

Studies and Development of Polymeric Materials from Acrylated Epoxidized Olive Oil

J. Johnsy Rose¹ & Dr. S. Begila David²

¹Research Scholar & ²Assistant Professor (Research Supervisor)
Department of Chemistry, Scott Christian College (Autonomous), Nagercoil,
Affiliated to Manonmaniam Sundaranar University, Abishekapatti,
Tirunelveli – 627 012, Tamil Nadu, India.

Abstract

The polymers are obtained from natural oils. These are generated from renewable natural sources. The plant oil like olive oil is obtained from the fruit of olea europaeo family oleaceae. This study concerns with the preparation and properties of a biodegradable polymers from olive oil was carried out. In this work, polymers were obtained by thermal polycondensation technique on the effect of olive oil based acrylated epoxidized resin with monomers such as methylacrylate, tegma with addition of catalyst. The oil, prepared epoxy resin and acrylated epoxidized resin were characterized using FTIR (Fourier-Transform Infrared Spectroscopy) and ¹H NMR (Nuclear magnetic Resonance) spectroscopy. Newly synthesized copolymers were also characterized by solubility studies, TG-DTA, (Thermo Gravimetric – Differential Thermal Analysis) and mechanical analysis, SEM analysis, and chemical studies.

Keywords: Biodegradation, Epoxidization, Acrylation, Methlacrylate (MA), Triethylene glycoldimethacrylate (TEGMA), Olive Oil.

1. INTRODUCTION

Plant oils are triglycerides of fatty acid. Olive oil mainly composed of the mixture of triglyceride esters of oleic acid and palmitic acid.

A technological improvement in the industrial production of olive oil seems to be represented by the manufacturing procedure with considers the use of stoned olives.^{1,2} The benefits of the destoning process the phenolic compounds have been shown in some studies.³ Many enzymes of degradation that are present in stones, in fact, once removed, do not affect the phenolic heritage of the oil during the process of extraction, preserving the antioxidant profile. Also, higher amounts of volatile compounds were observed for oil produced from stoned olives.⁴

Nowadays, there is a growing interest to produce biopolymers. Oil based bio polymers have many advantages compared with polymers prepared from petroleum based monomers. Recently bio based, thermosetting polymers from vegetable oils, such as an epoxy olive oil, epoxy sunflower oil etc have been synthesized in several possesses functional epoxie group which can be react with suitable curing agents to form an elastomeric net work.⁵ Epoxidized fatty oil and their derivatives have showed a promising effect when used as reactive resins, since the oil contains unsaturation that can be chemically modified through simple reactions. These reactions permit to introduce polymerizable groups^{6,7} as epoxy or acrylates which are available give products with practical useful properties and characteristics.^{8,9}

2. EXPERIMENTAL

2.1 Materials Used

Commercially available olive oil was used.

The chemicals like Hydrogen peroxide (H_2O_2), glacial acetic acid, Sulphuric acid, Acrylic acid, Triethyl amine and Benzene were used.

The monomers such as methylacrylate and Triethyleneglycosdimethacrylate (TEGMA) were purchased from Sigma-Aldrich Chemical Co. and used as such.

2.2 Formation of Epoxidized Olive Oil

Olive oil was epoxidized using glacial acetic acid with H_2O_2 were placed in 250 ml round bottomed flask and the mixture was heated to $80^\circ C$ for 12 hours. The mixture was separated using separating funnel and the epoxy resin is collected in a beaker.

2.3 Formation of Acrylated Epoxidized Olive Oil

The epoxidized olive oil was then acrylated using acrylic acid. Triethylamine was used as catalyst and benzene as solvent. The reaction mixture was again refluxed about 20 minutes at $80^\circ C$ - $100^\circ C$ under constant agitation in nitrogen atmosphere and collected in the beaker to produce acrylated epoxidized olive oil (AEOO).

2.4 Synthesis of Polymers from Olive Oil

Acrylated epoxidized resin of olive oil were co-polymerized with co-monomers like Methylacrylate (MA) and Triethyleneglycosdimethacrylate (TEGMA). Benzoyl peroxide was used as the initiator and N,N^1 dimethyl aniline as the accelerator. The mixture was casted on clean silicon oil spread glass plate cured for 1 hour at $100^\circ C$. All the cured materials showed high toughness, elastometric and good transparency. The acrylated epoxidized olive oil (AEOO) was prepared using the olive oil shown by the Figure 1.

