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Synthesis and Comparative Study of Novel Cross Linked Bio Polymers from Linseed Oil.

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Abstract
Novel cross linked biopolymers were synthesised from naturally available linseed oil. Epoxidation of linseed oil was carried out by per acetic acid method. Further an acrylated epoxidized resin (AELO) was synthesised from the epoxidized linseed oil (ELO). The (AELO) was characterised by spectral and physicochemical properties (Specific gravity, viscosity, Saponification value, iodine value).The Novel cross linked biopolymer were prepared by using AELO with Triethylene glycol trimethacrylate(TEGMA) . The mechanical properties of cross linked biopolymer was improved by adding filler like wood flour. The environmental degradation was assessed by sem analysis. The outcome of the studies revealed that the newly prepared cross linked biopolymers are potential biodegradable material for various consumer applications like package materials, sporting goods and floor mats.

Key words: Biodegradation, Epoxidation, Linseed oil, Tensile modulus.

I. 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 co_2 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.

II. Experimental

2.1 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.

2.2 Synthesis of novel cross linked Bio polymers

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 15minutes at 80^0 C .Reaction of the epoxy functionalized triglyceride with acrylic acid incorporates acrylates into the triglyceride [12]. Two bio polymers were prepared by free radical polymerisation of AELO resin of linseed oil with cross linking of co-monomer Triethylene 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 100^0C.All the cured material showed high toughness, elastomeric and good transparency.

2.3 Characterisation of Biopolymers

The AELO resin were subjected to extensive analysis for the determination of specific gravity, iodine value, saponification value, as per the ISO standard 840-1964. The resins were analysed by UU,IR spectral analysis. The FT-IR spectral analysis of the biopolymers was done by Magna-IR 550 Spectrophotometer. Tensile strength of the bio polymers 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 biopolymers 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 3months, 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 SEM analysis.

III. Results and Discussion

Linseed 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 function alisation [13, 14] .Under the present experimental conditions epoxidation takes place at the double bonds of the triglyceride units. The reaction of epoxidized linseed oil with triethyl amine catalyst by acrylic acid leads to the formation of Acrylated epoxidized linseed oil resin (AELO). The analytical data are given in Table 1. Finally the cross linking of AELO resins involves the reaction of unsaturated sites in the co-monomer which may of TEGMA to form bio polymers.

Table.1.Physical properties

Parameters	Corn oil	Epoxy resin	Acrylated epoxy resin
Specific gravity gm/cc at 30^0c	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 30^0c	68.6	218	96
Molecular weight/calculated	1096	1186	1498
Hydroxyl Number	-	-	4.01
Molecular weight/ Saponification value	987	1082	1259

3.1Spectral analysis of AECO resin

3.1.1UV spectral analysis

The UV spectra of linseed oil, epoxidized and acrylated epoxidized resin are shown in Figure 1. The linseed oil shows an absorption peak at 230nm (ester). Epoxy lnseed oil resin exhibited peak at 220 nm due to the substitution of the unsaturated groups. In acrylated epoxy linseed oil 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].

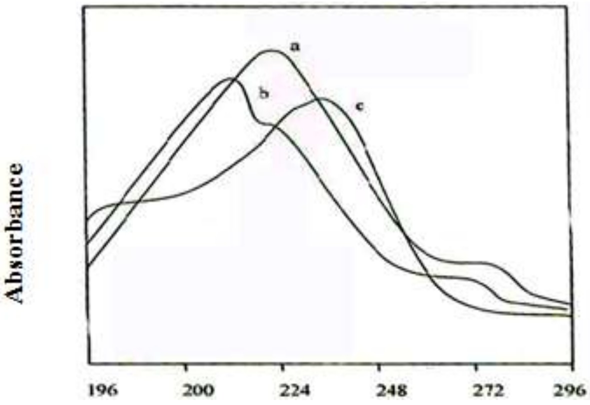

Figure 1. UV Spectra of
a) Linseed oil
b) epoxidized linseed oil resin
c) Acrylated epoxidized linseed oil resin

3.1.2 IR spectral analysis

The linseed oil, epoxidized linseed oil resin (ELO) and AELO resins can also be monitored by Fourier transform infrared (FTIR) spectroscopy shown figures (2-5). The room temperature infrared data was determined and reported previously by Obaleye and Orjiekwe [16, 17]. The linseed oil showed a very strong and sharp band at 1743 cm^{-1} due to the ester carbonyl group. The oil composition affects the exact position of the band and yields shifts when the proportion of the fatty acid changes. Linseed oil showed a maximum absorption at 3009 $^{cm-1}$ due to the higher proportion of linolenic or linoleic acid groups.

