Studies on the development of oil based polymer from methyl-methacrylate and vinyl acetate co-monomer

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***Abstract:** The polyester elastomers are obtained from natural oils. These are generated from renewable natural sources. This study concerns with the preparation and properties of a biodegradable polymers from non-volatile oil like sunflower oil was carried out. In this work, polyesters were obtained by thermal poly condensation technique on the effect of sunflower oil based acrylated epoxidized resin with monomers such as methyl methacrylate, vinyl acetate with addition of catalyst .The prepared epoxy resin and acrylated epoxidized resin were characterized using FT-IR (Fourier-Transform Infrared Spectroscopy) and ^{1}HNMR spectroscopy. The new polymeric material exhibited tensile stress strain behavior ranging from soft rubbers relatively brittle plastics. Thermal characterization such as differential thermal analysis [DTA] and thermo Gravimetric Analysis [TGA] were carried out. Biodegradability test was carried out using hydrolytic test, chemical test. These polyester exhibited wide range of mechanical and degradation profile that can be tuned by the choice of monomers.*

***Index Terms** - Biodegradation, Epoxidation, Vinyl Acetate (VA), Methyl Methacrylate (MMA), Sun flower oil.*

Plant oils are triglycerides of fatty acid. Sunflower oil is non-volatile oil having number of excellent properties. So they could be utilized in producing valuable polymeric materials. In recent years biodegradable polyester elastomers have attached much intension as green engineering including tissue engineering and drug delivery where cell seeded constructs and designed to replace damaged or diseased tissues [1,2]. Plant oil are predominately made up of triglyceride molecules contains many actives sites such as double bond, the allylic carbons, the ester group and the carbon alpha to the ester group. These active sites can be used to introduce polymerizable groups on the triglyceride, similar to the synthesis of petroleum –based polymer. In this study the sunflower oil based polyesters having the advantage of mimicking many features of extra cellular matrix and have the potential of the cells during tissue scaffolds wound healing and stabilization of transported cells [3]. This work refers initially to the polymerization of biodegradable polymers prepared by the polymerization of acrylated epoxidized sunflower oil with co-monomer such as methyl methacrylate and vinyl acetate (VA).

2. Experimental:

2.1 Materials and methods

Sunflower oil was purchased from local market at Nagercoil. The chemicals like H_2O_2 100, glacial acetic acid (100%), triethylene glycol dimethyl acrylate (TEGMA), vinyl acetate, methyl methacrylate were supplied by Sigma – Aldrich Co and used as such.

2.2 Formation of Epoxidized Sunflower Oil

Sunflower 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°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 Sunflower Oil

The epoxidized sunflower 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°C-100°C under constant agitation in nitrogen atmosphere and collected in the beaker to produce acrylated epoxidized sunflower oil (AESO). The structure of sunflower oil, epoxidized sunflower oil and acrylated sunflower oil was given by the Fig.1, 2 and 3.

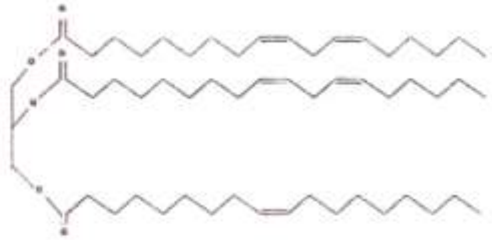

Fig.1 Structure of Sunflower oil

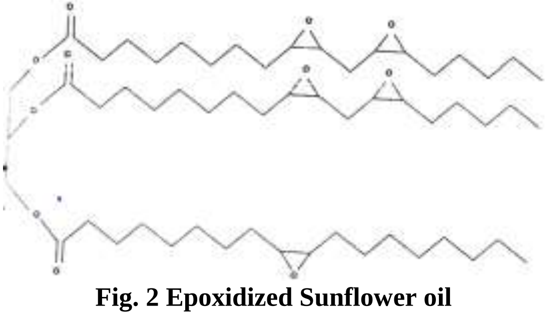

Fig. 2 Epoxidized Sunflower oil

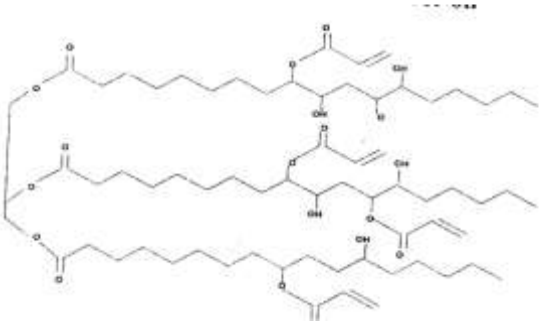

Fig. 3 Acrylated Sunflower oil

2.4 Synthesis of polyesters:

The acrylated epoxidized resin thus prepared was polymerized with different concentration of MMA, VA using benzoyl peroxide as initiator and N, N dimethyl aniline as accelerator. One ml of TEGMA was added as cross linking agent. The mixture was then casted on a clean silicon oil spreaded glass plate and dried in air to produce polyester. The procedure was followed for the preparation of various polymers by mixing the resin with different concentration of VA, MMA, as co-monomer. All the cured material showed high toughness, elastomeric and good transparency.

