



Synthesis and Characterisation of Novel Cross Linked Biopolyesters from Olive Oil as Eco-friendly Biodegradable Materials

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Abstract: Novel cross linked biopolyesters were synthesised from naturally available olive oil, oligomeric polytriglyceride fumarate (*o*-PTF) was prepared by glycerolysis of the olive oil followed by condensation with maleic anhydride. The (*o*-PTF) was characterised by spectral (FTIR, UV, NMR) and physicochemical properties (specific gravity, viscosity, saponification value, iodine value). The molecular weight of *o*-PTF was estimated using gel permeation chromatography (GPC). The cross linked biopolyesters were prepared by treating *o*-PTF of olive with *N*-vinyl-2-pyrrolidone and vinyl acetate. The cross linked biopolyesters were evaluated for spectral properties (FT IR), cross linked density, thermal properties, mechanical properties and biodegradation. The potential antifungal and anti bacterial activities of the newly prepared biopolyesters were evaluated. The environment degradation was assessed by soil burial test. The outcome of the studies has revealed that the newly prepared cross linked biopolyesters are potential biodegradable material for various consumer application like package materials and agricultural applications.

Keywords: Biopolyesters, Olive oil, *N*-Vinyl-2-pyrrolidone, Vinyl acetate

Introduction

The replacement of petroleum-based raw materials by renewable resources constitutes a major contemporary challenge in terms of both economical and environmental aspects¹.

Natural vegetable oils are considered to be one of the most important classes of renewable sources because of the wide variety of possibilities for chemical transformations, universal availability and low price and they are preferred by the chemical industry as alternative²⁻⁴. The main components of the triglyceride vegetable oils are saturated and unsaturated fatty acids which in its pure form are also available as platform chemicals for polymer synthesis^{4,5}. Plant oils are triglycerides (tri-esters of glycerol with long chain fatty acids), with varying composition of fatty acid depending on the plant, the crop, the season and growing conditions⁶. There has been renewed interest recently in developing new polymers from soybean and other plant oils as offer a renewable feed stock against finite and unreliable petroleum sources. Larock *et al*⁷ have developed a family of chemically modified plant oils which can be polymerised using free radical initiators, into rigid composites, rubbers and adhesives⁷. Sperling *et al*⁸ have prepared soft rubbers from epoxidised oil cured with acid anhydrides like maleic anhydrides and used the interpenetrating networks to apply on roof tops⁸. Cross linked biodegradable polymers have been prepared from edible oils with unsaturated anhydrides or acids have useful applications as adhesives, fillers and elastomers⁹. 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 oil olive oil for the preparation of the novel cross linked biopolyesters as eco-friendly biodegradable material of various consumers application like packaging material and agricultural application.

Experimental

Olive oil purchased from Vaighai Chemical Industries Ltd Madurai, India. Formic acid (CDH), hydrogen peroxide (Rankhem), ether (Merck) maleic anhydride (CDH), morpholine (Sigma Aldrich), *N*-vinyl-2-pyrrolidone (Sigma Aldrich), vinyl acetate (Sigma Aldrich) were purchased from respective dealers. All the materials were used without purification.

Synthesis of o-PTF resins

Glycerolysis of olive oil were carried out using 30% hydrogen peroxide and formic acid, in ice water bath. The reaction was vigorously stirred over night. The resulting product was poured into a separator funnel and extracted with ether and the ether extracted product was then reacted with maleic anhydride and the mixture was refluxed for 5 h at 70 °C - 80 °C at 160 °C for 30 minutes under vacuum condition using rota mantle to yield a yellow transparent liquid *o*-PTF resins.

Synthesis of novel cross linked biopolyesters

The four biopolyesters were prepared by free radical polymerisation of *o*-PTF resin of olive oil with cross linking co-monomer *N*-vinyl-2-pyrrolidone and vinyl acetate at room temperature with benzoyl peroxide as free radical indicator and dimethyl aniline as accelerator. To prevent oxygen free radical reaction the resin was purged with nitrogen gas prior to curing and then casted on a clean silicone oil spreaded glass plate, cured for six hours at room temperature. All the cured material showed high toughness, elastomeric and good transparency.

