International Journal of Chemical Studies

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Photo and biodegradation of thermosetting polymers from linseed oil

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Abstract
Photo degradation and biodegradation of thermosetting polymers prepared by the free radical polymerization of alkyd resin of linseed oil with monomers like vinyl acetate (VA) and N- vinyl 2-pyrrolidone (VP) was studied. Monoglyceride of linseed oil was first prepared by glycerolysis of linseed oil at 220-230 °C. Then the resin was prepared by the reaction of the monoglyceride formed with cyclohexane dicarboxylic anhydride at 80 °C for 2 hours. Cross linked polymers were synthesised by the polymerisation of the resin with vinyl acetate (VA) and N- vinyl 2-pyrrolidone (VP) comonomers in the presence of benzoyl peroxide as initiator. Biodegradation of the polymers were tested by soil burial test. SEM micrographs were taken to assess surface damage and to look for the presence and nature of microbial growth. Photo degradation of the polymers was studied by exposing the polymers to direct sunlight and UV light. The reaction was followed by H^{1}NMR and FT-IR spectroscopy. The polymers prepared to be degradable and thus serve as replacement in numerous potential applications.

Keywords: Biodegradation, vinyl acetate (VA) and N- vinyl 2-pyrrolidone (VP), linseed oil monoglyceride, photo degradation.

1. Introduction

Developments in science and technology, especially over the last two decades, have increased the amount of synthetic polymers produced worldwide each year. Each year, approximately 140 million tons of synthetic polymers are produced [1]. Many synthetic polymers, resistant to chemical and physical degradation, are produced and utilized. The presence of these substances in the environment brings about important problems, including a challenge to wastewater treatment plants and pollution of groundwater and surface water. Synthetic polymers are recognized as major solid waste, environmental pollutants. Disposal of agricultural plastic wastes is another important problem. For agricultural plastic wastes, an alternative method of disposal is biodegradation [2].

The study of polymer degradation and stabilization is one of the multipurpose processes by which one may modify the materials to overcome the environmental concerns regarding safe disposal and decomposition of polymers [3- 5]. It provides useful information about material's stability, degradation behavior, mechanism of degradation, mechanical changes which occur during the course of their application [6].

The urgent need of today is to develop polymers that are biodegradable so that they become environmentally friendly [7-9]. The most important aspect of synthesizing biodegradable polymers relates to their ability to undergo degradation within the biosphere on coming into contact with micro-organisms, enzymes, or under natural environmental conditions. The main problem associated with designing biodegradable polymers is the optimization of their chemical, physical and/or mechanical properties, as well as their biodegradability [10, 11].

Scientists are searching for new raw materials that can be synthesized into environmentally friendly polymers so as to make available the materials needed by various industries at lower costs [12, 13]. Some examples of these resources are polysaccharides, such as cellulose and starch, and glycerol esters of fats and oils [14]. Nowadays, there is a growing interest to produce vegetable oil based polymers due to their ready availability, inherent biodegradability and low toxicity [15].

Biodegradable plastics can be made from oil or from plant-based products. The most important aspect of synthesizing biodegradable polymers relates to their ability to undergo degradation within the biosphere on coming into contact with micro-organisms, enzymes, or under natural environmental conditions. The main problem associated with designing biodegradable

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polymers is the optimization of their chemical, physical and/or mechanical properties, as well as their biodegradability [16]. Photo degradation is favored among few popular methods of accelerated degradation studies. The photon energy in solar radiation is the most damaging component of the outdoor environment, serving to initiate a wide variety of chemical changes in polymeric materials [17]. The energy of ultraviolet photons is comparable with that of the dissociation energies of polymeric covalent bonds, which lie in the range of approximately 290-460 kJ/mole. Such photons have the capability of altering the polymer's chemical structure. Many chemical entities often found in polymers, however, have characteristic ultraviolet absorptions.

Photolysis with UV light and the γ-ray irradiation of polymers generate radicals and/or ions that often lead to cleavage and cross linking. Oxidation also occurs, complicating the situation, since exposure to light is seldom in the absence of oxygen. Generally this changes the material's susceptibility to biodegradation. Similarly, photo oxidation of polyalkenes promotes (slightly in most cases) the biodegradation [18, 19]. The formation of carbonyl and ester groups is responsible for this change.

The aim of this work is the preparation of cross linked polymers of linseed oil as an alternative to petroleum based polymeric materials with vinyl acetate and N-vinyl-2-pyrrolidone co-monomers. Photo degradation of the polymers was studied by exposing the polymers to direct sunlight and UV light and measuring the weight loss and changes in mechanical properties. Biodegradation of the polymers was also studied by soil burial test.

2. Materials and Methods
2.1 Materials
Linseed oil was purchased from local markets at Trivandrum. The chemicals Cyclohexane dicarboxylic anhydride(Sigma–Aldrich), Triethylene glycol dimethyl acrylate(TEGMA) (Sigma–Aldrich), Glycerol, Vinyl acetate, N-vinyl-2-pyrrolidone, Benzoyl peroxide and N,N – dimethyl aniline were used without purification.

