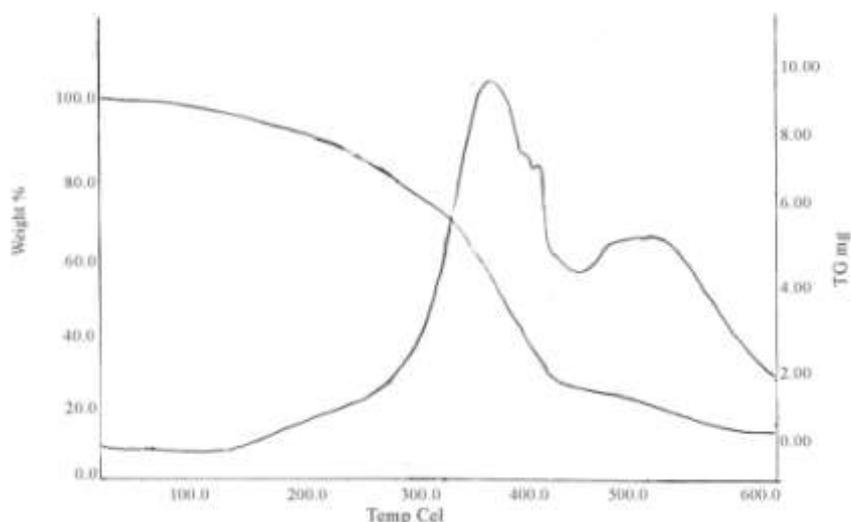


Fig-11: TGA-DTA curve of AECODEGMAWF

DTA analysis

DTA curves are recorded simultaneously with TGA curves. DTA curves shows first order transition namely crystallization and melting appears speaks in the exothermic and endothermic direction respectively. After melting material may undergo decomposition

reaction at higher temperature which give broad peaks, these may be generally exothermic but are some times more complex in nature. DTA analyses are shows in (Table 3) a weak one around ranging from 230°-420°c and a strong one above ranging from 330°c and 520°c.

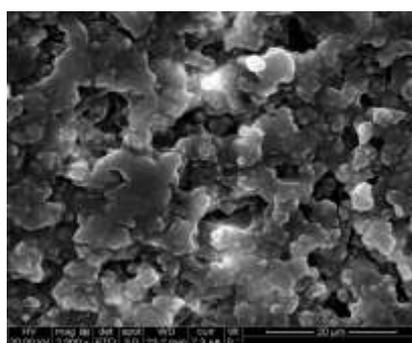
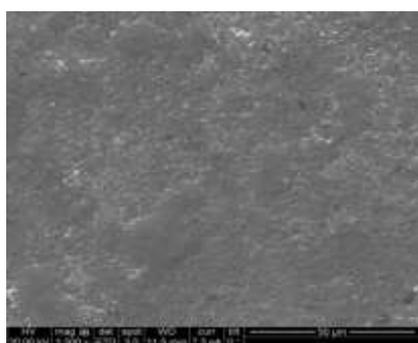
Table -3: Differential thermal analysis of the polymer sample

Sample	1 st exotherm	2 nd exotherm
AECODEMA	230	420
AECODEMAWF	330	520

Biodegradation Test

In soil burial degradation the effect of microorganisms arises on the surface of the polymer film [21, 22]. The calculation of biodegradation rate from weight loss of polymer films in soil burial test constitutes a practical problem, since the soil sticks onto the film surface, and weight measurements are not

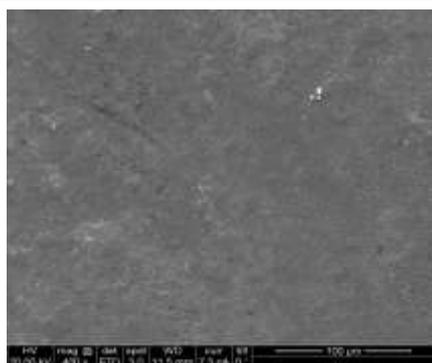
accurate. Kimura et.al. in his study of degradation of plastics was mainly caused by bacteria and fungi and that different soil conditions affected the rate of degradation of plastics [23]. Fig12 shows the SEM micrograph of polymeric samples before and after soil burial test.



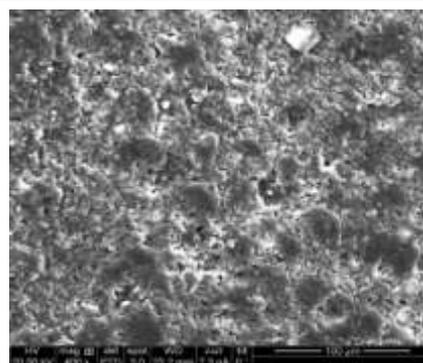
Before soil burial

After soil burial

Fig 12(a) : AECODEMA



Before soil burial



After soil burial

Fig 12(b):AECODEMAWF

CONCLUSION

Polymers are widely used in modern society because they are light in weight, low in cost and easy to process materials. Biodegradable polymers have a wide range of potential applications in market currently dominated by petroleum based materials. Plant oils are expected to be inexpensive renewable resources in the development of new polymeric materials. The purpose of this work is to prepare high molecular weight polymers and it alternative to petroleum based polymeric materials that range from soft and flexible rubbers to ductile or rigid plastics, as well as high-performance bio composites and nanocomposites. The present method of prepared corn oil based polymers have mechanical properties compared to of petroleum based polymeric materials and serve as replacement in numerous potential applications. The outcome of this studies revealed that newly prepared cross linked bio polyesters are various consumer applications like horticultural containers, packaging, automobiles, building construction, electronics and biodegradable agricultural films.

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