Studies on the Development of Oil based Polymers from Triethyleneglycol Dimethacrylate and Vinyl Pyrrolidone

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ABSTRACT: This study concerns with the preparation and properties of a biodegradable polymers from non-petroleum oil specifically, linseed oil was carried out. Epoxidation of linseed oil was carried out by peracetic acid method. Further an Acrylated epoxidized resin was synthesized from the epoxidized linseed oil [ELO]. Two new polymeric materials were prepared by varying the concentration of comonomers triethylene glycol dimethacrylate [TEGMA] and vinyl Pyrrolidone [VP]. The new polymeric materials exhibited tensile stress strain behaviour ranging from soft rubbers to 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 polymeric materials display a wide range of thermophysical and mechanical properties and should find useful applications as alternatives to their petroleum-based counterparts.

Keywords: epoxidation, acrylation, comonomer, thermalanalysis.

INTRODUCTION

More attention is being paid to studying and developing environment biodegradable plastics in order to retard or eradicate plastic pollution [1,2]. One of the current priorities in polymer chemistry is to explore biobased polymers from renewable resources. Among those polymers, vegetable oils are expected to be an ideal alternative chemical feedstock, owing to their low cost and environmental friendliness. [3,4] Triglyceride oils are one of the most important sources for biopolymers. Triglycerides from plants, such as soy bean, palm, rapeseed or sun flower, can be utilized. The triglyceride compound must be isolated and purified, and also functionalized to obtain the requested reactivity. Various chemical modification reactions are possible; the most common ones proceed an epoxidation reaction. Therefore, the use of plant oil based resins in liquid molding resins not only reduce volatile organic compounds emissions, there by reducing health and environmental risks, but it also promote global sustainability[5]. Triglycerides are composed of three fatty acid chains joined by a glycerol center.

Oil-based biopolymers have many advantages compared with polymers prepared from petroleum-based monomers. They are biodegradable and in many cases, cheaper than petroleum polymers. Vegetable oil constituents are complex multicomponent mixtures of different triglycerols that are an ester of glycerol and fatty acids [6]. Recently biobased, thermosetting polymers from vegetable oils such as an epoxy soy beanoil, epoxy castor oil, epoxy palm oil, epoxy linseed oil and epoxy canola oil have been synthesized in several ways. Epoxidized vegetable oil possesses functional epoxide group which can react with suitable curing agents to form an elastomeric network [7]. One of the major efforts in this field has taken advantage of either the original carbon-carbon double bonds of the vegetable oils for cationic polymerization[8,9] or the carbon-carbon double bonds of vegetable oil derivatives for free radical polymerization[10]or olefin metathesis polymerisation. [11]. Other major processes have involved the conversion of vegetable oils or fats into epoxidized vegetable oils (EVOs) [12, 13]or polyols [14]. Epoxidized vegetable oils can be cationically polymerized by latent thermal catalysts or cured by amines [15] or anhydrides [16] to produce thermosetting

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resins, where as the polyols can react with diisocyanates to produce vegetable oil based polyurethane thermosets [17,18] or waterborne polyurethane dispersions [19]. Naturally occurring linseed oils are triglycerides consting of a mixture of saturated and unsaturated (oleic,linoleic and linolenic) fatty acids which can be modified via hydroperoxide, peroxide, epoxide and perepoxide formation. [20, 21]. Epoxidized linseed oil can be used as a reactive modifier epoxy resin systems. The epoxy groups are however available for further chemical modification reactions.

The introduction of acrylate or methacrylate function in a polymer or oligomer is generally made with the aim of polymerization or copolymerization of the double bonds leading to network or grafted copolymers. Radiation curable acrylates can be derived from epoxidized oils by their reacting with the acrylic acid [22].

This work describes acrylated epoxidized linseed oil[AELO] has been prepared using the epoxidized linseed oil. Linseed oil is the most widely used drying oil in paint formulation and for varnishes and raw materials for uralkyd and alkyd resin [23, 24]. Prepared AELO was incorporatd with comonomers polymeric materials are prepared. These materials possess viable mechanical properties and thus are suitable replacement for petroleum based polymeric materials in numerous application. The advantages of these polymeric materials are low cost, availability from a renewable natural resource and their possible biodegradability.