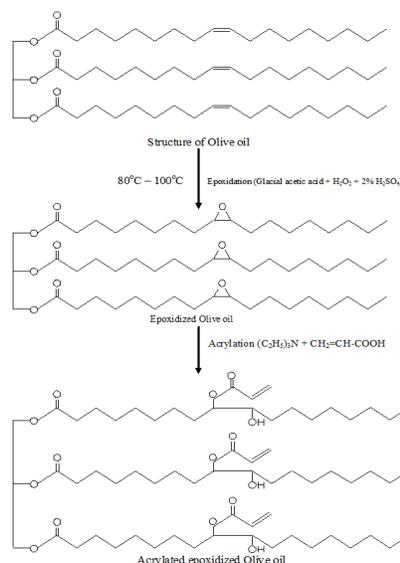


Figure 1: Synthesis of Acrylated epoxidized olive oil resin

2.5 Characterization Techniques

2.5.1 Spectral studies

FTIR spectra of the polymers were obtained using THERMO NICOLET, AVATAR 370 FTIR SPECTROMETER with KBr crystal in the range of $4000-400cm^{-1}$ at $27^\circ C$. 1H -NMR spectra of the oil, epoxidized resin and acrylated resin were dissolved in $CDCl_3$ and recorded using BRUKER AVANCE111400MHz FT NMR SPECTROMETER. The chemical shift in ppm for 1H -NMR Spectra were obtained relative to Tetra Methyl Silane (TMS) as internal reference.

2.5.2 Thermal analysis

Thermal studies of the polymers was determined by TG-DTA analysis. Thermo gravimetric analysis (TGA) was performed by perkins elimer thermo gravimetric analyzer over the temperature ranging from 30°C to 700°C at a heating rate of 10°C/min under nitrogen gas atmosphere.

2.5.3 Mechanical Studies

The tensile strength of the polymers prepared were determined using dumb-bell shaped cut from the specimen using Instron UTM, 10 ton static universal testing machine. The values represented were the mean of about 3-4 samples. The new polymeric material exhibited tensile stress strain behaviour relatively to plastics. The cross link densities were determined from the rubbery modulus plateau based on the theory of rubber elasticity $E^1 = 3\nu_e RT$.^{10,11} Where E^1 in the storage modulus no of cross linked co-polymer in the plateau region. R in the universal constant (8.314 J-mol⁻¹.K⁻¹) and T is the absolute temperature.

2.5.4 Biodegradation – Soil burial Tests

Biodegradation of polymers were studied by soil burial test. For the soil burial test the replicates pieces of the sample (5x3cm) were buried in the garden soil at the depth of 30cm from the ground surface for 3 months, inoculated with the sewage sludge having ability to adhere and degrade the polymer film.¹² 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 by measuring the weight loss after 30 and 60 days which is calculated using the relation.¹³

$$\text{Degree of biodegradation, } D = \frac{W_o - W_t}{W_o} \times 100$$

Where,

W_o - weight of original film.

W_t - weight of residual film after degradation for different time.

2.5.5 Chemical Resistance

Chemical resistance of the newly prepared polymer samples were studied by immersing the polymer sample in various solvents such as CCl₄, CHCl₃ diethyl ether, toluene and DMSO measuring the dimensional changes after 1 week and 4 weeks. The weight loss also measured after 45 days.

3. RESULTS AND DISCUSSIONS

3.1 Spectral analysis

3.1.1 FT-IR Spectra

The FT-IR Spectroscopy is a rapid, non-destructive technique that has been widely applied in the characterization of different functional groups with characteristic absorption bands in infrared region of the electromagnetic spectrum.^{14,15} The FT-IR spectra of olive oil epoxidized resin and acrylated epoxidized resins are shown in the figures 2,3 & 4. The oil composition affects the exact position of the band and yield shifts when the proportion of the fatty acid changes.