Characterisation of o-PTF resins

The *o*-PTF resins were subjected to extensive analysis for the determination of specific gravity, iodine value and sap value as per the ISI standard 840 - 1964. The molecular weight was determined by GPC using μ styragel column, 100 A⁰ and 500 A⁰, UV detector and 280 nm filter. The *o*-PTF were analysed by UV, IR, NMR spectral analysis.

Characterisation of biopolyesters

The AT – IR spectral analysis of the four biopolyesters was done by perkin 597 infrared spectrophotometer. The Tensile strength of the biopolyesters were determined using Dumbbell shaped cut from the specimen using ISO 527 – 2:1993 (E) specimen type SA die. The values represented are an average mean of about 6-10 samples. The thermal analysis of the biopolyesters were determined by simultaneous DTA – TGA and DSC using SDT - 2960 TA instruments INC derived from ASTM E 1131 – 03.

Test for biodegradability

Soil burial test

The replicate pieces of the sample (5x3 cm) were buried in the garden soil at the depth of 30 cm 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.

Microbial studies

Bacterial adhesion and antimicrobial activity were evaluated by agar diffusion method the microbial strains used are *Escherichia coli* (gram positive bacteria) and *Candida albicans* (fungi).

Results and Discussion

Olive oil is a mixed glyceride of unsaturated components (linoleic acid, oleic 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^{11,12}. Under the present experimental conditions hydroxylation takes place at the double bonds of the triglyceride units. The reaction of hydroxylated olive oil with maleic anhydride catalysed by morpholine lead to the formation of oligomeric-poly triglyceride fumarate (*o*-PTF) resin, the analysis of these resins reveals the formation of *o*-PTF resins. The analytical data are given in Table 1, finally the cross linking of *o*-PTF resins involves the reaction of unsaturated sites in the polymer chain with a co-monomer which may be of vinyl type such as vinyl acetate and *N*-vinyl-2-pyrrolidone to form biopolyesters of olive oil.

Table 1. Physical properties

Parameter	olive oil	Gly-olive	O-PTF olive
Specific gravity gm/cc at 30 °C	0.924	0.889	0.722
Sapvalue mg KOH / gm	190.4	164.9	86.6
Iodine Index	120.32	6.72	53.72
Visosity	0.925	1.264	1.22
Mol Wt / Sap test	886	1024	1939.95
Mol wt / Cal	882	1018	1938
Mol wt (GPC)	892	1032	1946
Hydroxyl Number	-	9.72	0.723

Iodine value represents the degree of unsaturation (= bonds) in the triglyceride oil. The high iodine value of olive oil indicates the higher concentration of unsaturated compound in

the parent oil. In the hydroxylated resin iodine value is decreased drastically revealing that the double bond is replaced by hydroxyl group. The hydroxyl value determined the number of hydroxyl groups. The iodine values is increased significantly in the *o*-PTF resins due to the unsaturated fumarated side chain in the *o*-PTF resins

Saponification is applied to the hydrolysis of fatty acid ester under alkaline condition. Saponification number is used for the determination of the size, average molecular weight of the fatty acid and to estimate the non fatty impurity if present. Therefore the molecular weight of the compounds were determined from the relation $\text{molecular weight} = 168,000 / \text{Sap value}$. The molecular weight determined by this method match the calculated value. The saponification value reveals that the molecular weight of *o*-PTF resin has increased compared to the oil

Spectral analysis of o-PTF resin

The UV spectrum of olive oil shows an absorption peak at about 230 nm (ester). The UV spectrum show a shift of peak from 230 nm for oil to 259 for hydroxylated resin due to the hyper chromic effect which is attributed to the substitution of the unsaturated group. In the *o*-PTF resins the peak is again shifted back to 235 nm due to hypo chromic effect which is attributed to the distortion of geometry by the introduction of fumarate group¹³.

IR spectral analysis

The IR spectra of olive oil, HTO resins, (*o*-PTF) resins are recorded between 500 cm^{-1} to 4500 cm^{-1} (Figure 1-3). In hydroxylated triglyceride resins, the IR spectra showed a strong absorption band at 3465.84 cm^{-1} , due to the present of free -OH group in the molecule. The corresponding peak is completely reduced in the *o*-PTF resins indicates the -entire OH group get substituted. A strong absorbance band in 2925.81 cm^{-1} is due to the presence of C=O of the glycerol ester moiety. A strong band in 2854.45 cm^{-1} is due to the symmetrical -C-H bond in -CH₂-group of the side chain.

