

SYNTHESIS AND CHARACTERIZATION OF BIOPOLYMERS FROM LINSEED OIL MONOGLYCERIDE CYCLOHEXANE DICARBOXYLATE WITH METHYL ACRYLATE AND METHYL METHACRYLATE CO-MONOMERS

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[Received-24/03/2014, Accepted-14/04/2014]

ABSTRACT

In this study novel biodegradable polymers were synthesized by the free radical polymerization of linseed oil monoglyceride cyclohexane dicarboxylate with comonomers like methyl acrylate(MA) and methyl methacrylate(MMA). Linseed oil monoglyceride(LOMG) was first prepared by the glycerolysis of linseed oil followed by the reaction with cyclohexane dicarboxylic anhydride to produce cyclohexane dicarboxylate esters of LOMG (alkyd resin). The reactions were followed by FT-IR and H¹NMR spectroscopy. Finally, radical copolymerization of the LOMG cyclohexane dicarboxylate with different concentration of methyl acrylate and methyl methacrylate was performed to produce rigid, thermoset polymers. The thermal and mechanical properties of the cured polymers were analyzed. Bio degradation of the polymer samples were also studied by soil burial test. The outcome of these studies revealed that the newly prepared cross linked bio-polymers were potential biodegradable material for various consumer applications.

Key words: Cyclohexane dicarboxylic anhydride, Methyl acrylate (MA), Methyl methacrylate (MMA), linseed oil monoglyceride(LOMG), Alkyd resin.

[I] INTRODUCTION

The urgent need of today is to develop polymers that are biodegradable so that they become environmentally friendly [1–3]. 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. In addition, the natural resource of petroleum is being exhausted at a fast rate [4]. The escalating cost of petrochemicals and the high rate of depletion of this natural resource present a

serious challenge to the innovative potential of chemists [5]. 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 [6,7]. Some examples of these resources are polysaccharides, such as cellulose and starch, and glycerol esters of fats and oils [8].

Nowadays, there is a growing interest to produce vegetable oil-based biopolymers due to their ready availability, inherent biodegradability and

low toxicity.[9] Vegetable oils have been used in paints and coatings for centuries, because the unsaturated oils can oligomerize or polymerize when exposed to the oxygen in air[10]. These polymers have many advantages compared with polymers prepared from petroleum-based monomers (Williams and Hillmeyer, 2008). They are biodegradable and in many cases cheaper than petroleum-based polymers[11]. Cross linked biodegradable polymers have been prepared from edible oils with unsaturated anhydrides or acids have useful applications as adhesives, fillers and elastomers (Park *et al.*, 2004). Due to the presence of fatty acid chains within the polymeric structure, these polymers present improved physical properties such as higher flexibility, adhesion and resistance to water and chemicals.[12]

Recently there have been many attempts to convert vegetable oils and fatty acids to useful polymers and several different approaches have been described [13–15]. Triglycerides, as the main component of vegetable oils, contain several reactive positions useful in many synthetic transformations. Linseed oil is a triglyceride oil consisting mainly of linolenic acid (53%), oleic acid (18%), linoleic acid (15%), palmitic acid (6%) and stearic acid (6%) [16]. Linseed oil is considered a good drying oil, used mainly for the preparation of paints and varnishes [17]. It is also used in enamels, linoleum, oilcloth, patent leather, printer's ink and as waterproofing for raincoats, slickers and tarpaulins [18]. The present study is preparation of alkyd resin from linseed oil and explore the potential utility for the preparation of novel cross linked ecofriendly biodegradable polymers as an alternative to petroleum based polymeric materials.

[II] MATERIALS AND METHODS

2.1 Materials

Linseed oil is purchased from local market at Trivandrum. The chemicals Cyclohexane dicarboxylic anhydride (Sigma–Aldrich), Triethylene glycol dimethyl acrylate (TEGMA) (Sigma–Aldrich), Methyl acrylate, Methyl

methacrylate, Benzoyl peroxide, 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 methyl acrylate (MA) using benzoyl peroxide as initiator and N,N-dimethyl aniline as accelerator. 1 ml of triethylene glycol dimethyl acrylate (TEGMA) was 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 hrs and the temperature was increased upto 100°C and curing takes place at this temperature for 2 hrs.