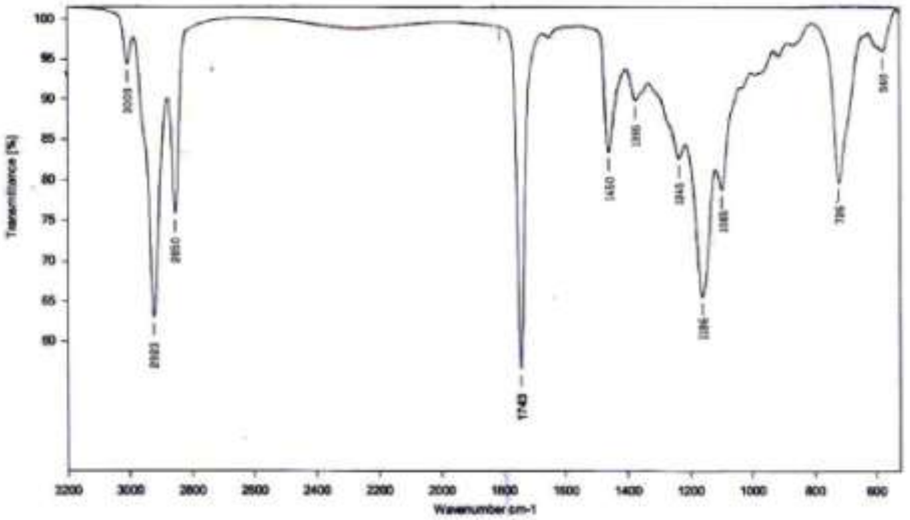

Figure: 2 FTIR Spectrum of Linseed oil

In ELO 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 [18]. The peak at 1245 cm^{-1} corresponds to the epoxy group. The region of other two bands are broader, the portion of the maximum depending on the structure of the epoxide. These absorption bands appear between 950cm^{-1} and 860cm^{-1} and between 865 cm^{-1} and 785 cm^{-1}.

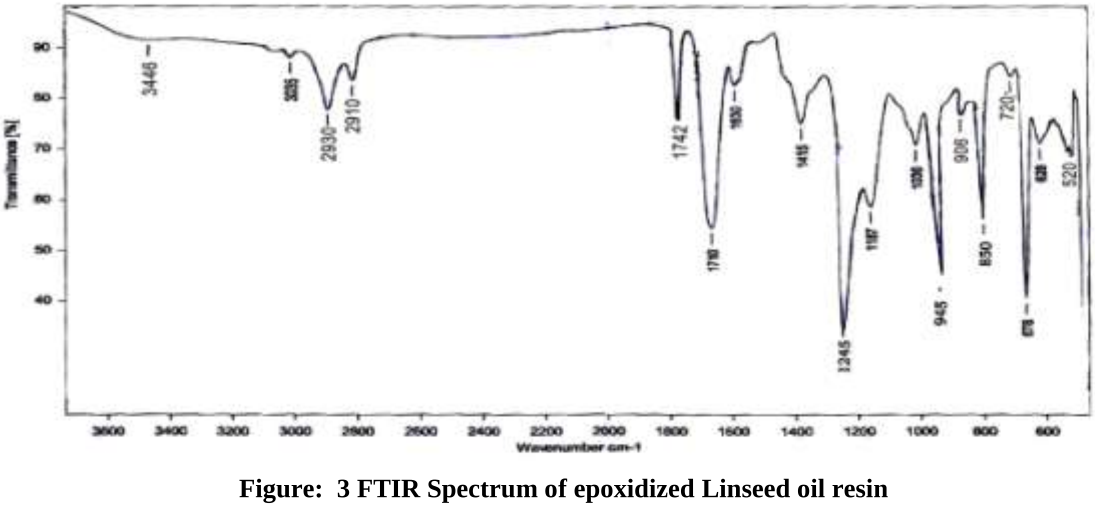

Figure: 3 FTIR Spectrum of epoxidized Linseed oil resin

In AELO- 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 3401cm^{-1} associated with hydrogen bond of -0H groups. Strong absorption band for the carbonyl group C=O of the acrylated compound appears at 1714cm^{-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 [CH_2=CH(CO)-O].