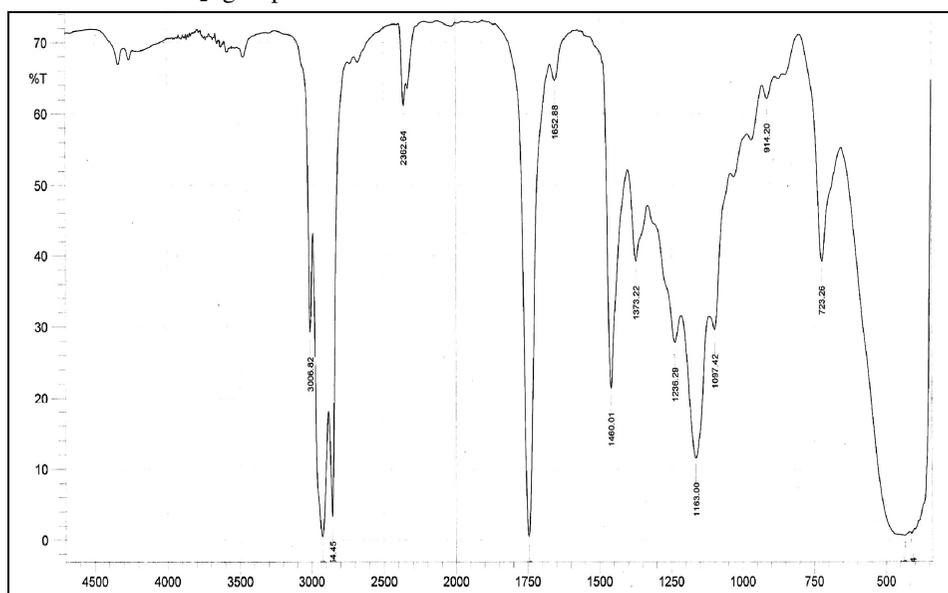


Figure 1. IR spectrum of olive oil

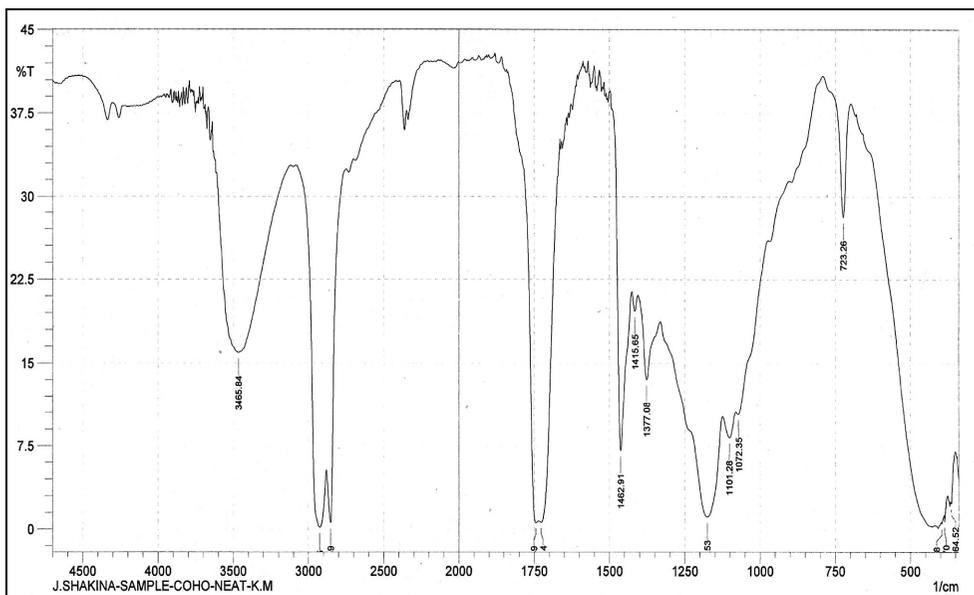


Figure 2. IR spectrum of hydroxylated olive oil

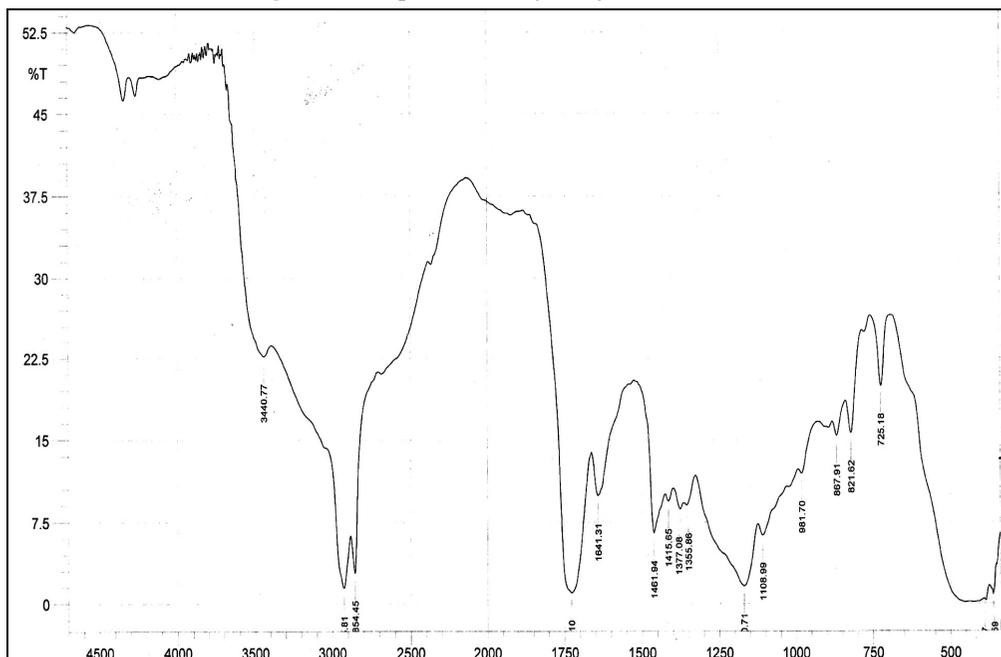


Figure 3. IR spectrum of o-PTF resin olive oil

The IR spectrum of o-PTF - olive oil -co- vinyl acetate polyesters are shown in the Figure 4. The responses at 2925 cm⁻¹ is due to the aliphatic C-H group in the chain, the peak at 1730 cm⁻¹ (C=O stretch in esters) and peak at 1454 cm⁻¹ is due to CH₂ linkages and the peak at 1372 cm⁻¹ is due to CH₃ group and 3500 cm⁻¹ is due to OH group.