2.5 Characterization Techniques:

2.5.1 Spectral studies

FTIR spectra of the polymers were obtained using THERMO NICOLET, AVATAR 370 FTIR SPECRTOMETER with KBr crystal in the range of 4000-400cm^{-1} at 27°C. ^{1}H-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 ^{1}H-NMR Spectra were obtained relative to Tetra Methyl Silane (TMS) as internal reference. TG/DTA thermograms of the post polymers were obtained at a scanning speed of 10°C min^{-1} in the range of 30°C-700°C under the flow of nitrogen gas using PERKIN ELMER, DIAMOND TG/DTA.

2.5.2 Thermal Analysis

Thermal studies of the biopolymers was determined by TG-DTA analysis. Thermo Gravimetric Analysis (TGA) was performed by Perkin's Elimer thermo gravimetric analyzer over the temperature ranging from 30°C to 700°C at a heating rate of 10^{o}C /min under nitrogen gas atmosphere.

2.5.3 Mechanical studies

The tensile strength of the biopolymers prepared were determined using dumb-bell shaped cut from the specimen using Instron Universal Testing Machine (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 behavior relatively to plastics. The cross link densities ν_e were determined from the rubbery modulus plateau based on the theory of rubber elasticity $E^1=3\nu_e RT$ [4,5] where E^1 is the storage modulus (Young's) of cross linked co-polymer in the plateau region. R is the universal constant [8.314Jmol^{-1}K^{-1}] and T is the absolute temperature.

2.5.4 Biodegradation –Soil burial test

Biodegradation of polymers were studied by soil burial test. For the soil burial test the replicate pieces of the sample [5×3 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 [6]. 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 [7].

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

Where,

W_0- 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 CCl_4, $CHCl_3$, diethyl ether, Dimethyl Sulphoxide (DMSO), Toluene etc and 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

The chemical reaction was studied by analyzing FT-IR and ^{1}H-NMR spectra of sunflower oil, epoxy resin and acrylated epoxidized resin. Fig. 4,5 and 6 shows the FT-IR spectra of sunflower oil, epoxy resin and acrylated epoxidized resin.