The procedure was followed for the preparation of various polymers by mixing the resin with different concentration of Methyl methacrylate (MMA) co-monomer. All the cured materials showed high toughness, elastomeric and good transparency.

[III] CHARACTERIZATION

3.1 Spectral studies

The progress of the reaction was studied by analyzing the FT-IR and ¹H NMR spectra of the oil, monoglyceride and the resin.

3.2 Thermal and mechanical studies

The tensile strength of the biopolymers prepared were determined using Dumbbell shaped cut from the specimen using Instron UTM; 10 ton static Universal Testing Machine. The values represented were an average mean of about 4-5 samples. The new polymeric materials exhibited tensile stress–strain behavior relatively to plastics. The crosslink densities, ν_e , were determined from the rubbery modulus plateau based on the theory of rubber elasticity $E' = 3\nu_e RT$ [19, 20]. where E' is the storage modulus (Young's) of cross linked polymer in the plateau region, R is the universal gas constant (8.314 J·mole⁻¹·K⁻¹) and T is the absolute temperature (K).

The thermal analysis of the biopolymers was determined by TG-DTA analysis. Thermo gravimetric analysis (TGA) was performed by Perkin's Elmer thermo gravimetric analyzer over the temperature ranging from 30 to 700 °C at a heating rate of 10 °C/min under nitrogen gas atmosphere.

3.3 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, [21]

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

Where M_o – weight of original film

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

3.4 Swelling analysis

The swelling analyses of the polymeric samples were carried out in different solvents viz., saline (20% NaCl), alkaline (2% NaOH), acidic (2% H₂SO₄) and toluene. The polymeric samples were allowed to remain in the solution for 72 hours at room temperature and then weighed as soon as they were removed from the solvent. The samples were weighed after 2, 4, 6, 8, 12, 24, 48 and 72 hours. The swelling ratio, q_v of various polymers at equilibrium [22] was determined using the Equation

$$q_v = \frac{\text{volume of swollen polymer}}{\text{volume of dry polymer}}$$

3.5 Chemical resistance

Chemical resistance of the newly prepared polymer samples were studied by immersing the polymer samples in various solvents such as CCl₄, CHCl₃, diethyl ether, benzene, toluene, H₂O₂, HCl, ethanol, H₂O, NaCl etc. and

measuring the dimensional changes after 1 week and 4 weeks[23]. The weight loss also measured after 30 days.

IV] RESULTS AND DISCUSSIONS

4.1 Spectral analysis

The progress of the chemical reaction was studied by analyzing FT-IR, and H¹ NMR spectra of the oil, monoglyceride and the resin. Fig 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 1460.81cm⁻¹, 1374.03 cm⁻¹ and 722.21 cm⁻¹ corresponds to the C-H bending vibration of CH₂ and CH₃ 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 (CO groups in different environment) which is due to the formation of alkyd resin. Also broadening of the peak at 2925.48 is due to the CH₂ groups in cyclohexane ring.