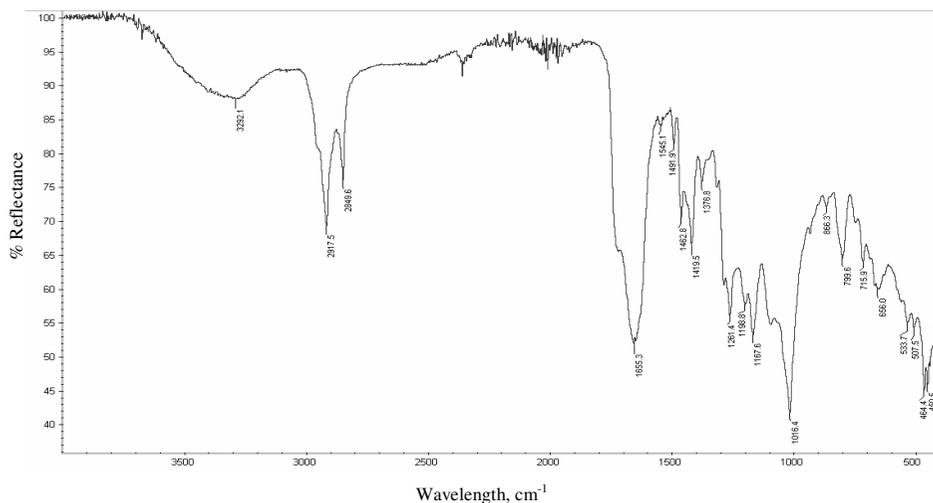


Figure 4. IR spectrum of *o*-PTF - olive oil -co- vinyl acetate polyester

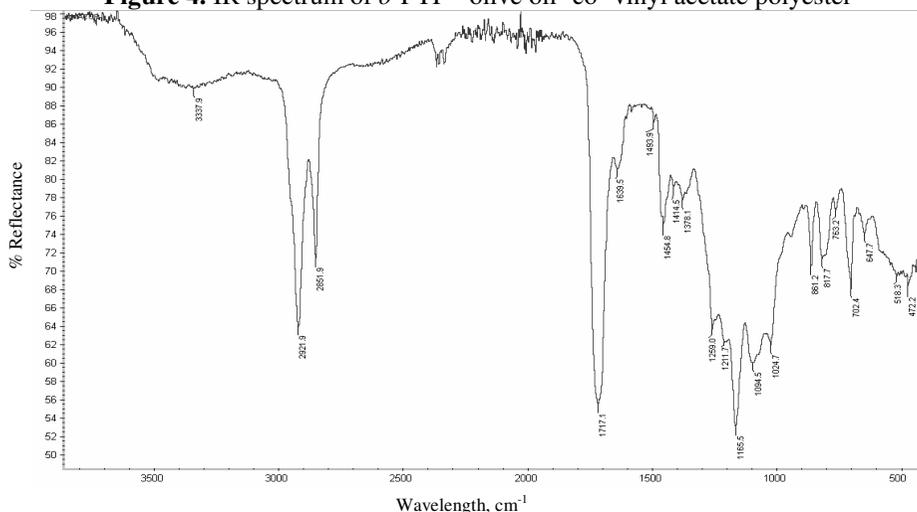


Figure 5. IR spectrum of *o*-PTF - olive oil -co *N*-vinyl pyrrolidone polyester

The IR spectrum of *o*-PTF-olive oil-co - *N*-vinyl-2-pyrrolidone biopolyesters are shown in Figure 5. The spectrum shows responses at 2924 cm^{-1} due to the aliphatic -CH groups in the chain, the peak at 1723 cm^{-1} C=O stretch in esters and peak at 1645 cm^{-1} is due to CH bending of trans CH=CH and the peak at 1021 is due to C=C stretching.

The possible peaks in ^1H NMR for quantitating unsaturated fatty acids are those of olefinic protons (5.3-5.4 ppm), protons attached to the bis-allylic carbons (2.7-2.8 ppm), protons attached to allylic carbon (2.0-2.1 ppm), methylene -CH₂- (1.2-1.4 ppm) and the terminal methyl protons (0.8-0.9 ppm) shown in the (Figure 6). The corresponding olefinic protons peak in the glycerolysis product has almost disappeared (Figure 7), showing the double bonds in oil is replaced by the hydroxyl group. This peak is shifted to 3.1-3.2 ppm in the *o*-PTF resins due to the deshielding effect of hydroxyl and carboxylate ester linkages (Figure 8).

Table 2. Chemical shift and assignment of the signal in the ^1H NMR spectrum of olive oil in pyridine- d_5 / chloroform - d solvent

Signal δ	protons	Attribution
5.40	CH=CH	All unsaturated fatty acids
5.37	CH-OCOR	triglycerides
4.22,4.42	CH ₂ -OCOR	triglycerides
2.87	CH=CH-CH ₂ -CH=CH	linolenyl and linoleyl chain
2.32	CH ₂ -COOH	all acyl chains
2.06	CH ₂ -CH=CH	all unsaturated acyl chain
1.63	CH ₂ -CH ₂ COOH	all acyl chain
1.30	(CH ₂) _n	all acyl chain
0.95	CH=CH-CH ₂ -CH ₃	linolenyl chain
0.88	CH ₂ -CH ₂ -CH ₂ -CH ₃	all acyl chains except linolenyl chain