3.1.1-IR spectral studies

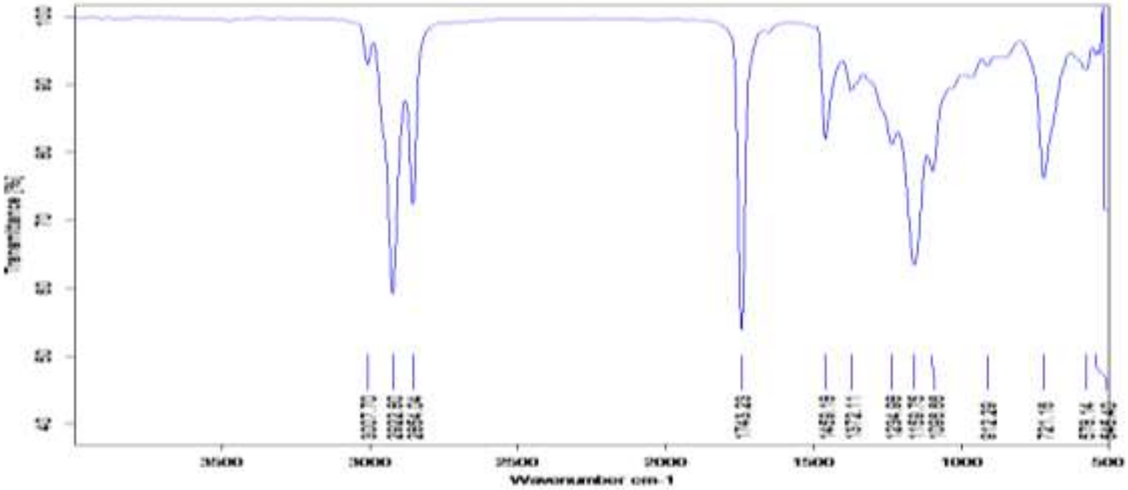

Fig. 4 FT-IR Spectra of Sunflower Oil

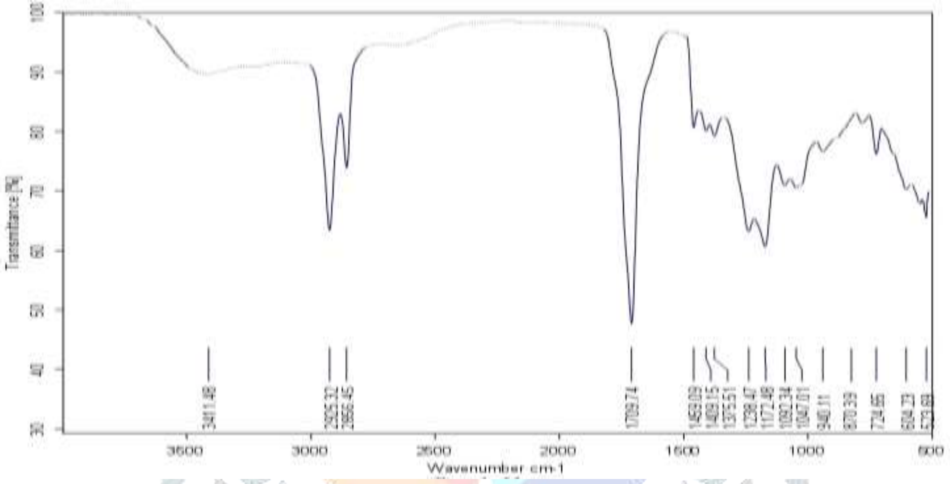

Fig. 5 FT-IR Spectra of Epoxy Resin

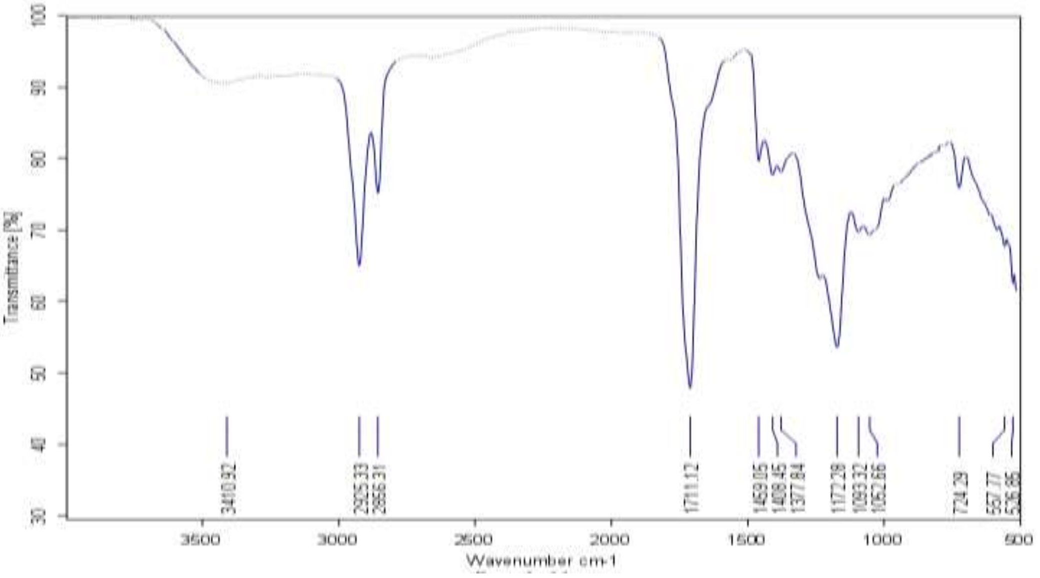

Fig. 6 FT-IR Spectra of Acrylated Epoxidized Resin

In FT-IR spectrum of sunflower oil the peak at 3007 cm^{-1}, 2922Cm^{-1} and 2854 cm^{-1} corresponds to C-H stretching frequencies of olefinic, methylene and methyl groups. The infra red data was determined at room temperature and reported previously by Obaleye and Orjiekwe [8,9]. The sunflower sample shows a very strong and sharp band at 1743.23cm^{-1} due to the ester group. The peak at 1459.18cm^{-1}, 1372.11cm^{-1} and 721.16cm^{-1} corresponds to the bending vibrations of –CH$_2$– and –CH$_3$ groups. The epoxy group showed three characteristic absorption bands (1240-1250cm^{-1}, 950-860cm^{-1}, 865-785cm^{-1}). The epoxy group gave the bands at 1250cm^{-1}, 950cm^{-1}, because of the symmetric and asymmetric ring stretching [10]. The IR spectrum of epoxy Resin (Fig.5) shows peak at 1238.47cm^{-1}, 940.11cm^{-1} and 870.39cm^{-1} which corresponds to the epoxy group formation.