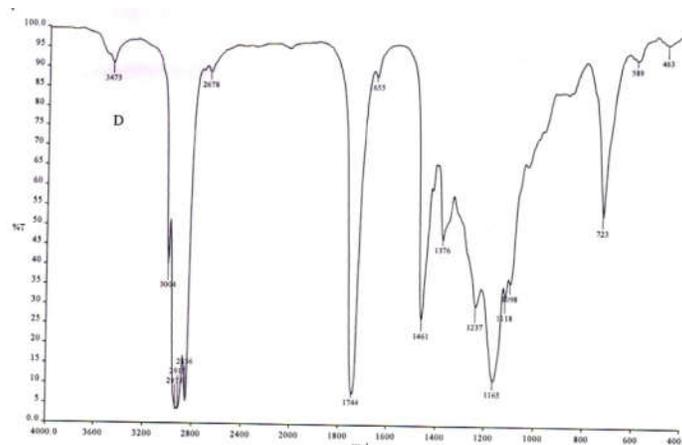


Figure 2: FT-IR Spectra of Olive Oil

In FT-IR Spectrum of olive oil, the peak at 3004 cm^{-1} , 2933 cm^{-1} and 2856 cm^{-1} corresponds to $-\text{CH}-$ stretching frequencies of olefinic, methylene and methyl groups. The infrared data was determined at room temperature and reported pervious by Obaleye and Orjiekwe.^{16,17} The Olive oil sample shows a very strong and sharp band at 1744 cm^{-1} due to the ester group. The peak at 1461 cm^{-1} , 1165 cm^{-1} , 723 cm^{-1} corresponds to the bending vibrations of methylene and methyl groups.

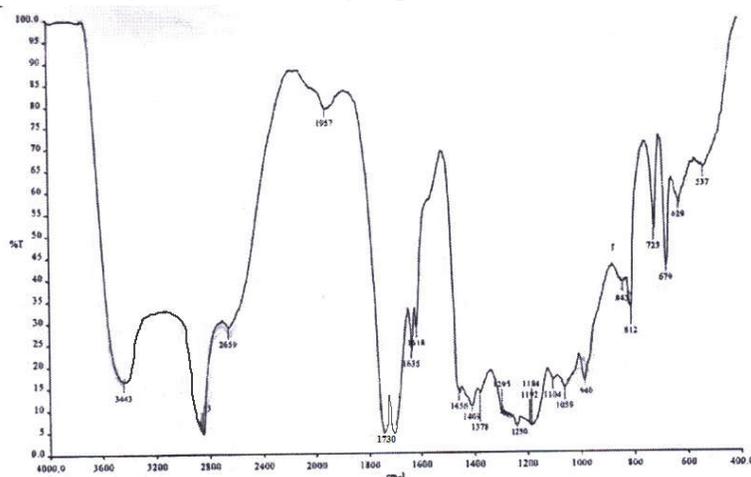


Figure 3: FT-IR spectra of Epoxidized resin

The epoxy group showed three characteristic absorption bands, ($1240\text{-}1250\text{ cm}^{-1}$, $925\text{-}860\text{ cm}^{-1}$ and $865\text{-}785\text{ cm}^{-1}$). The epoxy groups gave the band at 1250 cm^{-1} and 950 cm^{-1} , because of the symmetric and asymmetric ring stretching.¹⁸ The IR spectrum of epoxy resin (fig 3) shows peak at 1250 cm^{-1} is small, it corresponds to the epoxy group formation. The region of other two bands appear at 946 cm^{-1} and 723 cm^{-1} in the epoxy resin corresponds to the stretching vibration of $-\text{CH}-$ and $-\text{CH}_2-$ groups. The epoxy resin also shows carbonyl band of triglyceride ester group at 1742 cm^{-1} and in acrylated epoxy resin and 1730 cm^{-1} .