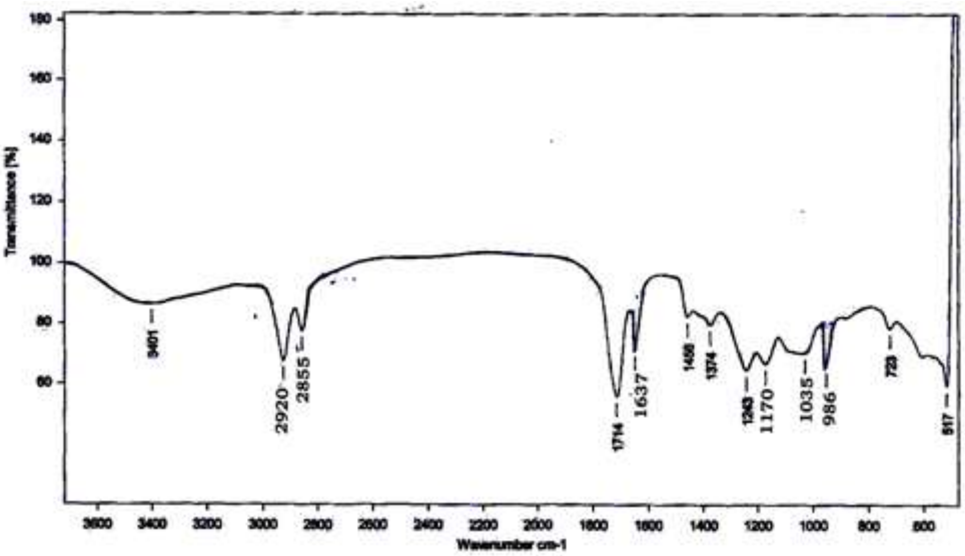

Figure 4 FTIR Spectrum of Acrylated Expoxidized Linseed oil resin

The spectra of curved 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 1743cm^{-1} is shifted to1714cm^{-1} in acrylated epoxy resin and 1723cm^{-1} in AELOTEGMA . 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 3401cm^{-1} is shifted to 3006cm^{-1} indicates extra hydrogen bonding interaction with the hydroxyl group present in the curved samples.

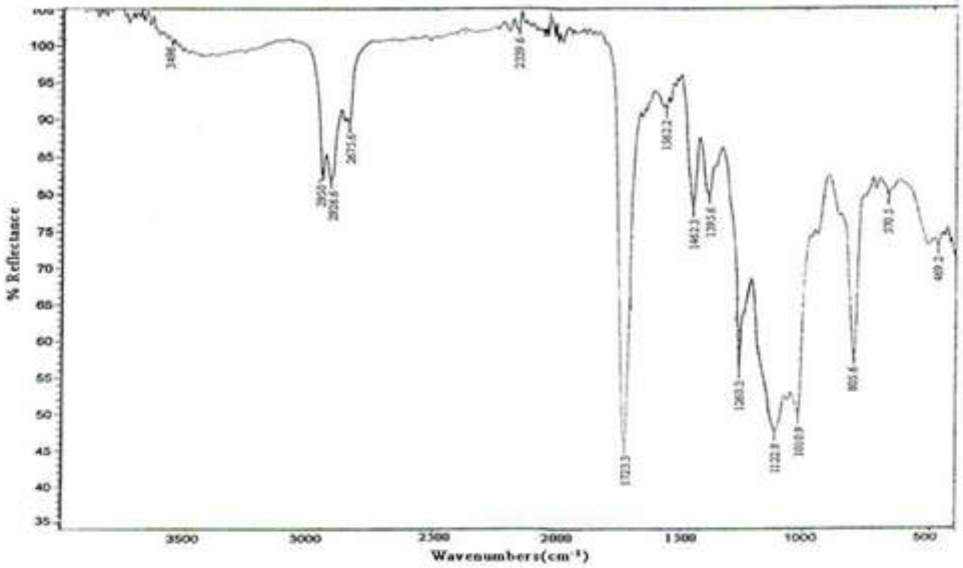

Figure 5. IR spectrum of AELO resin with TEGMA polymer

3.2 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 polymer [AELOTEGMAWF] made by AELO resin, wood flour and TEGMA than polymer [AELOTEGMA] made by AELO resin and TEGMA. 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 [19].

Table 2. Mechanical properties of Polymers

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

Fig 6 shows the stress and strain behaviour of the bio polymers. Higher stress strain behaviour obtained in biopolymer made by using wood flour (AELOTEGMAWF) than biopolymer made by pure monomer (AELOTEGMA). 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 biopolymers.