These absorption bands appear between 950cm^{-1} and 860cm^{-1} and between 865cm^{-1} 785cm^{-1}. The band obtain at 870.39cm^{-1} and 724.65cm^{-1} in the epoxy resin corresponds to the stretching vibration of –CH= and –CH$_2$–groups. Bands in the far 1R region at 590cm^{-1} and 370cm^{-1} are also reported [11]. The band in the far 1R region observed at 604cm^{-1}in the epoxy resin is absents in oil and acrylated resin.

3.1.2 NMR spectral studies

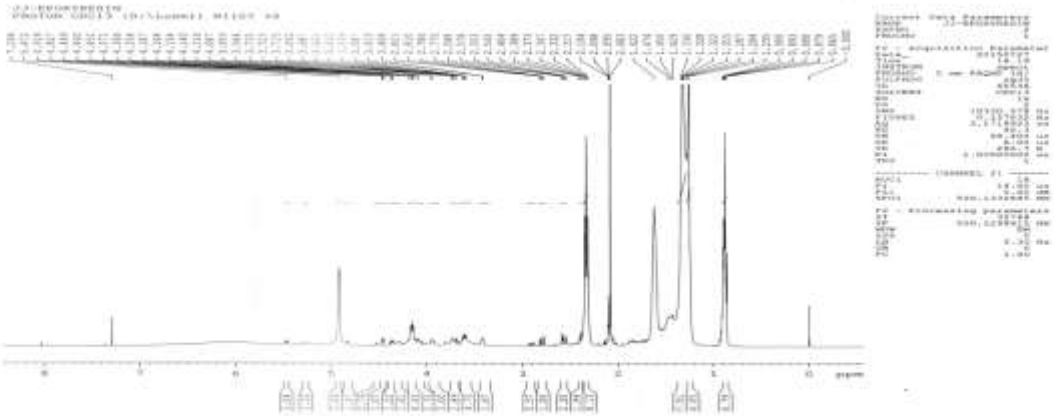

Fig. 7 ^{1}H NMR Spectrum of Sunflower Oil

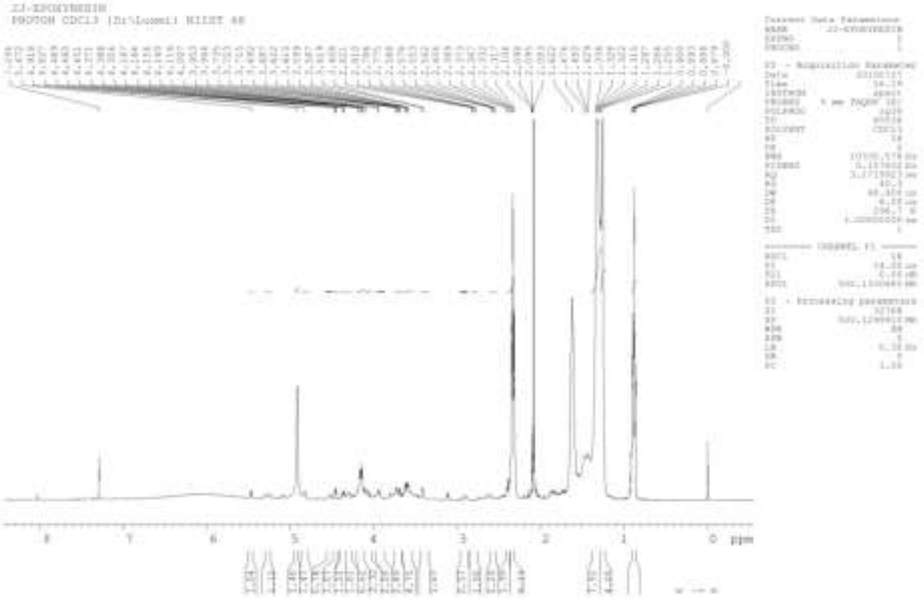

Fig. 8 ^{1}H NMR Spectrum of Epoxy Resin

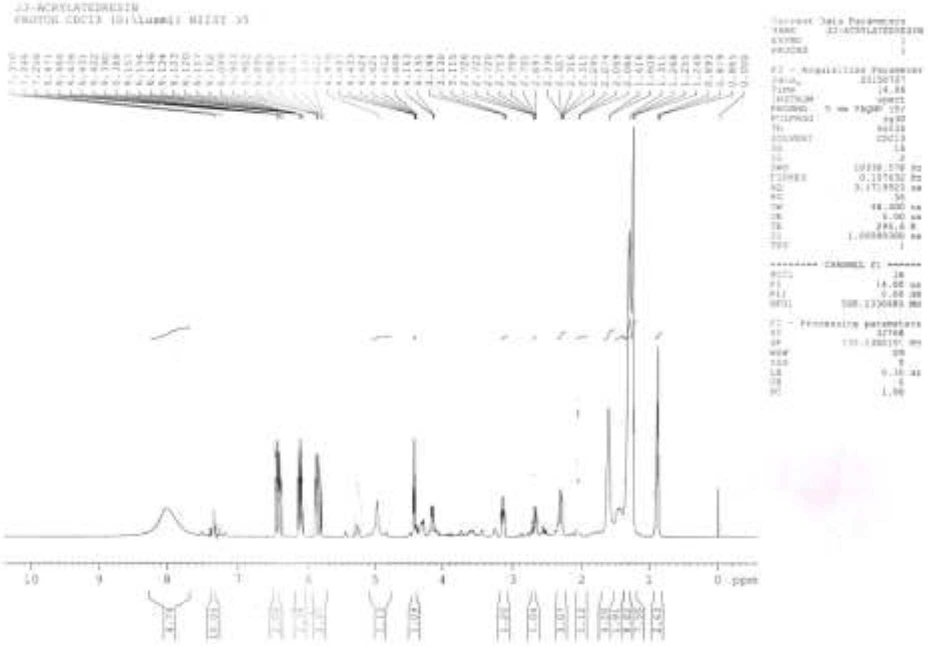

Fig. 9 ^{1}H NMR Spectrum of Acrylated Epoxidized Resin

The ^{1}H NMR spectrum of sunflower oil, epoxidized sunflower oil, and acrylated epoxidized sunflower oil are shown in Fig. 7, 8 and 9. In the ^{1}H NMR spectra of sunflower oil the peak at 5.2 to 5.3 ppm corresponds to the unsaturated vinylic hydrogen [12]. This peak disappeared in the epoxy product but shifted in the acrylated epoxy resin at 5.8 to 6.1 ppm upon conjugation [13]. In the sunflower oil peak at 4.1 to 4.3 ppm originates from the proton in the $–CH_2$ group of the triglyoxides. The peak at 2.75 ppm which corresponds to the proton in the $–CH_2$ group between two carbon–carbon double bonds completely disappears in the epoxy product. The strong peak at 1.3ppm in attributed to the long chain more than five methylene groups [14]. The peak at 0.86 to 2.3 ppm was due to the long aliphatic side chain.

3.2 Thermal analysis

TGA was used to investigate the thermal stability of the polymer Fig. 10 and Fig. 11 shows the decomposition behavior of the polymer samples of sunflower oil methyl methacrylate [SUNAEMMA] and sunflower oil vinyl acetate [SUNAE-VA] polymers under nitrogen atmosphere. Two distinct temperature regions are observed were the samples experienced significance weight loss 250°C – 350°C and 350°C – 450°C [15].