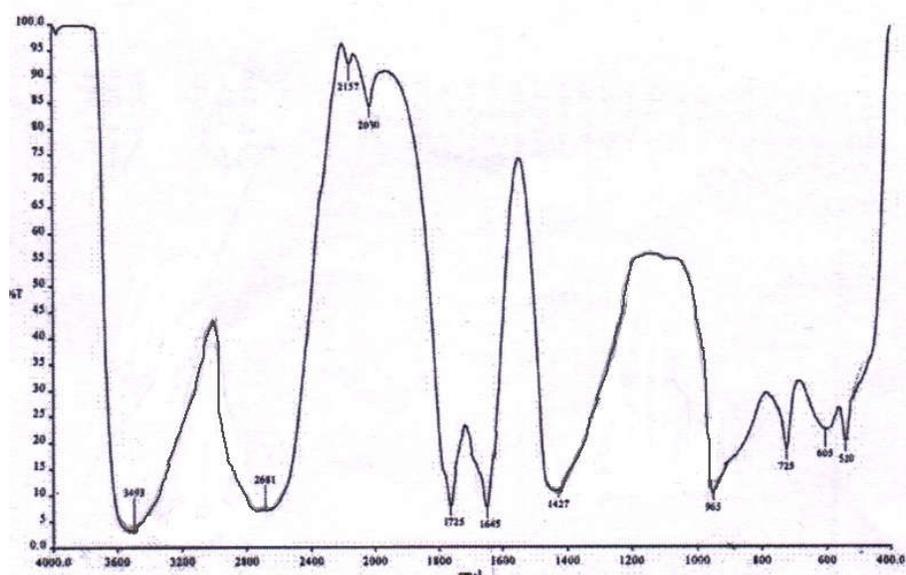


Figure 4: FT-IR Spectra of acrylated epoxidized resin

The FT-IR spectra of acrylated epoxidized resin shows that the epoxide group completely converted into acrylated functionality. This is indicated the presence hydroxyl functionality of resin at absorption band of 3493cm^{-1} associated with hydrogen band of $-\text{OH}$. A strong absorptim band at 1725cm^{-1} indicating the acrylated epoxidized compound formation. Another different absorption band at 1645cm^{-1} indicating the vinyl functionality ($-\text{CH}=\text{CH}_2$). The presence of vinyl functionality of acrylated resin in supported by the absorption peak at 965cm^{-1} as vinyl carboxyl group ($\text{CH}_2=\text{CH}-\text{CO}-\text{O}$). The band in the far IR region at 590cm^{-1} and 370cm^{-1} are also reported.¹⁹ The bands are observed at 605cm^{-1} in oil and 520cm^{-1} in acrylated epoxidized resin due to symmetric stretching vibration of alkyl group.

3.1.2 ^1H NMR Spectral analysis

^1H NMR spectra of olive oil, epoxidized resin and acrylated epoxidized resins are shows in figures 5,6 & 7.

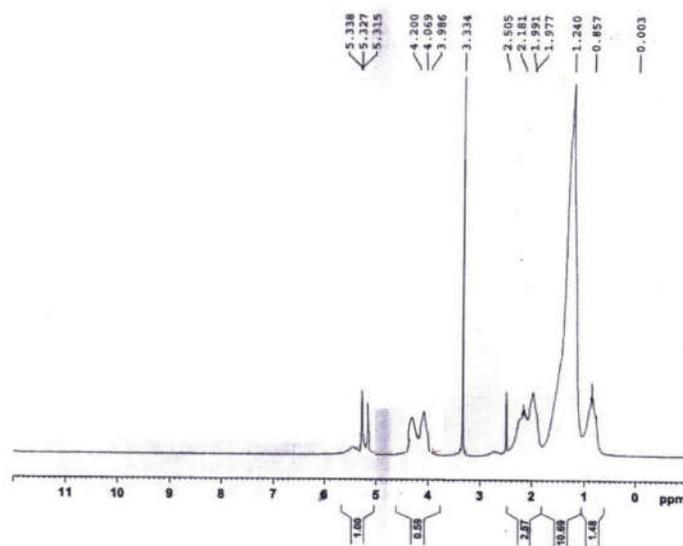


Figure 5: ^1H NMR Spectra of Olive Oil

In the ^1H NMR spectra of olive oil, the peak at 0.857 ppm corresponds to the hydrogen of the ending methyl groups $(-\text{CH}_2 - \text{CH}_3)$. Peak at 1.2 ppm originate from aliphatic methylene hydrogen $(-\text{CH}_2)-$.²⁰ The peak at 2.1 ppm corresponds to allyl hydrogen $(-\text{CH}_2 - \text{CH} = \text{CH}-)$. The peak at 4.06 to 4.2 ppm due to methylene hydrogen from the glyceride moiety.²¹ The peak at 5.31 to 5.33 ppm corresponds to the unsaturated vinylic hydrogen.²²