2.2 Methods
Preparation of polymers
Glycerolysis of linseed oil was carried out by heating 2:1 mixture of linseed oil and glycerol at 220-230 °C for 5 hours. The monoglyceride formed and cyclohexane dicarboxylic anhydride in the ratio 2:1 was heated to 80 °C for 2 hours. The resin, thus prepared was polymerized with different concentration of vinyl acetate (VA) using benzoyl peroxide as initiator and N, N- dimethyl aniline as an accelerator. 1 ml of triethylene glycol dimethyl acrylate (TEGMA) is added as cross linking agent. The mixture was then casted on a clean silicone oil spreaded glass plate and was placed in an oven at 50°C for 2 hours and the temperature was increased upto 100°C and curing takes place at this temperature for 2 hours.

The procedure was followed for the preparation of various polymers by mixing the resin with different concentration of N-vinyl-2-pyrrolidone (VP) co-monomer.

3. Characterization
3.1 Spectral studies
The progress of the reaction was studied by analyzing the FT-IR and H[1]NMR spectra of the oil, monoglyceride and the resin. Photo degradation of the polymer samples was also studied by IR spectroscopy.

3.2 Biodegradation- Soil burial test
Biodegradation of the polymers were studied by soil burial test. For the soil burial test the replicate pieces of the sample (5 x 3 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 (Gandini, 2008). 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 measuring the weight loss after 30 and 60 days, which is calculated using the relation, [20].

$$\text{Degree of biodegradation, } D = \frac{(Mo - Mt)}{Mo} \times 100$$

Where,

Mo – weight of original film

Mt – weight of residual film after degradation for different time.

Physical factors such as fragmentation and embrittlement can also be assessed in these tests. SEM micrographs were taken to assess surface damage and to look for the presence and nature of microbial growth.

3.3 Photo degradation
Photo degradation of the polymers was studied by exposing the polymers to direct sunlight and UV light and measuring the changes in the mechanical properties. The extent of degradation was examined by measuring the weight loss after 30 and 60 days.

4. Results and Discussions
4.1 Spectral analysis
The progress of the chemical reaction was studied by analyzing FT-IR, and H[1]NMR spectra of the oil, monoglyceride and the resin. Figure 1a, 1b and 1c shows the FT- IR spectra of linseed oil, linseed oil monoglyceride and linseed oil monoglyceride cyclohexane dicarboxylate resin.

In the FT-IR spectrum of linseed oil the peaks at 3008.1 cm^{-1}, 2925.48 cm^{-1} and 2855.1 cm^{-1} corresponds to the C-H stretching frequencies for olefinic, methylene and methyl groups. The peak at 1745.26 cm^{-1} corresponds to the C=O stretching frequency of ester group. The peak at 1460.81 cm^{-1}, 1374.03 cm^{-1} and 722.21 cm^{-1} corresponds to the C-H bending vibration of CH_2 and CH_3 groups. The peak at 1236.15 cm^{-1}, 1163.83 cm^{-1} and 1099.23 cm^{-1} corresponds to the C-C and C-O stretching vibrations. The presence of additional peak at 3413.39 cm^{-1} in the FT-IR spectrum of linseed oil monoglyceride corresponds to the presence of OH groups (i.e. confirms the formation of partial glycerides). The broadening of the peak at 1740.44 cm^{-1} in the FT-IR spectrum of the resin indicates the presence of different CO groups which is due to the formation of alkyd resin.

Figure 2a, 2b and 2c shows the H[1]NMR spectrum of linseed oil, linseed oil monoglyceride and linseed oil monoglyceride cyclohexane dicarboxylate resin.

In the H[1]NMR spectrum of linseed oil, the peak at 0.8 - 1.0 corresponds to the terminal methyl protons, the peak at 1.3 and 1.6 corresponds to CH_2 and CH protons, the peak at 2.0 and 2.3 for protons in allylic and bis allylic carbons, the peak at 2.7 -2.8 for protons in CH_2 -O carbon, the peak at 4.1 - 4.3 for the methylene protons in the ester group and the peak at 5.2 - 5.4 corresponds to the olefinic protons (protons of glycerol