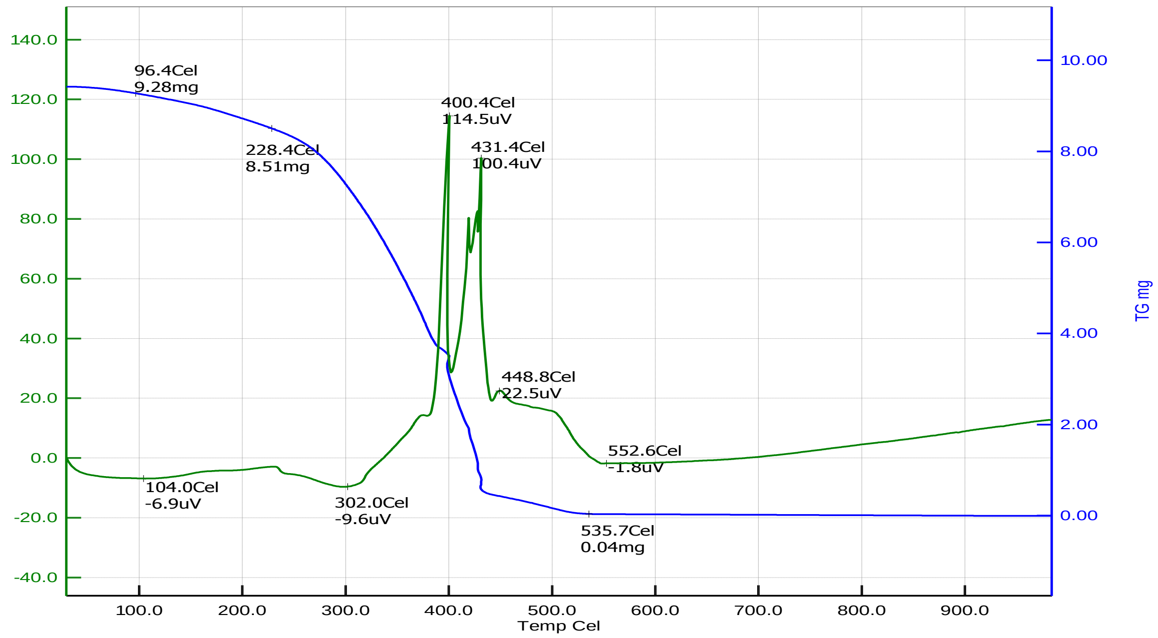

Fig. 10 TG-DTA curve of Sunflower Oil Methyl Methacrylate

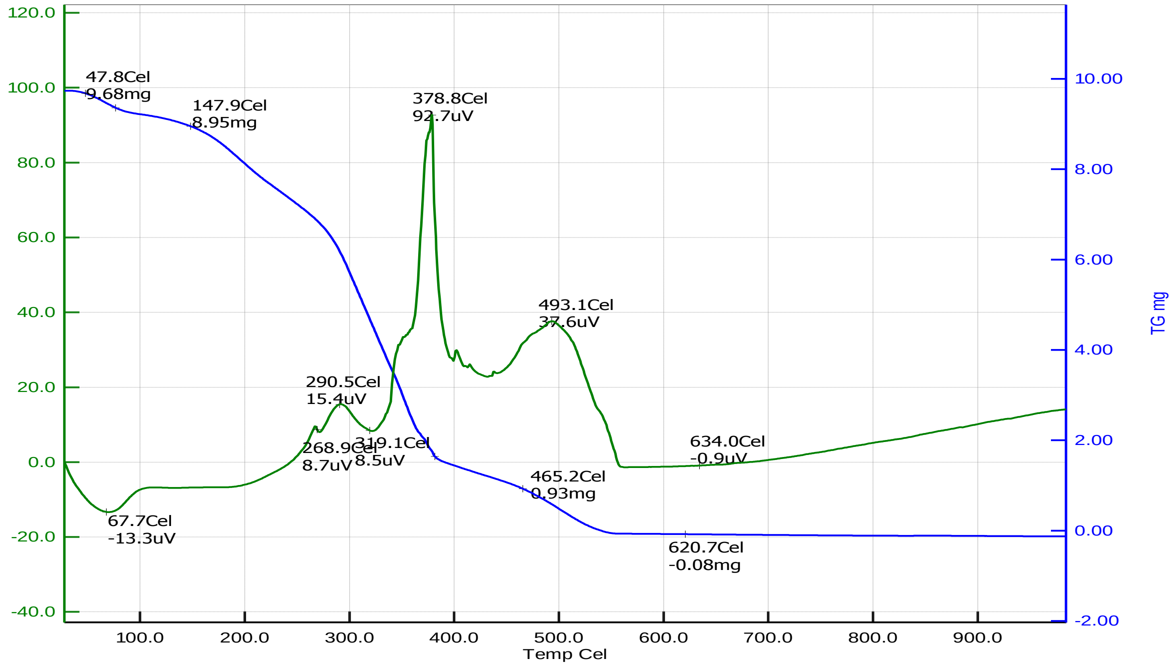

Fig. 11 TG-DTA curve of Sunflower Oil Vinyl acetate

It is clear from the figure that most of the unreacted free oil disappears at the temperature between 250°C – 350°C [Stage 1] i.e. the 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 temperature greater than 350°C [Stage 2]. This decomposition stage corresponds to the carbonization of the cross link polymer network. Stage 1 in the TGA curves involves two major steps i.e. diffusion of free oil to the surface of the bulk polymer and subsequent evaporation. This diffusion of the free oil is retarded by highly cross linked material, but the evaporation of the free oil from the polymer surface occurs rather rapidly at high temperature. From the proceeding results it is clear that the thermal stability of the polymer is limited by the first decomposition stage in the TGA thermogram, which is directly related to the amount of unreacted free oil in the bulk polymer.