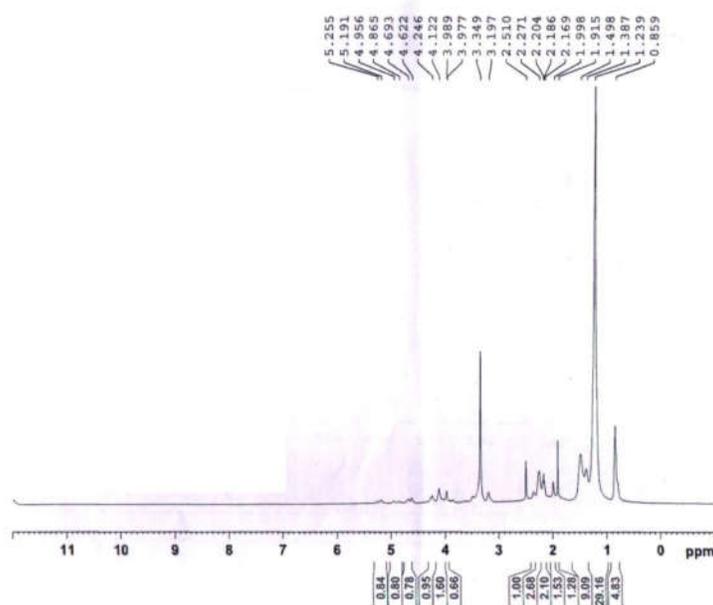


Figure 6: ^1H NMR Spectra of epoxidized resin

In the ^1H NMR spectrum of epoxidized resin showing that the double bond is replaced by epoxy group. These peaks were disappeared but reappeared in the acrylated epoxy resin due to the presence of unstated group in fig (4.7). The peak corresponds to the epoxy group were appeared at 2.5 ppm. The peak at 3.1 ppm to 3.3 ppm indicates $-\text{CH}-$ hydrogen between two epoxy groups and peak at 1.4 ppm corresponds to $-\text{CH}-$ hydrogen adjacent to epoxy groups.

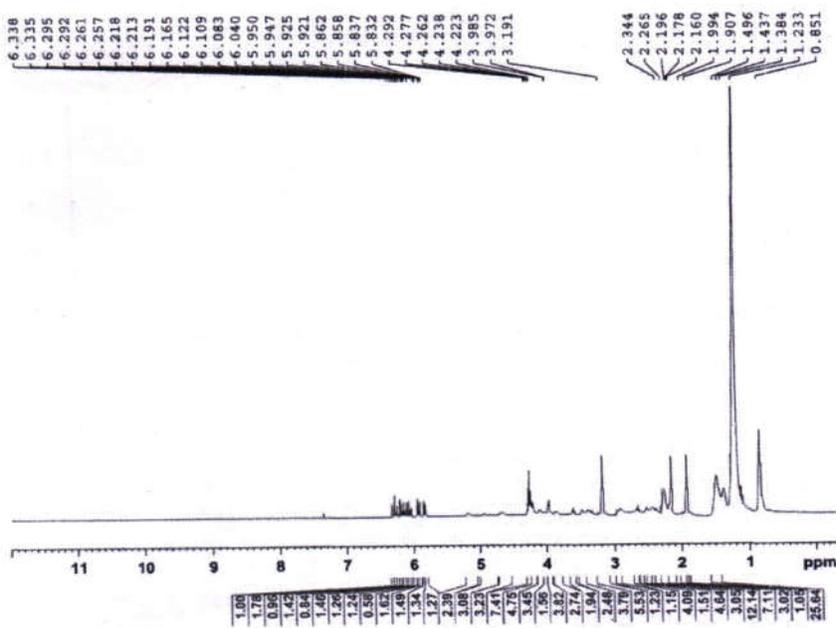


Figure 7: ^1H NMR Spectra of acrylated epoxy resin

In the ^1H NMR spectrum of acrylated resin showing that the esterification reaction take place between the epoxidized olive oil and acrylic acid in the presence of triethyl amine, epoxide resins react with carboxylic acid to form esters. In acrylated epoxidized resin, the epoxide group 2.5ppm is disappear and was this peak was shifted 3.1ppm, due to the deshielding effect of hydroxyl and carboxylate ester linkages. The strong peak at 1.3ppm is attributed to the long chain (more than 5 methylene groups).²³ The peak at 0.85 to 2.3 ppm is due to the long aliphatic side chain.

3.2 Thermal analysis

Thermogravimetric analysis (TGA) was used to investigate the thermal stability of the polymers. Figures 8 and 9 are the TG-DTA curves of OLIAEMA and TEGMA which show the decomposition behavior of the polymers samples under nitrogen atmosphere. The bulk polymer is thermally stable under 100°C followed by the decomposition temperature region 100°C – 250°C Stage [1], 250°C – 450°C stage [2], above 450°C [stage 3]. The first decomposition step [stage 1] of the bulk polymer is mainly due to evaporation and decomposition of unreacted free oil. The decomposition temperature of the highly cross linked polymer is above 400°C at the heating rate of 20°C /min, approximately that of stage 2 of the decomposition of the bulk polymer. This steps corresponds to degradation and char formation of the cross linking polymer network. Above 460°C in the char residues gradually oxidize to the air. Therefore the last temperature region is same for all the polymers.