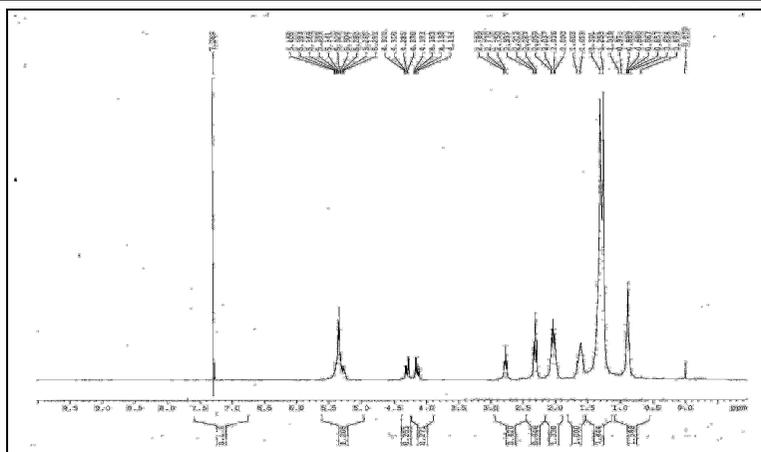


Figure 6. NMR Spectrum of olive oil

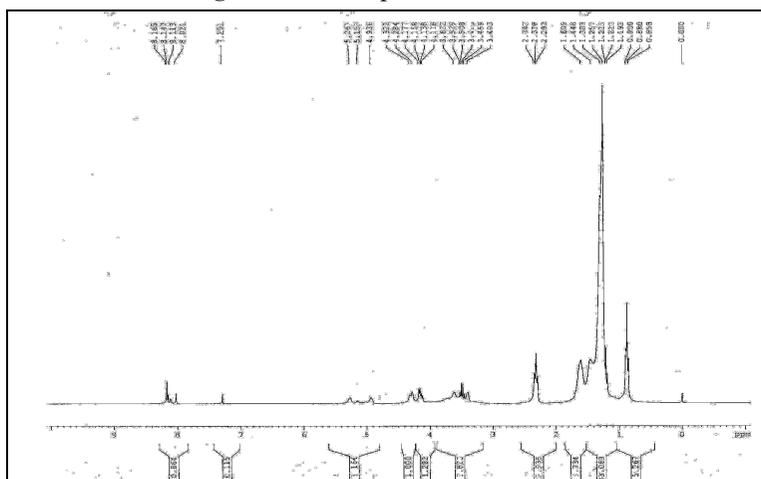


Figure 7. NMR spectrum of hydroxylated olive oil

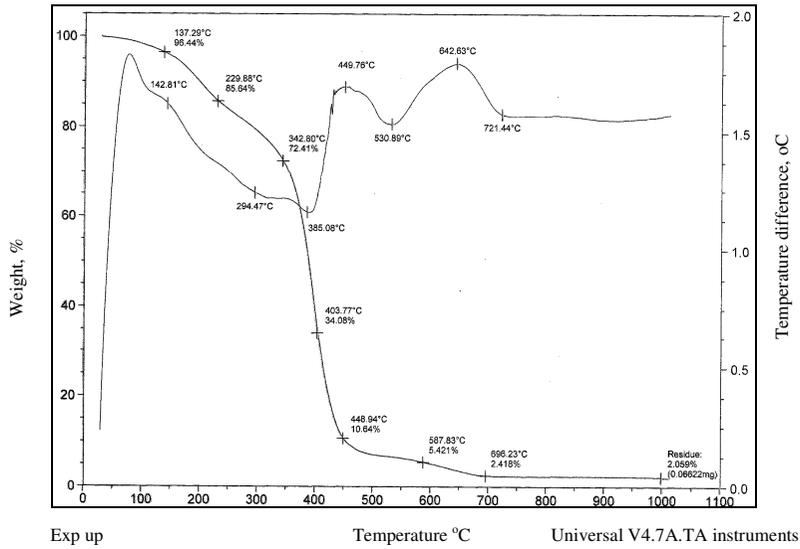


Figure 9. The TGA-DTA curve for OLIVA

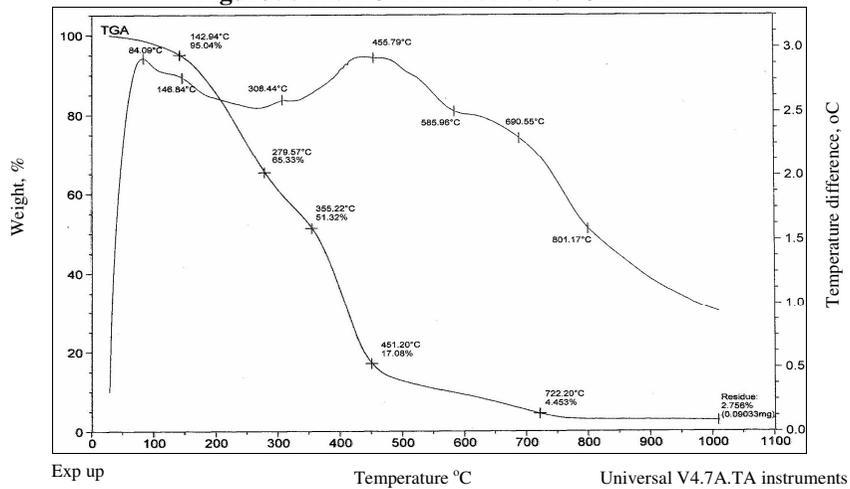


Figure 10. The TGA-DTA curve for OLINVP

Table 4. DSC characterisation

Biopolyesters	T _g °C	ΔH _m , °C
OLIVA	63.36	173.79,477.96
OLINVP	77.68	184.91,328.0,471.22

Mechanical properties

The data of mechanical properties of all the cure samples are shown in the Table 3. The higher tensile strength and modulus are observed in vinyl acetate biopolyesters than *N*-vinyl-2-pyrrolidone biopolyesters. The modification with MA increases the chemical functionality of the biopolyester resins results in a increasing cross linked density thus from these results

the modulus and strength of triglyceride based biopolyesters can be increased by simply increasing the chemical functionalities of the triglycerides¹⁶. The high strength and high modulus reflect the strong and hard character of these poly esters (Table 5)

Table 5. Mechanical properties

Sample	Tensile strength MPa	Strain at Break %	Modulus
OLIVA	11.143±0.07	51.6±6.5	9.8±1.7
OLINVP	21.99±0.2	78.5±4.8	7.7±0.2

Biodegradation test

Soil burial test