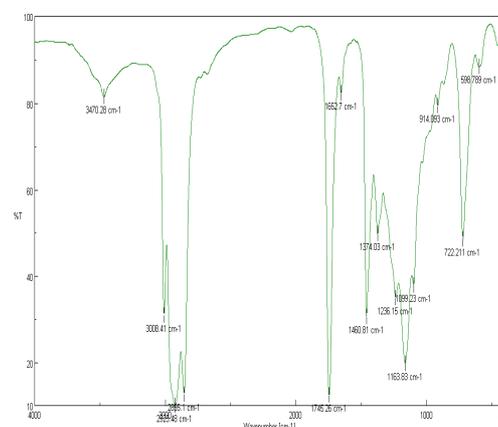


Fig 1a. FT-IR spectrum of linseed oil

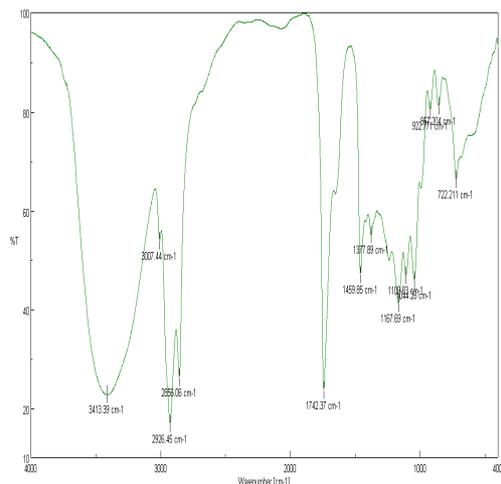


Fig 1b. FT-IR spectrum of linseed oil monoglyceride

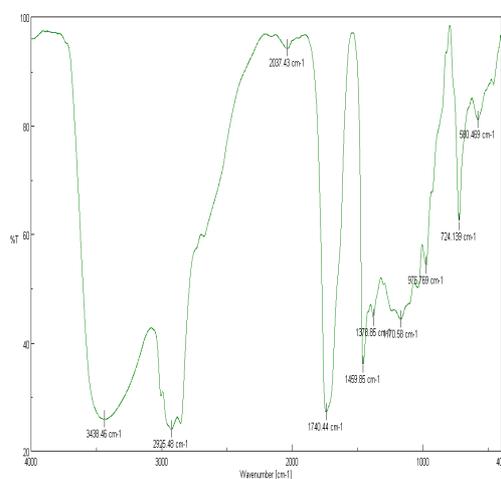


Fig 1c. FT-IR spectrum of linseed oil monoglyceride cyclohexane dicarboxylate (resin)