EXPERIMENTAL

Epoxidation of Linseed Oil

On industrial scale, the oil epoxidation is carried out by the prileshjew's reaction, where the oil double bonds react with organic peroxyacids. For safety reason peroxyacids are produced in situ in the reaction vessel by acid catalyzed oxidation of the corresponding organic acid with hydrogen peroxide. Epoxidation of oil using 30% hydrogen peroxide was carried out by per acetic acid method[25]. Refined linseed oil and acetic acid were charged in a three neck flask, equipped with the thermometer and Leibig's condenser. To start the epoxidation, 30% hydrogen peroxide solution was gradually charged into the mixture during first 2hrs of reaction (scheme1).

linseed oil

$80^{\circ}C$-$100^{\circ}C$ | H_2O_2/CH_3CooH

ELO

Scheme 1
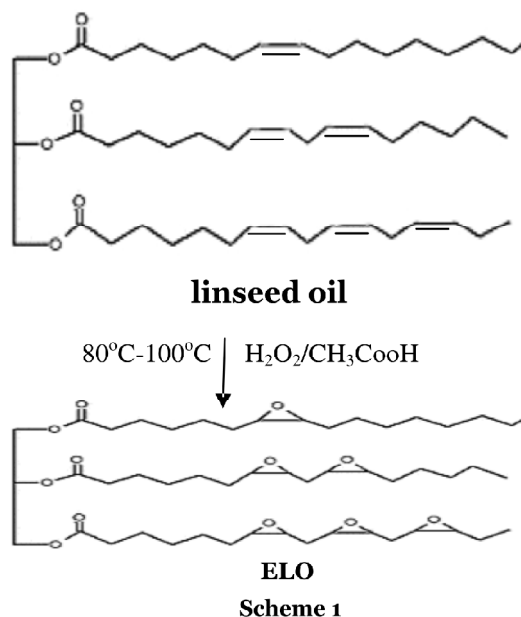
After the completion of charging H_2O_2. The reaction was further continued for 8hrs maintaining the temperature 80°-$100^{\circ}C$. The crude product was filtered and washed with warm water repeatedly until P^H is equal to 7.0.

Acrylation of Epoxidized linseed oil

A mixture containing 30 parts by weight of prepared epoxidized linseed oil, acrylic acid, catalyst triethylamine and inhibitor benzene were heated 70°-$80^{\circ}C$ at 1hr (scheme 2).

ELO

$(C_2H_5)_3N$ $H_2C=CH-\overset{O}{\underset{}{C}}-OH$

AELO

Scheme 2

Preparation of Polymer Materials

Acrylated epoxyresin [AELO] was then copolymerisd with comonomer triethylene glycol dimethacrylate [TEGMA] and vinyl pyrrolidone [VP],benzoyl peroxide is used as the initiator and dimethyl aniline as the accelerator. The mixture was casted on a glass plate and heated in the oven for 1hr at 100°C yield thermosetting polymers.

RESULTS AND DISCUSSION

Analysis of Synthesized ELO

Epoxidation of fatty acids is a reaction of a carbon-carbon double bond with an active oxygen, usually from a peroxide or a peracid, which results in the addition of an oxygen atom, converting the original-C=C-bond into a threemembered epoxide (oxirane) ring. Iodine value indicates the remaining unsaturation after the epoxidation reaction, the oxirane oxygen content indicates the epoxy groups present in the products. The reductions in iodine values indicated the consumption of unsaturation during epoxidation. The determined iodine value and Oxirane Oxygen % are shown in Table 1.

Table 1
Iodine Value and Oxirane Oxygen

Samples	Iodine value	Oxirane Oxygen %
Linseed oil	175.6	0
EpoxidizedLinseed oil	9.2	6.2

Fig. 1 Shows ¹H-NMR spectra of linseed oil. The peaks at 0.75 ppm corresponds to the hydrogens of the ending methyl groups (CH_3-$(CH_2)_n$-). Peak at 1.2-1.4 ppm originate from aliphatic methylene hydrogens (-CH_2-). The peak at 2.05 ppm corresponds to allyl hydrogens (-CH_2-CH=CH-). Peak at 2.7 ppm originates from hydrogen between two double bonds (-CH=CH-CH_2-CH=CH-). The peaks at 4.1-4.4ppm due to methylene hydrogens from the glyceride moiety (-CH-CH_2-O-). Finally vinyl hydrogens and methyne hydrogen from glyceride group (CH-O-C(O)-) was detected at 5.2-5.5 ppm.

This peaks disappeared in the epoxy resin showing that the double bond is replaced by the epoxy group but reappeared in the acrylated epoxy sample due to the presence of unsaturated group.

Figure 1:   ¹H - NMR of Linseed Oil

In Fig. 2. ELO. The peak corresponds to epoxy groups were appeared at 2.9 ppm. The peaks at 3.1 ppm shows -CH- hydrogens between two epoxy groups. The peaks at 1.45 ppm corresponds to -CH hydrogens adjacent to epoxy groups.