The biopolyester films 6x3 cm were buried in soil for 6 months for isolation of degrading microbe. It was found that a remarkable degradation was indicated in the sample (Figure 11). The percentage of weight loss was low between 30 and 40 days. After 40 days the degradation was rapid from this results triglycerides cross linked with hydrolysable bonds such as esters remain biodegradable¹⁷.

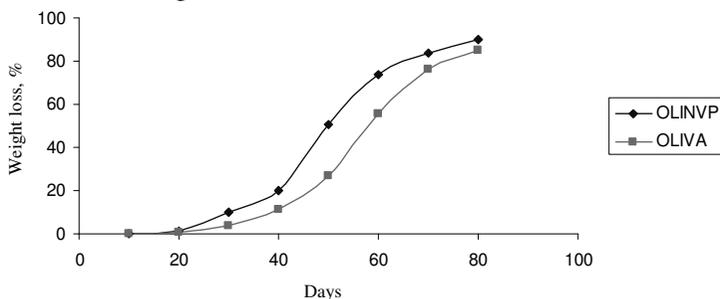


Figure 11. Analysis of soil burial test

Aerobic test

The aerobic biodegradability of polymeric resins in a aqueous medium was evaluated by determining the oxygen requirement in a closed respirometry (Germany standard ISO 9408 .1999) the degradation rate = BOD / COD x 100 was calculated. From the results (Table 6) the degradation rate is faster after 45 days *i.e.* longer the sample is subjected to the aerobic test, the faster the degradation rates. When compared to soil burial test aerobic degradation is much faster.

Table 6. Aerobic test

Sample Code	Average BOD	COD	Biodegradation, %	Degradation days
OLINVP	619	1.113	88	60
OLIVA	520	0.821	91	60

Bacterial adhesion test

The biopolyesters were incubated on mineral salt agar medium inoculated with isolated bacterial and fungi strain. Degradation of several of these polymers proceeds through adsorption of the micro organism to the polymer surface followed by hydrolytic cleavage. *S.aureus* species degrades polyesters.