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

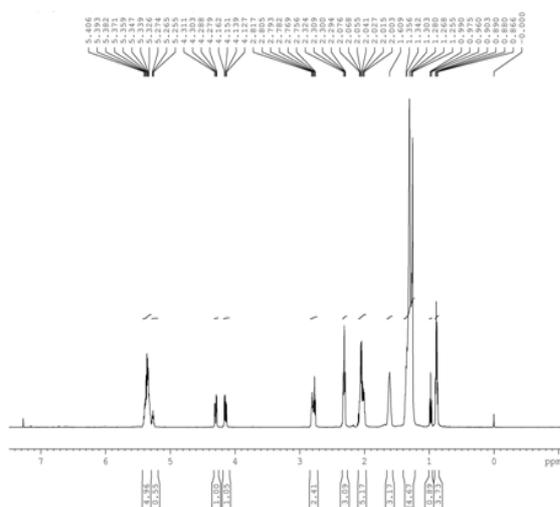


Fig 2a. NMR spectrum of linseed oil

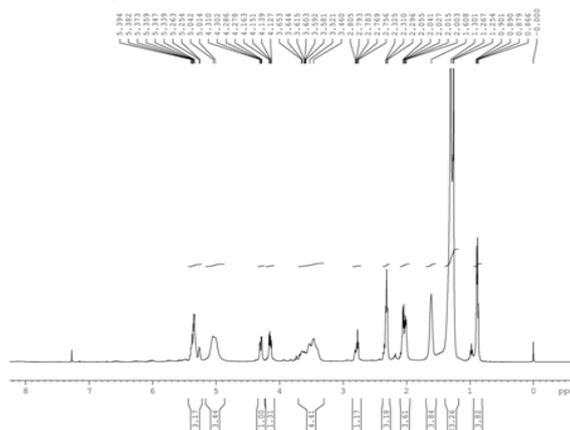


Fig 2b. NMR spectrum of linseed oil monoglyceride

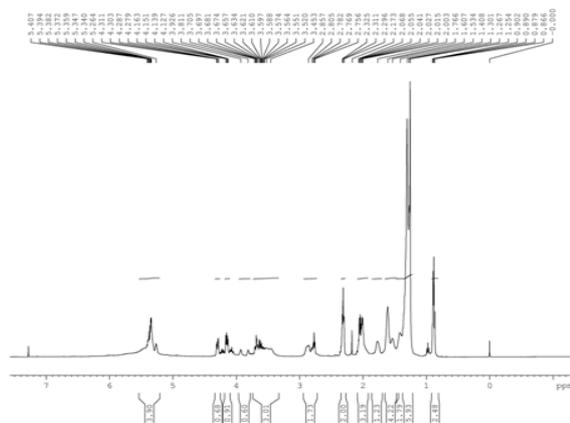


Fig 2c. NMR spectrum of linseed oil monoglyceride cyclohexane dicarboxylate resin

In the 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 CH₂ 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 CH₂ -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 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 CH₂ protons attached to the OH group. In the NMR spectrum of resin, the multiplet at 3.4 - 3.9 corresponds to the protons in the cyclohexane ring.

4.2 Thermal analysis

Thermo gravimetric analysis (TGA) was used to investigate the thermal stability of the polymers.

Fig. 3a & 3b shows the decomposition behavior of the polymer samples LINMGMA & LINMGMMMA under nitrogen atmosphere. Two distinct temperature regions are observed where the samples experienced significant weight loss (150-250°C and 300-450°C).

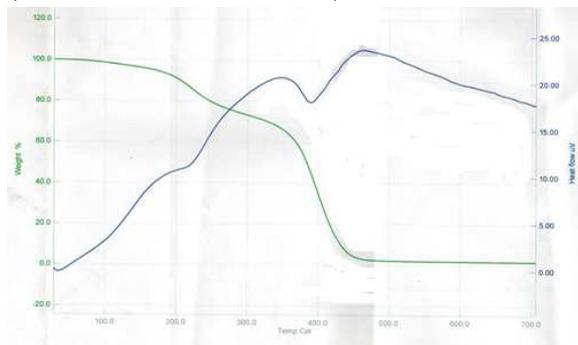


Fig 3a. TG-DTA curve of linseed oil monoglyceride cyclohexane dicarboxylate – methyl acrylate (LINMGMA) copolymer

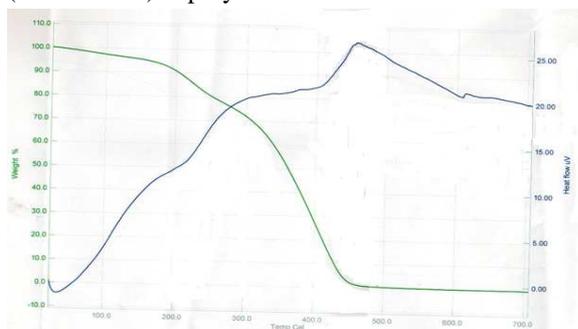


Fig 3b. TG-DTA curve of linseed oil monoglyceride cyclohexane dicarboxylate – methyl methacrylate (LINMGMMMA) copolymer

It is clear from the figure that most of the unreacted free oil disappears at the temperature between 150 and 250°C (stage 1), i.e. this region corresponds to the evaporation of the unreacted free oil. On the other hand, the insoluble substances were found to be highly cross linked thermosets that decompose at temperatures greater than 300°C (stage 2). This decomposition stage corresponds to the carbonization of the cross linked polymer network. Stage-I in the TGA curves involves two major steps, i.e. diffusion of the free oil to the surface of the bulk polymer and subsequent evaporation. The diffusion of the free oil is retarded by highly crosslinked materials, but the evaporation of the free oils from the polymer surface occurs rather rapidly at high temperatures. From the preceding

results, it is clear that the thermal stability of the polymers is limited by the first decomposition stage in the TGA thermograms, which is directly related to the amount of unreacted free oil in the bulk polymer.