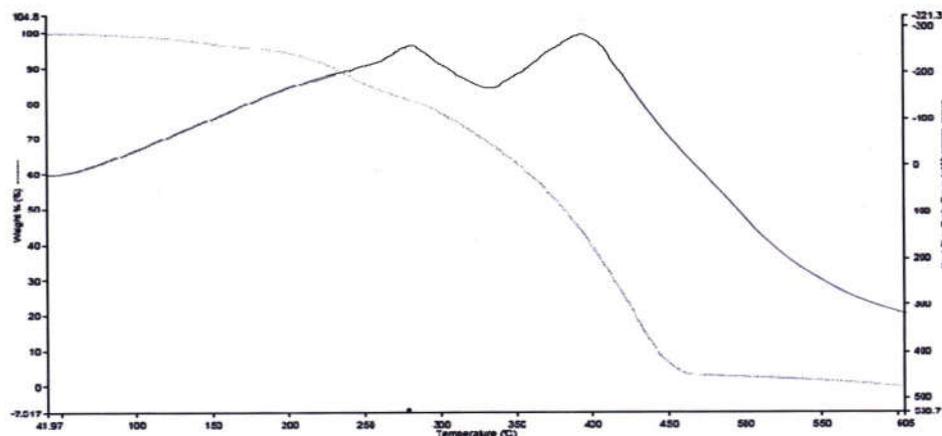


Figure 8: TG-DTA curve of olive oil methyl acrylate

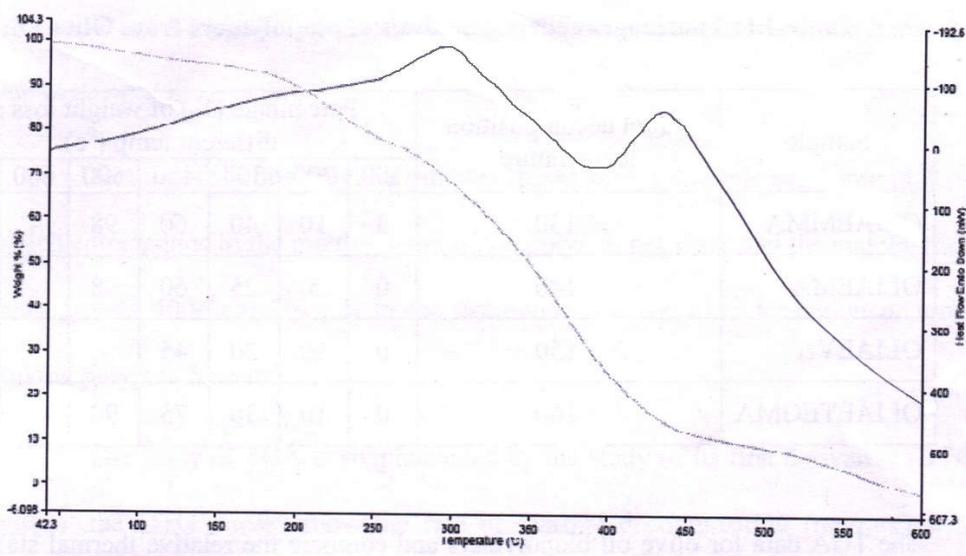


Figure 9: TG-DTA curve of olive oil TEGMA

The DTA curve of OLIAEMA polymer sample shows an endothermic peak around 320°C which corresponds to the melting point of the polymer network and 2 exotherms are seen in the samples. The first exotherm around 280°C which corresponds to the cleavage of long alkyl side chain. The second exotherm around 420°C in sample is strong and it corresponds to the decomposition and char formation of cross linking polymer network.

Similarly the DTA curve of OLIAETEGMA polymer sample show an endothermic peak around 400°C which corresponds to the melting point of the polymer network and 2 exotherms are seen in the sample at 250°C and 450°C. Comparing to the DTA curves, the melting point of OLIAETEGMA was slightly greater than OLIAEMA polymer.

3.3 Mechanical Properties

The mechanical properties of thermosetting polymers such as tensile strength, percentage of elongation, young's modulus, shore 'D' hardness are shown in Table 1.

Table 1: Mechanical Properties of polymers

Polymer Sample	Cross link density (X10 ⁻³)	Mol. Wt. between cross links (mol ⁻¹)	Tensile Strength ×10 ⁵ Pa	% of elongation	Young's Modulus ×10 ⁵ Pa	Shore D hardness
OLIAE50MA50	2.58	387	5.27	0.37	179	56.2
OLIAE75MA25	2.40	416	5.41	0.41	123	55.2
OLIAE25MA75	2.59	398	5.33	0.39	127	54.2
OLIAE50TEGMA50	3.93	254	27.38	7.01	273	60.5
OLIAE75TEGMA25	3.85	259	27.41	7.13	268	60.1
OLIAE25TEGMA75	3.94	254	27.21	6.96	254	57.7

In the above Table 1, the polymer samples like MA and TEGMA with different concentrations are given.

From the data, it is clear that the polymer samples prepared from these polymers, OLIAETEGMA has high tensile strength and high young's modulus and OLIAEMA polymer has low tensile strength and low young modulus. It is observed that the tensile strength and young modulus of elasticity of the polymers increases with increasing cross link density.