Table 7. Viable count / sample for biopolyester

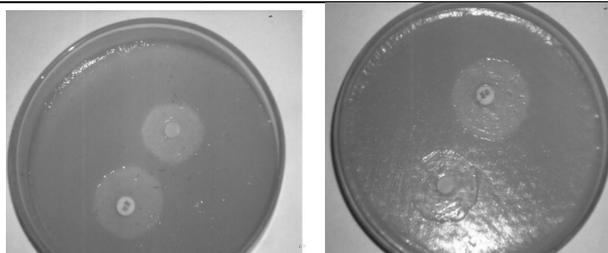
Sample code	Number of bacteria adhered / sample	
	<i>E.Coli</i> x 10 ⁶ cfu	<i>S.aureus</i> x 10 ⁶ cfu
OLINVP	0.51	2.32
OLIVA	2.63	2.52

Antimicrobial activity

The newly prepared biopolyesters have been studied against bacterial and fungi strains (Figure 12). The *N*-vinyl-2-pyrrolidone biopolyesters showed potential anti bacterial and anticandidal activity against micro organisms (Table 8).

Table 8. Antimicrobial studies with zone of inhibition (mm)

Sample code	<i>E.coli</i>	<i>Candida albicans</i>
OLINVP	17	13
OLIVA	6	4
Gentamycin-10 mg	24	19

**Figure 12.** Antimicrobial studies of OLINVP with zone of inhibition

Conclusion

Natural oils are expected to be inexpensive renewable resources development of new polymeric materials from vegetables oil is highly desirable. The purpose of this work is to prepare high molecular weight polymers and it would be alternative petroleum based polymeric materials such as plastic and rubber materials. The present method of *in situ* glycerolysis of the oil followed by condensation with maleic anhydride and the Four cross linked biopolyesters were prepared by treating *o*-PTF of olive oil with *N*-vinyl-2-pyrrolidone and vinyl acetate. The outcome of those studies has revealed that the newly prepared cross linked biopolyesters are potential biodegradable material for various consumer application like package materials and agricultural applications.

References

1. Williams C K and Hillmeyer M A, *Polym Rev.* 2008, **48**, 1-10.
2. Bierman U, Friedt W Lang S and Luhs W, Machmuller G, Metzger J O, Klaas M R, Schafer H J and Schneider M P, *Angew Chem Int Ed.*, 2000, **39**, 2206- 2224.
3. Clark J H, Budarin V, Deswarte F E I, Hardy J J E, Kerton F M, Hunt A J, Luque R, Macquarrie D J, Milkowssi K, Rodriquez A, Samuel O, Tavener S J, White R J and Wilson A J, *Green Chem.*, 2006, **8**, 853-860.
4. Guner F S, Yagci Y and Erciyes A T, *Prog Polym Sci.*, 2006, **31**,633-670.
5. Sharma V and Kundu P P, *Prog Polym Sci.*, 2006, **31**, 983-1008.
6. Meier M A R, Metzger J O and Schubert U S, *Chem Soc Rev.*, 2007, **36**, 1788-1802.

7. Lu Y and Larock R C, *Chem Sus Chem.*, 2009, **2**, 136-147.
8. Sperling L H, *Polymeric Multicomponent Materials, An Introduction*, Wiley, Newyork, 1997.
9. Juan Carlos Ronda, Gerard Lligadas, Marina Galià, Virgínia Cádiz, *Eur J Lipid Sci Technol.*, 2011, **113(1)**, 46-58
10. Park S J, Jin F L and Lee J R, *Macromol Rapid Comm.*, 2004, **25(6)**, 724-727.
11. Eren T and Kuisefoglu S.H and wool R, *J Appl Polym Sci.*, 2003, **90(1)**, 197-202.
12. Eren T, Kuisefoglu S H and Wool R, *J Appl Polym Sci*, 2005, **97**, 2264-2272.
13. Sharma V and Kundu P P, *Prog Polym Sci.*, 2008 **33**, 1199-1215.
14. Eren T and Kuisefoglu S H, *J Appl Polym Sci.*, 2004, **91(4)**, 2700-2710.
15. Sionakidis J, Sperling L H and Thomas D A, *J Appl Polym Sci.*, 1979, **24**, 1179.
16. Li F Hanson M V and Larock R C, *Polymer*, 2001, **42**, 1567-1579.
17. Güner F S Yagci Y and Erciyes A T, *Prog Polym Sci.* 2006, **31**, 633-670.



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