backbone). In the H[1]NMR spectrum of linseed oil monoglyceride, the additional peak at 5.0 for the OH protons which confirms the formation of monoglyceride and the multiplet peak at 3.4 - 3.7 corresponds to the CH$_2$ protons attached to the OH group. In the H[1]NMR spectrum of resin, the multiplet at 3.4 - 3.9 corresponds to the protons in the cyclohexane ring.
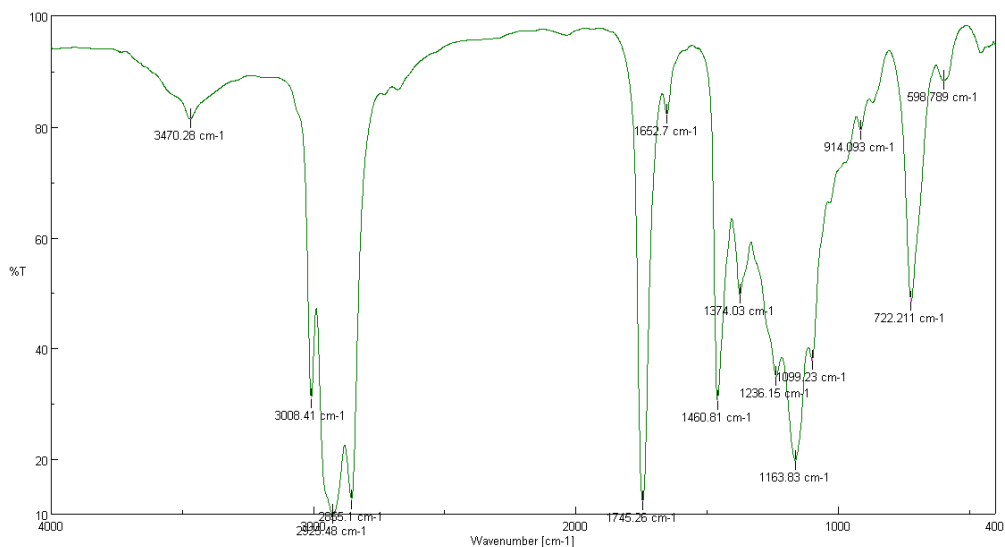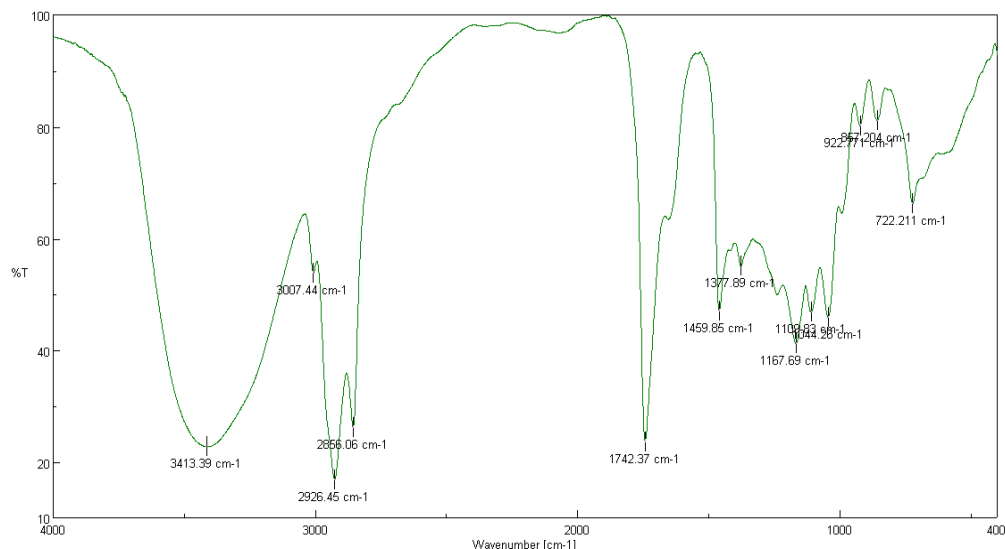
Fig 1a: FT-IR spectrum of linseed oil
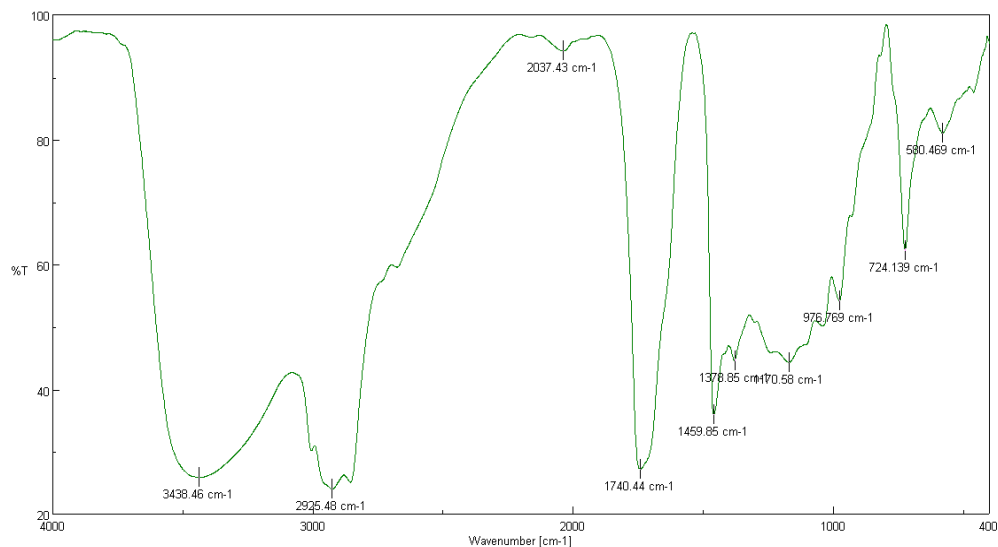
Fig 1b: FT-IR spectrum of linseed oil monoglyceride