In the DTA curve of LINMGMA polymer, the peak at 190°C owing to the glass transition temperature and the endothermic peak at 390°C correspond to the melting point of the polymer network. Similarly in the DTA curve of LINMGMMMA polymer, the peak at 190°C owing to the glass transition temperature and the endothermic peak at 410°C correspond to the melting point of the polymer network. Comparing the DTA curves melting point of LINMGMMMA was slightly greater than the LINMGMA polymer.

4.3 Mechanical properties

The mechanical properties of the polymer samples prepared are shown in table 1. From the data it is known that the polymer samples prepared having high tensile strength and modulus relative to other thermosetting plastics. Comparing the two samples analyzed, methyl methacrylate containing polymer is having high tensile strength and modulus.

Polymer sample	Cross link density ($\times 10^{-3}$)	Tensile strength $\times 10^5$ Pa	% of elongation	Young's Modulus $\times 10^5$ Pa
LINMGMA	1.57	7.67	107.76	118.8
LINMGMM A	7.62	14.02	103	576.6

Table 1. Mechanical properties of the biopolymers

4.4 Bio degradation - Soil Burial test

Bio degradation of the polymer samples prepared by the free radical copolymerization of linseed oil monoglyceride cyclohexane dicarboxylate with various concentration of the monomers like MA and MMA as reported in table 2.

Polymer sample	Degree of Biodegradation (%)	
	30 DAYS	60 DAYS
LINMG80MA	24	47
LINMG60MA	31	62
LINMG20MA	48	71
LINMG60MMA	35	65
LINMG40MMA	41	70
LINMG20MMA	57	87

Table 2. Percentage of biodegradation of polymer sample

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 shows more than 70% degradation within 60 days. From the datas obtained by soil burial test (table 2) it is known that, the extent of biodegradation increases with decrease in the concentration of monomers. Comparing the two polymers, the rate of biodegradation is high for methyl methacrylate polymer. The outcome of these studies revealed that the newly prepared cross linked bio-polymers are potential biodegradable material for various consumer application like package materials and agricultural applications.

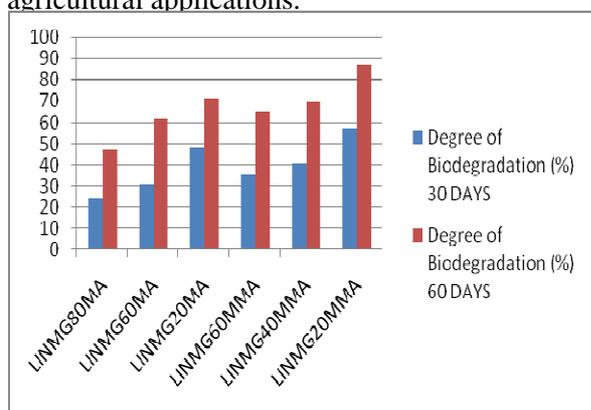


Fig 4. Percentage of biodegradation of various polymer samples

4.5 Swelling analysis

The samples have been tested for swelling in alkaline, acidic, and brine solutions, as well as in toluene. All the polymeric samples show minimum swelling in acidic and alkaline solution and maximum swelling in brine (NaCl) solution. In toluene swelling ratio almost remains constant ie there is no significant swelling.

Fig 5a and 5b shows the swelling ratios at different time intervals for the polymer samples in different solutions which represents the time dependence of the swelling ratios. A sharp rise in qv values is observed at the early stages of swelling. After 4 hours, the qv values show little change (almost remain constant). This may be explained in terms of the catastrophic rupture of the polymer network due to the internal stress

caused by diffusion of the liquid into the polymer network.