In DTA curve of SUNAEMMA polymers, the peak at 302°C owing to the glass transition temperature and the endothermic peak at 400°C corresponds to the melting point of the polymer network. Two exotherms are seen in the samples the first exothermic varying from 420°C-380°C in sample is relatively weak and it corresponds to the cleavage of the long alkyl side chain. The second exotherm varying from 440°C – 420°C in sample is strong and it corresponds to the decomposition and char formation of cross linking polymer network.

Similarly DTA curve of SUNAE-VA polymer, the peak at 268.9°C owing to the glass transition temperature and the endothermic peak at 400°C corresponds to the melting point of the polymer network. Two exotherms are at 378.8°C and 493.1°C also seen in the sample. Comparing to the DTA curves the melting point of SUNAEMMA was slightly greater than SUNAE-VA polymer.

3.3 Mechanical properties

The mechanical properties of the polymer samples prepared are shown in the Table 1and 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 having high tensile strength and modulus.

Table 1 Mechanical properties of the biopolymers

Polymer sample	Cross link density ($\times10^{-3}$)	Tensile strength ($\times10^{5}$ Pa)	% of elongation	Young's Modulus ($\times10^{5}$Pa)
SUNAEMMA	0.7	18.571	10.99	454
SUNAE-VA	0.6	14.285	17.79	129

3.4 Biodegradation –soil burial test

Biodegradation of the polymer sample prepared by the free radical copolymerization of sunflower oil acrylated epoxidized resin with various concentration of monomers like MMA, VA are reported in Table 2.

Table 2 Percentage of biodegradation of polymer samples from sunflower oil

Polymer sample	Degree of Biodegradation (%)	
	30 Days	60 Days
SUNAEMMA	3.14	7.32
SUNAE-VA	17.39	33.69

From the data obtained by soil burial test, it is known that, the extent of biodegradation increases with decreases the concentration of monomer. From this data biodegradation is high in vinyl acetate polymer.

3.5 Chemical resistance

The chemical resistance of various polymer samples in different media is determined by measuring the dimensional changes after 1 week and 4 week. The weight loss also measured after 45 days. Table 3 shows the weight loss of polymer sample after 45 days. The comparison of the stability of polymers SUNAEMMA, SUNAE-VA towards various chemical was shown in the Table 3 and Table 4. The newly prepared polymer samples where studied by immersing the polymer samples in various solvents such as Toluene, $CHCI_3$, DMSO, Diethyl ether and CCl_4. All the polymeric samples prepared are highly stable, but undergoes slight degradation in Toluene, $CHCI_3$, DMSO, Diethyl ether and CCl_4 due to their fragility. The polymer samples are higher chemical resistance in non polar organic solvents such as $CCl_{4,}$ $CHCI_3$, etc.

Table 3 Weight loss of polymers in various solvents

Solvents	Weight loss % in 45 days	
	SUNAE-MMA	SUNAE-VA
Toluene	5.93	12.26
$CHCl_3$	3.62	14.67
DMSO	1.89	14.28
Diethyl ether	3.33	10.16
CCl_4	0.87	11.92

Table 4 Chemical resistance of SUNAE-MMA bio-polymers

SOLVENT	SUNAE-MMA (INITIAL)	SUNAE-MMA (45 days)	Weight Loss %
Toluene	1.18	1.11	5.93
$CHCl_3$	0.939	0.905	3.62
DMSO	1.111	1.09	1.89
Diethyl ether	1.2	1.16	3.33
CCl_4	1.034	1.025	0.87