Fig 1c: FT-IR spectrum of linseed oil monoglyceride cyclohexane dicarboxylate (resin)
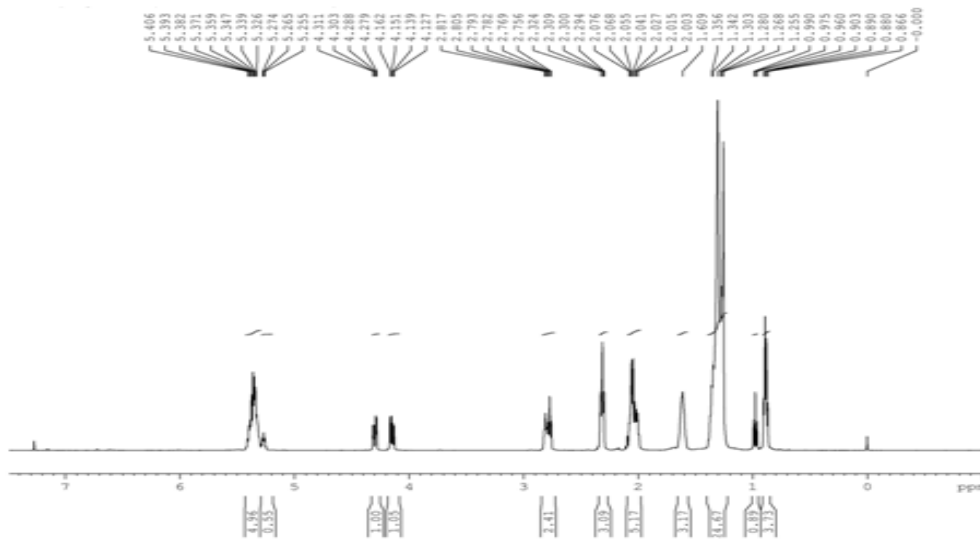
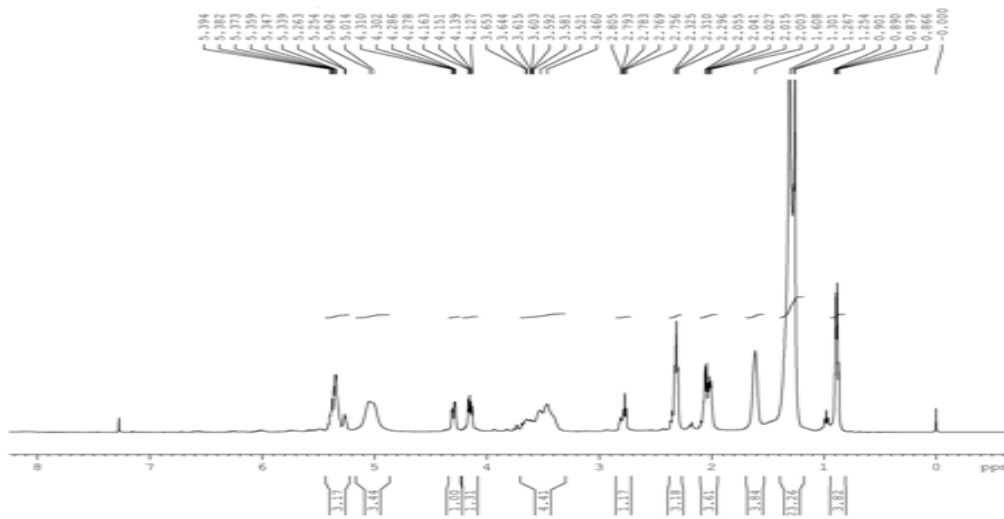**Fig 2a:** H[1]NMR spectrum of linseed oil

Fig 2b: H[1]NMR spectrum of linseed oil monoglyceride

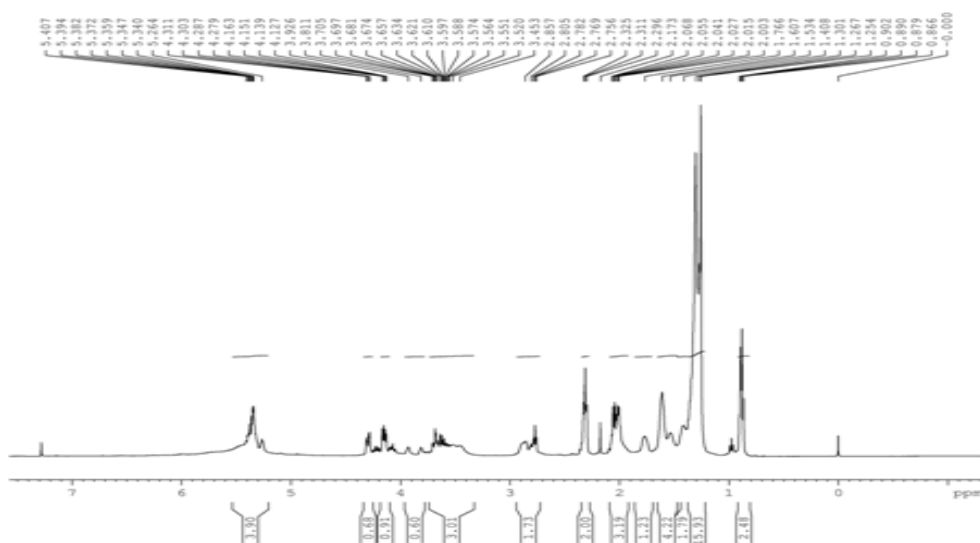**Fig 2c:** H[1]NMR spectrum of linseed oil monoglyceride cyclohexane dicarboxylate resin

4.2 Biodegradation - Soil Burial test

Biodegradation of the polymer samples prepared by the free radical copolymerization of linseed oil monoglyceride cyclohexane dicarboxylate with various concentrations of the monomers like VA and VP as reported in table 1.