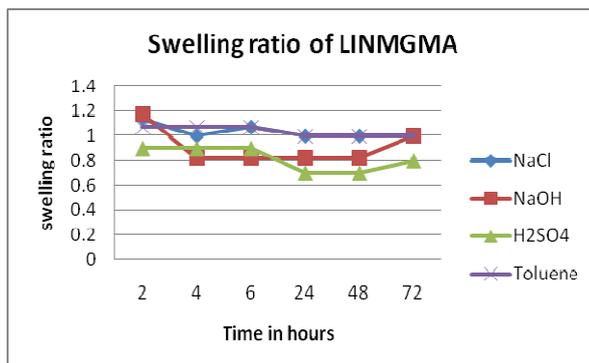


Fig 5a. Swelling of LINMGVA in various solvents

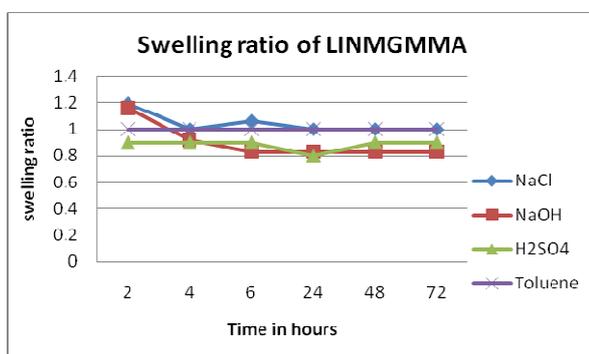


Fig 5b. Swelling of LINMGVMA in various solvents

4.6 Chemical resistance

Resistance of the polymers at various chemicals are determined by immersing the polymer samples in different media and measuring the dimensional changes after 1 week and 4 weeks. The weight loss also measured after 30 days. Table.3 shows the weight loss of polymer samples after 30 days. The comparison of stability of polymers LINMGMA AND LINMGMMA towards various chemicals was shown in the figure 6.

Solvents	Weight loss in 30 days (%)	
	LINMGMA	LINMGMMA
H ₂ O	15	18
Ethanol	35	25
HCl	0	0
H ₂ O ₂	5	5
NaCl	10	5
Benzene	5	0
Toluene	35	15

Diethyl ether	15	10
CCl ₄	0	0
CHCl ₃	0	0

Table .3 Chemical resistance of the biopolymers

All the polymeric samples prepared are highly stable but undergoes slight degradation in H₂O, ethanol NaCl and toluene. The dimension of the polymer samples immersed in HCl, H₂O and NaCl did not change after 4 weeks, but the dimension of the polymers immersed in organic solvents (CCl₄, diethyl ether and CHCl₃) changed after 1 week. The dimension could not be measured after 4 weeks due to their fragility.

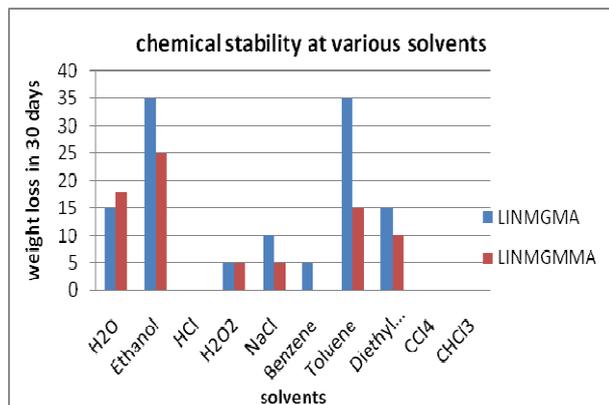


Fig 6. Chemical resistance of polymers in various chemicals

[V] CONCLUSION

1. A variety of novel bio degradable polymers have been synthesized by the free radical copolymerization of linseed oil monoglyceride cyclohexane dicarboxylate with MA and MMA, as comonomers.
2. The polymers are found to be typical thermosetting materials. They exhibited good tensile stress-strain behavior relatively to plastics.
3. Two distinct decomposition stages are found upon thermogravimetric analysis, which correspond to evaporation of the unreacted free oil present in the bulk polymer and carbonization of the crosslinked polymer. The thermal stability of the polymers is mainly

determined by the amount of the unreacted free oil present in the bulk polymer.

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

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