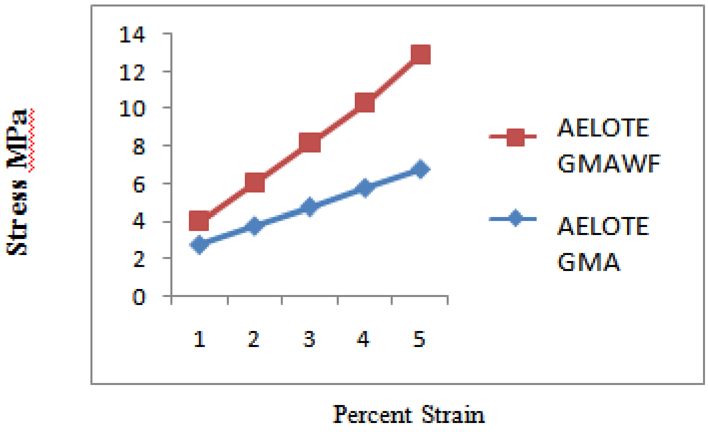

Figure 6 Mechanical properties of biopolymers

3.3Thermal properties

3.3.1.TGA analysis

All the samples were subjected to themogravimetric analysis. The biopolymer AELOTEGMAWF shows improved thermogram than AELOTEGMA. The initial decomposition temperature of AELOTEGMAWF was observed at 310˚C but AELOTEGMA 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 CH_3 and OH on the side chain .The biopolymer AELOTEGMA was more stable up to 430˚C after the addition of wood flour AELOTEGMAWF 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 biopolymers in oxydegradative manner.

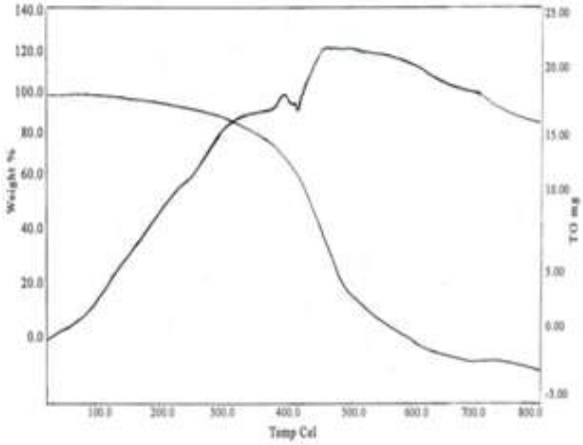

Figure. 7 TGA-DTA curve of AELOTEGMAWF

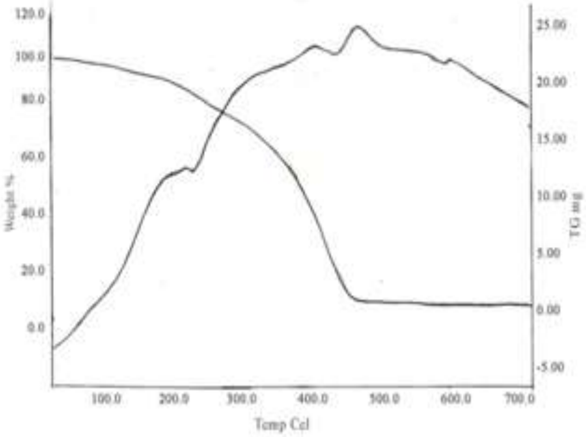

Figure .8 TGA-DTA curve of AELOTEGMA

3.3.2 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	**1st exotherm**	**2nd exotherm**
AELOTEMA	230	420
AELOTEMAWF	410	520

3.4 Biodegradation Test

In soil burial degradation the effect of microorganisms arises on the surface of the polymer film [20, 21]. 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. Kikmura 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 [22]. Fig.9 shows the SEM micrograph of polymeric samples before and after soil burial test. Figure 9 shows the SEM micrograph of polymeric samples before and after soil burial test.