Table 1: Percentage of biodegradation of polymer samples from linseed oil

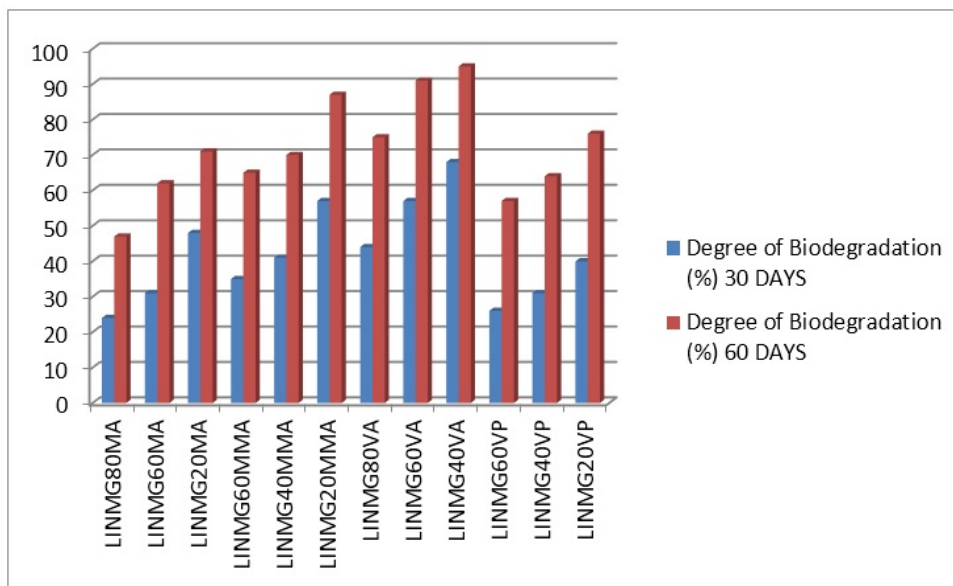| Polymer sample	Degree of Biodegradation (%)	
	30 DAYS	60 DAYS
LINMG80VA	44	75
LINMG60VA	57	91
LINMG40VA	68	95
LINMG60VP	26	57
LINMG40VP	31	64
LINMG20VP	40	76

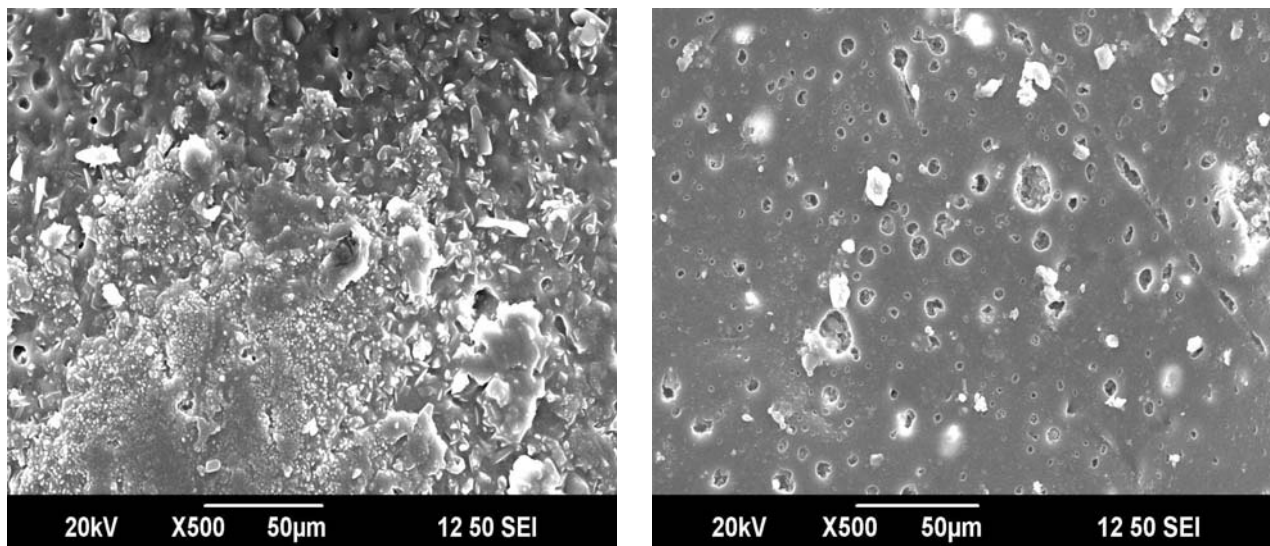**Fig 3:** Percentage of biodegradation of various polymer samples from linseed oil