3.4 Biodegradation – Soil burial Test

Biodegradation of the polymer samples prepared by the free radical copolymerization of olive oil acrylated epoxidized resin with various concentration monomers like MA and TEGMA are reported in Table 2.

Table 2: Percentage of Biodegradation of polymer sample from olive oil

Polymer Sample	Degree of Biodegradation %	
	30 days	60 days
OLIAEMA	4.42	9.7
OLIAE. TEGMA	2.54	6.6

From the data obtained by soil burial test, it is known that the extent of biodegradation increases with decreases the concentration of monomers. From this data biodegradation is high in OLIAEMA and low biodegradation in OLIAETEGMA polymer.

SEM Analysis

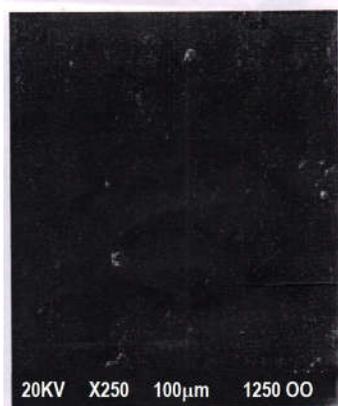
SEM is commonly used for studying both the surface morphology, and cellular response of bio materials. Figure 10 shows the SEM micrographs of the polymer OLIAEMA, OLIAETEGMA.



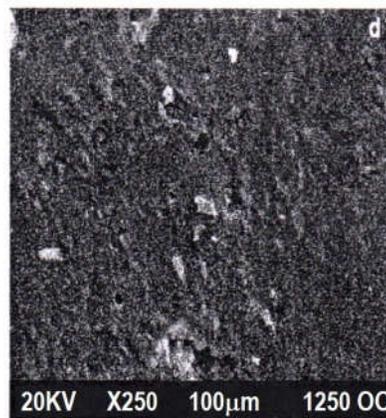
SEM Micrograph of OLIAEMA (Before)



SEM Micrograph of OLIAEMA (After)



SEM Micrograph of OLIAETEGMA (Before)



SEM Micrograph of OLIAETEGMA (After)

Figure 10: SEM Micrographs of Polymers before and after soil burial test

3.5 Chemical Resistance

The extent to which polymers are subjected to attack by chemical is determined by a number of parameters, related both to the chemical and the polymer involved. Chemical resistance of newly prepared polymer samples were studied by immersing the polymer samples in various solvents such as CCl_4 , Toluene, CHCl_3 , diethyl ether, DMSO and measuring the dimensional changes after 1 week and 4 weeks. The weight loss also measured after 45 days. All the polymeric samples prepared are highly stable but undergoes slight degradation in Toluene, CHCl_3 , diethyl ether, DMSO and CCl_4 (Table 3) due to their fragility. The polymer samples are higher chemical resistance and they are biodegradable.

Table 3: Weight loss of polymers in various solvents

Solvents	Weight loss % in 45 days	
	OLIAEMA	OLIAETEGMA
Toluene	4.5	2.3
Diethyl ether	4.09	2.5
CCl_4	5.74	3.8
CHCl_3	4.5	3.5
DMSO	4.39	2.6

The Comparison of stability of polymers OLIAEMA and OLIAETEGMA towards various chemicals is shown in Figure 11. The data shows that polymers in olive oil (OLIAEMA) has low chemical resistance than the other polymer OLIAETEGMA.