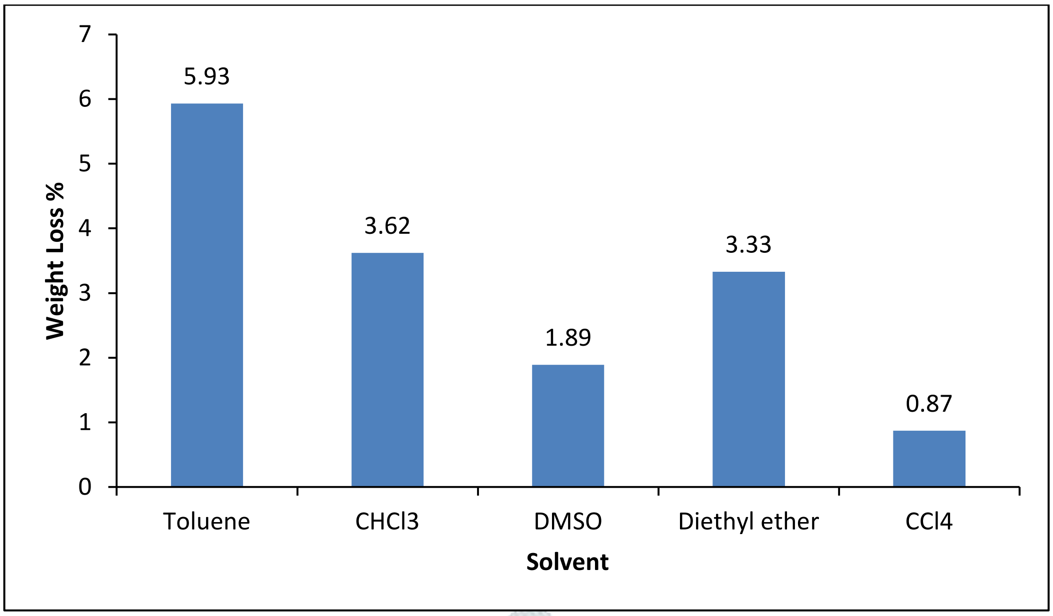

Fig. 12 Stability of SUNAE-MMA polymers in various solvents

Table 5 Chemical resistance of SUNAE-VA bio polymers

SOLVENT	SUNAE-VA (INITIAL)	SUNAE-VA (45 days)	Weight Loss %
Toluene	1.06	0.93	12.26
$CHCl_3$	1.09	0.93	14.67
DMSO	1.12	0.96	14.28
Diethyl ether	1.18	1.06	10.16
CCl_4	1.09	0.96	11.92

The comparison of the stability of the polymers SUNAEMMA, SUNAE-VA towards various chemical are shown in the Fig. 12 and Fig. 13.

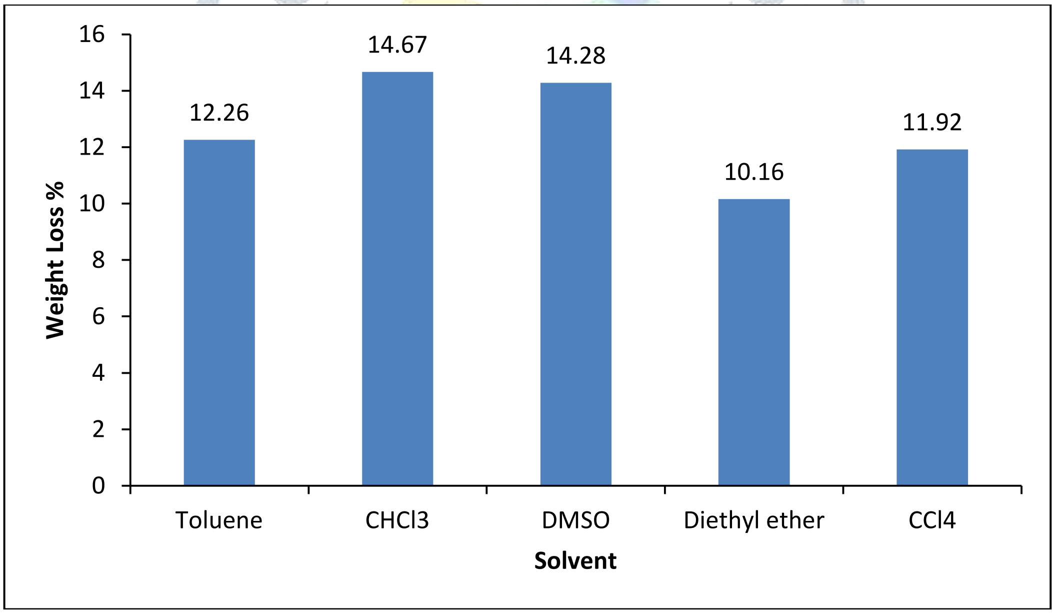

Fig. 13 Stability of SUNAE-VA polymers in various solvents

Conclusion

The plant oils are predominantly made up of triglyceride molecules. The sunflower oil derived from plant is a non volatile oil having number of excellent properties. The new polymeric samples prepared having high tensile strength and modulus relative to their thermosetting plastics. Thermo gravimetric analysis shows two distinct temperature regions corresponds to the evaporation and decomposition behavior of the polymer sample and it is used to investigate the thermal stability of the polymer. The soil burial shows that the newly prepared polymers are biodegradable and chemical resistance shows that the polymers sample are highly stable and less degradation.

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