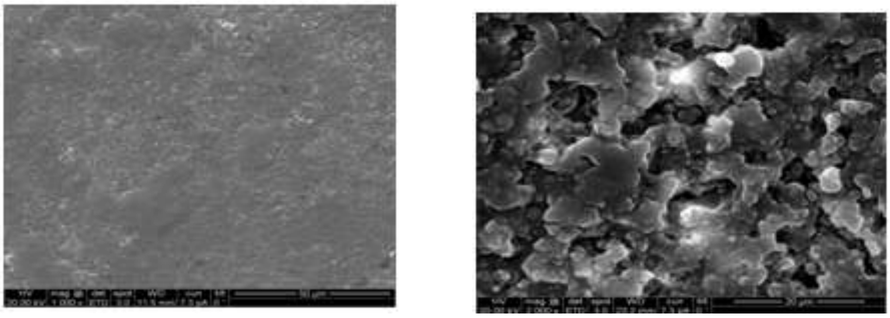

Fig **9(a) AELOTEMA before soil burial** **AELOTEMA after soil burial**

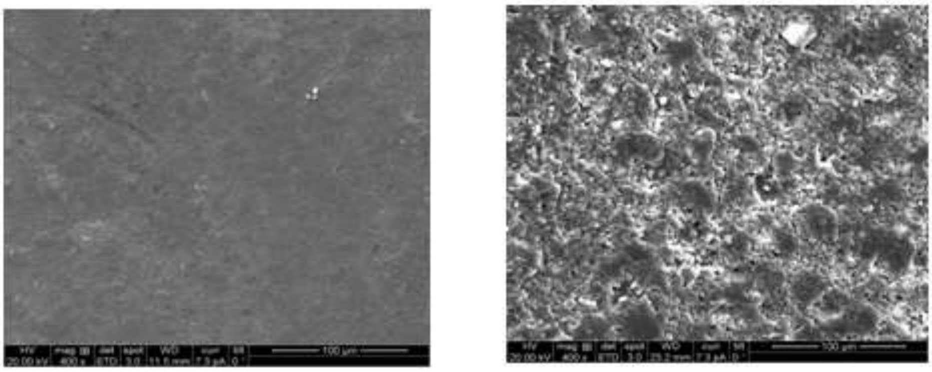

Fig 9(b) AELOTEMAWF before soil burial **AELOTEMAWF after soil burial**

IV. 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 linseed 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 biopolymers are various consumer applications like horticultural containers, packaging, automobiles, building construction, electronics and biodegradable agricultural films.

References

[1] M. Eissen J.O. Metzger, E. Schmidt, U. Schneidewind, Angew. Chem. 2002, 114, 402-25; *Angew. Chem. Int.* Ed, 2002, 41, 414 - 436.

[2] L. N. Padma, *Polym Rev*.2000, 40, 1-21.

[3] E.A. Macgregor, C.T. Greenwood, *polymers in Nature*, *John wiley & sons, New York*, 1980.
[4] *Industrial uses of vegetable oils* (Ed;S.Z.Erhan) AOCS press, champaign, IL, 2005.
[5] F.S . Guner, Y. Yagci. and A. T. Erciyes *prog polym Sci*, 2006,31,633-670.
[6] V. Sharma and P.P. Kundu, *Prog Polym Sci*, 2006,31,983-1008.
[7] Y. Lu and R.C. Larock, *chem. Sus chem*., 2009, 2, 136-147.
[8] Juan Carlos Ronda, Gerard Lligadas, Marina Galia, Virginia cadiz, *Eur J Lipid sci Technol.*, 2011, *113(1)*, 46-58.
[9] A.K. Mohanty, M .Misra, L.T. Drzal, S.E. Selke, B.R. Harte, G. Hinrichsen *in Natural Fibers, Biopolymers and Bio composites* (Eds: A.K. Mohanty, M. Misra L.T. Drzal) CRC Press, F.L. Boca Raton. 2005, PP.1-36.
[10] S.J.Park, F.L. Jin and J.R.Lee, *Macromol Rapid Comm*. 2004, *25(6)*,724-727.
[11] Milton sack and H.C.Wohlers, *J. Am.oil chem... Soc*.36; 1959; 623-627.
[12] A. Cunningham, A. Yappa and U.S. Patent. 1974, 382-993.
[13] T. Eren and S.H.kuisefoglu and R.J.wool, *Appl polym Sci*..2003, *90(1),* 197-202.
[14] T. Eren and S.H. kuisefoglu and R.J. wool, *Appl polym Sci*..2005, 97, 2264-22732.
[15] O.P. Lamba, S. Lal, M.C. Yappert, M.F. Lou, and D. Borchman , 1994. *Free radical biology and medicine*, *16(5)*: 591-601.
[16] J.A. Oaleye , and C.L. Orjiekwe ,1995. *Ind. J.Chem . 34a* 310-312.
[17] J.A. Obaleye and C.L. Orjiekwe, 1992. Synth. *React. Inorg. Met.Org. Chem, 22(7);* 1019-1029.
[18] L. Karunanayake and P.N.Fernando. J, 2006, J.Natn.Sc.Foundation Srilanka, 34(2) ; 97-102.
[19] Y.W. Mai, Z.Z. Yu, *Polymer nanocomposites,* Woodhead and CRC, F.L. Boca Raton, ,2006.
[20] B.D. Ahn, S.H. Kim, Y.H. Kim, J.S. Yang, *J Appl Polym Sci*.82; 2001:2808-2826.
[21] S.H. Lee, S.W. Lim, K.H. Lee, *Polym Int.48(9);*1999:861-867.
[22] M. Kikmura, K. Toyota, M. Jwatsuki, H. Sawada, *Proceedings of the third international scientific worship on biodegradable plastics and polymers,* Osaks Japan 1994; 92-109.