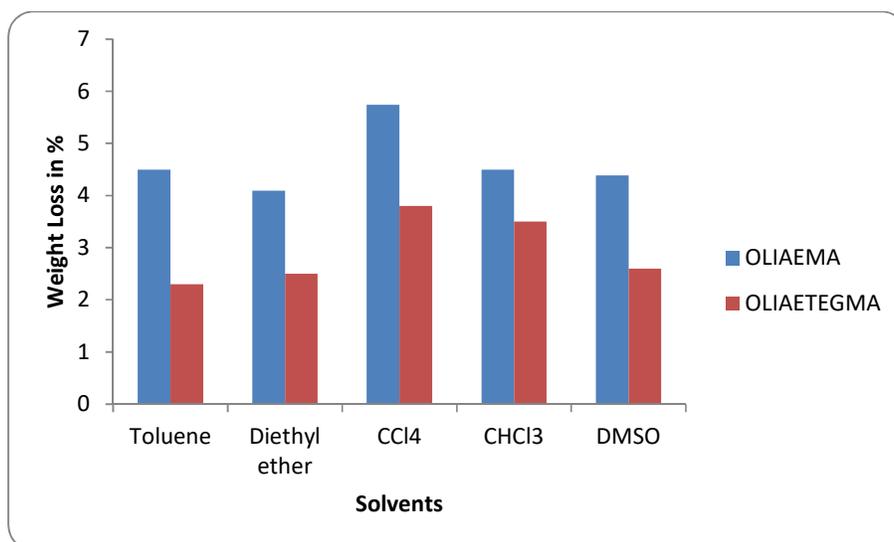


Figure 11: Chemical resistance of polymers in various chemicals

3.6 CONCLUSION

Plant oils are predominantly made up of triglyceride molecules. The olive oil from plant is a non volatile oil having number of excellent properties. The new polymeric samples like OLIAEMA and OLIAETEGMA prepared from acrylated epoxidized olive oil resins. From this polymers OLIAETEGMA has high tensile strength and high young modulus. This indicates the sample is very hard and flexible like plastics. The sample like OLIAEMA has low tensile strength and young modulus, indicates that the sample is soft and rubbery. It is also observed that the hardness of the polymers increases with increasing cross link density.

The soil burial test shows that the polymer samples prepared are slight biodegradable the chemical analysis shows that the polymer samples are highly stable.

REFERENCES

- [1] Amirante R. cini E, Montel GL, Pasquolone A (2001). Influence of mixing and extraction parameters on virgin olive oil quality grasas. *Y Aceites* 52, 198-201.
- [2] Frega N, Cagtioti L, mozzon in (199) oil extracted from olives pitted olivo and olio 12, 40-44.
- [3] De Nilo A, D: Donna L, mozzotti F, Sajjad a, Sindona G, etal. (2008). Oleuropein expression in olive girls produced from drupes stoned in a spring pitting apparatus food chem. 106, 677-684.
- [4] Amirante p. Gloodeveo ml, DugoG, leone A. Tamborrino A (2006) Advance technology in virgin olive oil production from traditional and elestoned pastes. *Food chem.* 98, 797
- [5] Shrikant N, and khol L, *J sci* 2001, 83, 703.
- [6] Raghavachar R. Sarneck G. Baghdach J and massingill J. *Jeoat Tech* 2000, 72, 125.
- [7] Biermann U, Friedt W, Lang S, et al *Angewandte Chemie int edn*, 2000,39,220.
- [8] Hilker I Bothe D, Press, J and Warnock H. *chem.. Eng Sci.* 2001, 56, 427.
- [9] Scala J stands J, Orlick J et al *polymer* 2004, 45, 7729.
- [10] Hory P.J. *Principles of Polymer Chemistry* Cornell University press Ithaca (1958).
- [11] Nielse L.e. Landel R.F. *mechanical Properties of polymers and composites* Marcel dekker new York (1994).
- [12] M.N Belgacem and A. Gandini in *Monomers Polymers and composition from renewable resonicesed* Amstar of am 2008, pp 39-66.

- [13] *M. Karunanithi, R. Nanthini, A. Ravi and V. Jai Sankar Synthesis and characterization of biodegradable aliphatic polyester. Asian journal of chemistry, vol.22 No.10 (2010)7699-7705.*
- [14] *Jualumnukal N and Intarat R. J metals, matter, minerals 2006, 16, 53.*
- [15] *Hendlo, howeu I Lowery I and Jones anal clinica acta 2001, 427, 75.*
- [16] *Obaleye JA and Orjiekwe C.L 1995 Int. J. Chem 34a, 310-312.*
- [17] *Obaleye, Ja and Orjiekwe, C.L. 1992 Syn. Reaw Inorg met org chem., 27(7) 1019-1029.*
- [18] *Vegirkahraman M, Gulay Bayvamoğlu Wilhan Kayaman Apohan and Atilla Gungor. J. Relative and functional polymers 2007,67,97-103.*
- [19] *May C.A and Tanaka Y. Epoxy resin Chemistry and Technology, mareel Deekev Inc. New York 1973, P.677.*
- [20] *Mythili C.V, Malar retna, and Gopalakrishnan S. 2004 J. Material Science 27; 235-241.*
- [21] *Li, F Hanson, M.V. Larock, R.C. 2001. J. Polymor, 42. 15667-1579.*
- [22] *Kyu-wan Lee, Bai Xue mei: Quan Bo, Young wenlim, keun-woo chang; yohan Han, Inf Engg. Chem 2007, 13(4): 530-536.*
- [23] *Mythili C.V, Malar Retna A, and Gopala Krishnan & J. Mater Sci. 2004, 27, 235-24.*