Fig 4: SEM image of LINMGVA before and after degradation
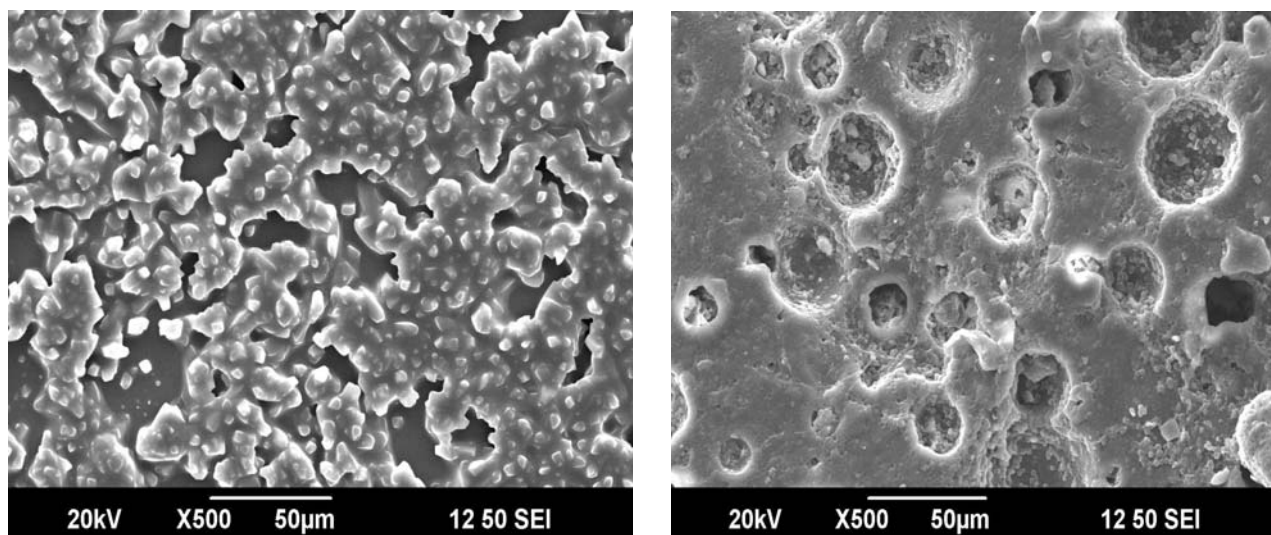
Fig 5: SEM image of LINMGVP before and after degradation

From the soil burial test, it is known that the polymer samples prepared are highly biodegradable and undergoes more than 50% degradation within 2 months. Some of the polymers show more than 90% degradation within 60 days. From the soil burial test (figure 3) it is known that, the extent of biodegradation increases with decrease in the concentration of monomers. Comparing the polymer samples prepared, the rate of biodegradation is high for vinyl acetate polymer. The outcome of these studies revealed that the newly prepared cross linked biopolymers are potential biodegradable material for various consumer application like package materials and agricultural applications.

Surface damage and microbial growth on the polymers were studied from SEM analysis. Scanning electron microscope (SEM) is used to study the morphological behavior of polymers. SEM micrographs of the polymers before and after soil burial were analyzed which shows the degradation of the polymers by microbial action. Figure 4 and 5 shows the SEM micrographs of the polymers LINMGVA and LINMGVP before and after degradation.

4.3 Photo degradation

Photo degradation of the polymers were studied by exposing the polymers to direct sun light (dry and wet condition) and UV light and measuring the weight loss and changes in the mechanical properties. The extent of degradation was examined by measuring the weight loss after 30 and 60 days. (Table 2 and 3) As a consequence of this change, the material becomes more brittle with a reduction in its tensile, impact and elongation strength. Discoloration and loss of surface smoothness accompany photo-oxidation. High temperature and localized stress concentrations are factors that significantly increase the effect of photo-oxidation.

Figure 6a,6b and 7a,7b shows the FT-IR spectrum of the polymer samples LINMGVA and LINMGVP before and after photo irradiation. In the FT-IR spectrum of the polymer samples after degradation, the presence of additional peaks in $3000\text{-}4000\,cm^{-1}$ region indicates the formation of number of free radicals by the photolysis of polymer sample.

Table 2: Photo irradiation of polymer samples (dry condition)

Polymer sample	Degree of Photo degradation (%)	
	30 DAYS	60 DAYS
LINMG80VA	5	9
LINMG60VA	7	13
LINMG40VA	10	18
LINMG60VP	10	16
LINMG40VP	11	18
LINMG20VP	13	21

Table 3: photo irradiation of polymer samples (wet condition).

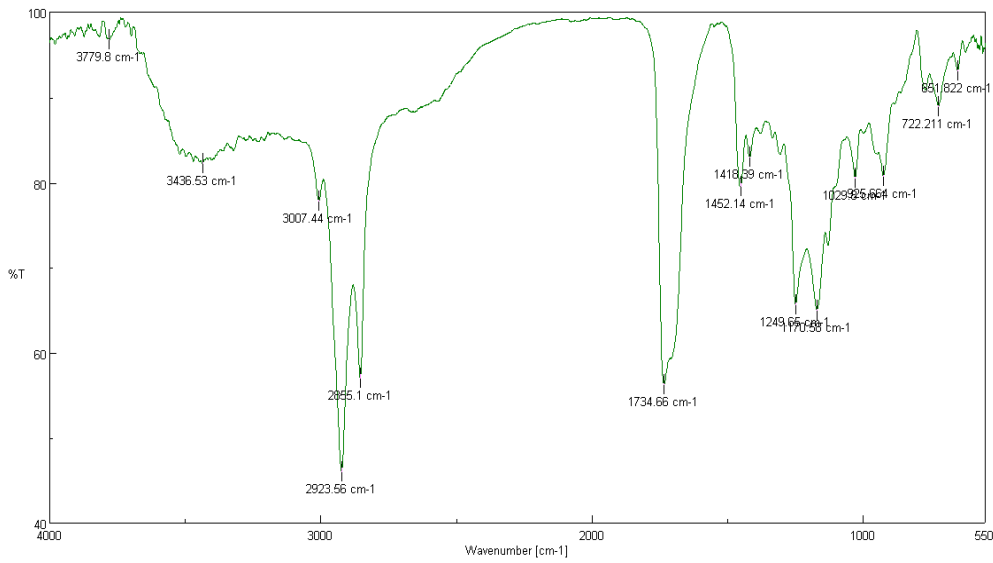| Polymer sample	Degree of Photo degradation (%)	
	30 DAYS	60 DAYS
LINMG80VA	38	43
LINMG60VA	45	49
LINMG40VA	48	55
LINMG60VP	45	48
LINMG40VP	49	54
LINMG20VP	55	60

Fig 6a: IR spectrum of LINMGVA before photo irradiation
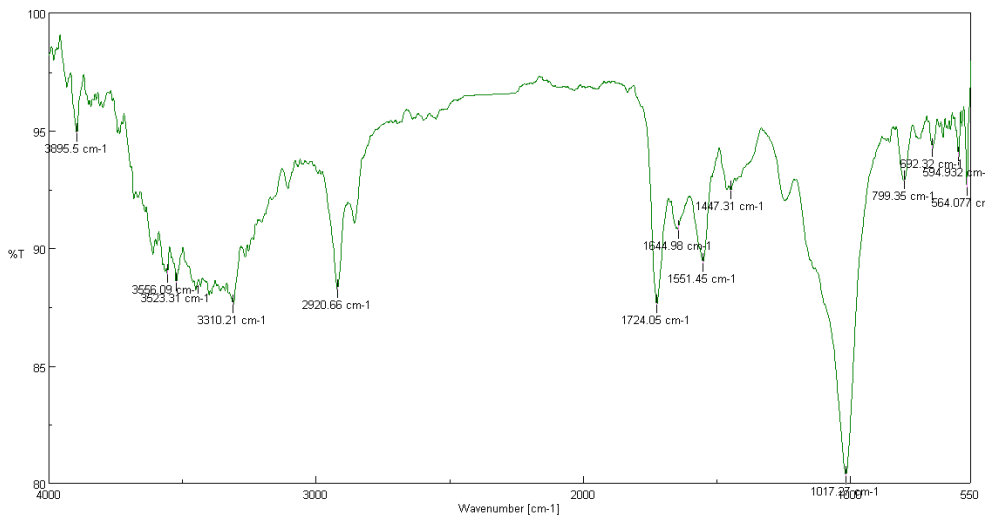

Fig 6b: IR spectrum of LINMGVA after photo irradiation
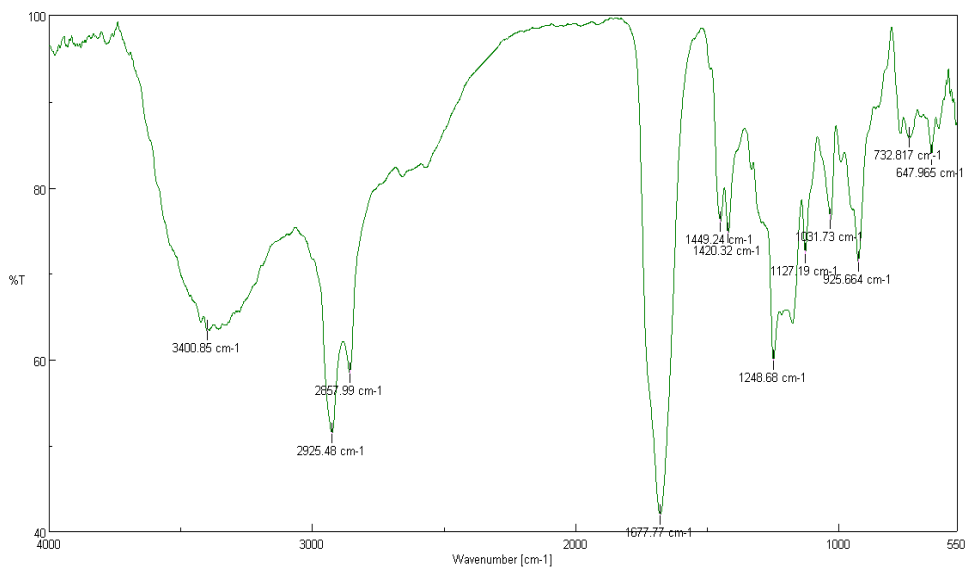

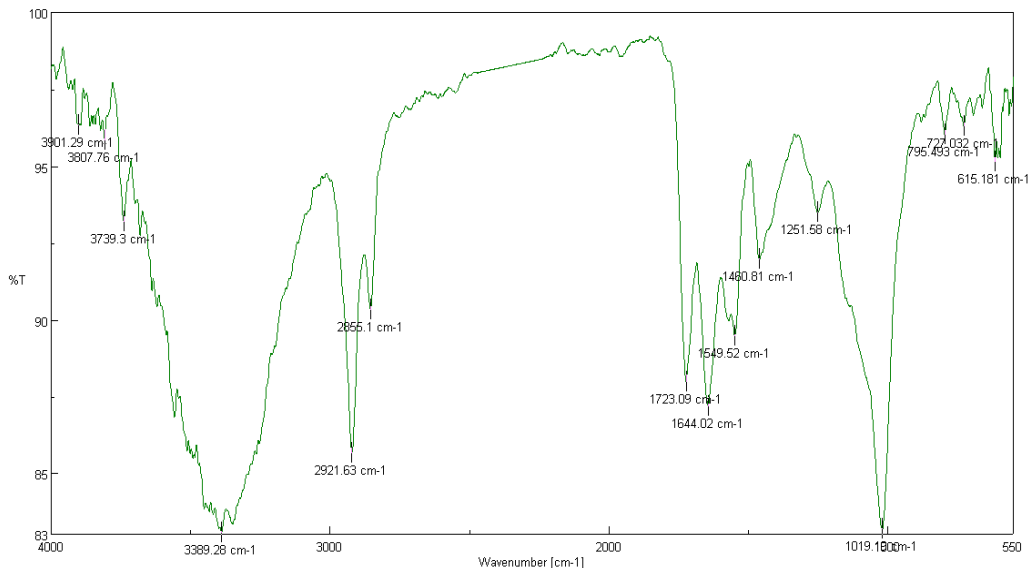**Fig 7a:** IR spectrum of LINMGVP before photo irradiation

Fig 7b: IR spectrum of LINMGVP after photo irradiation

4.4 Comparison of photo and biodegradation

From the data (table 1, 2 and 3), it is known that the percentage of photo degradation of the polymer samples under wet condition is greater than the photo degradation under dry condition and which is almost similar to the percentage of biodegradation of the polymer samples. Figure 8 and 9 shows the comparison of biodegradation of polymer samples prepared with photo degradation under dry and wet condition
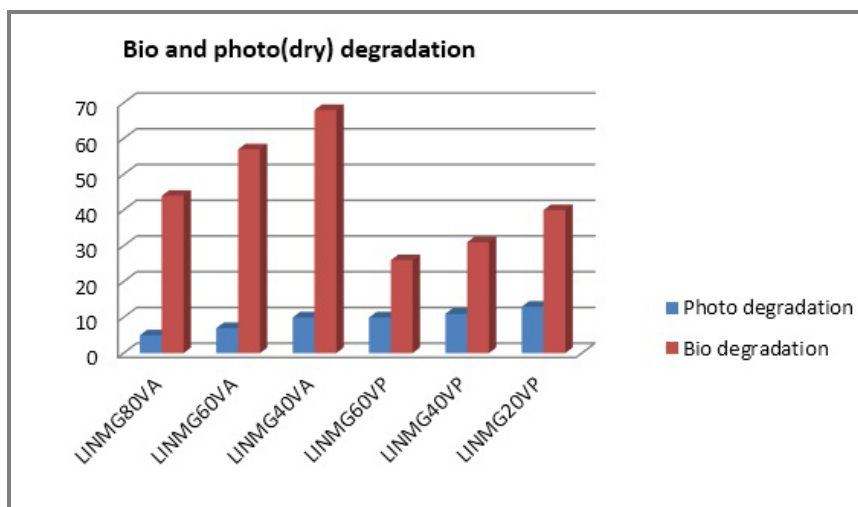

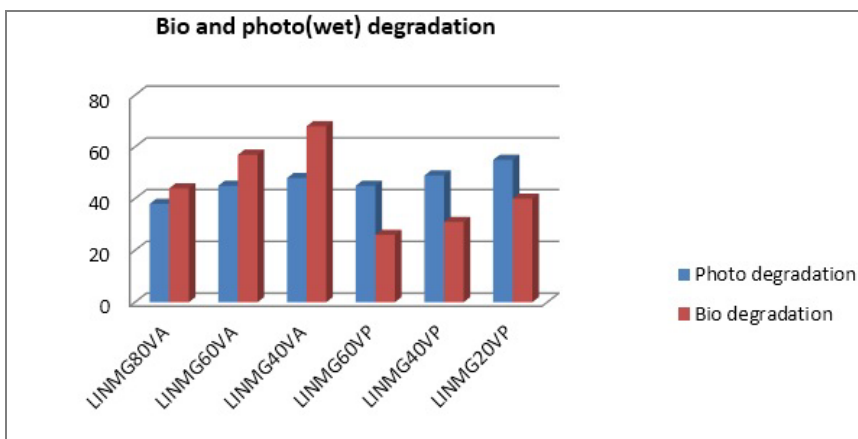**Fig 8:** Bio and photo degradation (dry condition)

Fig 9: Bio and photo degradation (wet condition)

5. Conclusion

1. A variety of novel biodegradable polymers have been synthesized by the free radical copolymerization of linseed oil monoglyceride cyclohexane dicarboxylate with VA and VP as co-monomers.

2. The polymers are found to be typical thermosetting materials. They exhibited good tensile stress–strain behavior relatively to plastics.

3. From the soil burial test it is known that the newly prepared polymers are biodegradable and can play very important role in biological applications.

4. Photo degradation of the polymer samples were also studied by exposing the samples to direct sunlight. Photo degradation by direct sun light in wet condition is greater than the photo degradation in dry condition. Thermal stability of the polymer samples were also changed by photo irradiation.

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