Figure 2:   ¹H -NMR of ELO

Analysis of Synthesized AELO

The esterification reaction takes place between the epoxidized linseedoil and acrylic acid in the presence of triethyl amine. Epoxide resins react with carboxylic acid to form esters. The reaction takes place between the carboxyl group of the acid

and both the epoxy and hydroxyl groups of the epoxides. This was confirmed by ^{1}H-NMR spectrum of the AELO. This peak is shifted to 3.1-3.2 ppm in the acrylated epoxy resin due to the deshielding effect of hydroxyl and carboxylate ester linkages. The strong peak at 1.3 ppm is attributed to the long chain (more then five methy lene groups).The peaks at 0.95 to 2.3 ppm is due to the long aliphatic side chain. Fig. 3.

Figure 3:   ^{1}H - NMR of AELO

Analysis of Polymer Sample

Two different polymeric materials were prepared by varying concentration of comonomers TEGMA and VP. The nomenclature adopted in this work for the samples are LTI and LT2. LTI series of samples corresponds to a polymer prepared from acrylated epoxy resin [AELO] and TEGMA at different concentrations. LT2 series of samples corresponds to the polymer prepared from AELO and VP at different concentrations. The samples prepared have been designated as follows. As an example LTIAELO50T50 means that the sample contains about 50% by weight of acrylated epoxidized resin of linseed oil [AELO] and 50% by weight of TEGMA.

Mechanical Properties

The two samples of varying composition obtained using different comonomers varies from rubber to hard plastics. They appear to be plastics with crosslink densities ranging from 7.23×10^3 to 4.49×10^3. The results indicate that the products are thermosetting polymers with density crsslinked structures. Crosslink densities differ significantly from one another. which is the direct result of the different degrees of unsaturation of different comonomers employed. LT1 samples of varying composition posses high crosslink density and LT2 sample have the lowest crosslink density. Crosslinking increases the tightness of the polymer network and reduces the molecular mobility of the chains between the junction.[26]. shown in Table 2.

Table 2
Mechanical Properties of Linseed Oil Polymers

Polymer	Tensile Strength MPa	Tear Strength KN / m	% Elongation at break	Hardness Shore (A)	Crosslink density Mol / m³
LT1 AELO50T50	Brittle	23.34	Brittle	65	7.23×10^3
LT1AELO75T25	Brittle	25.20	Brittle	67	7.20×10^3
LT2AELO25T75	Brittle	20.12	Brittle	64	7.22×10^3
LT2AELO50V50	3.1±0.3	12.76	8.9±2	43	4.46×10^3
LT2AELO75V25	3.0±0.2	12.74	8.7±2	44	4.47×10^3
LT2AELO25V75	2.9±0.2	12.79	8.4±1	42	4.49×10^3

Thermal Properties: Thermogravimetric analysis (TGA)

All the samples were subjected to thermogravi mertic analysis. The samples of the same series exhibited common thermal characteristics and hence the thermogram of samples from each series are presented here. TGA and DTA thermograms are given in fig. (4a) and (4b). The bulk polymer is thermally stable under 100°C followed by two decomposition temperature regions. The initial decomposition temperature of LTI, and LT2 are 238°C and 200°C respectively. In the first step of thermal degradation 200°C-460°C weight loss up to 27% is observed. This may be caused by thermal degradation of small fragments. The sample LTI and LT2 are thermally more stable up to 430°C.

The weight loss around 80% in the second stage of thermal degradation (470°C-600°C) may be due to the depolymerisation and cleavage of the compound in the oxydegradative manner.
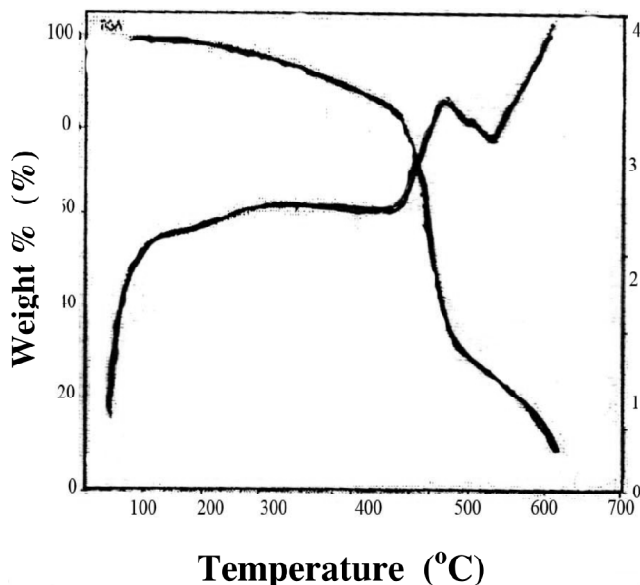

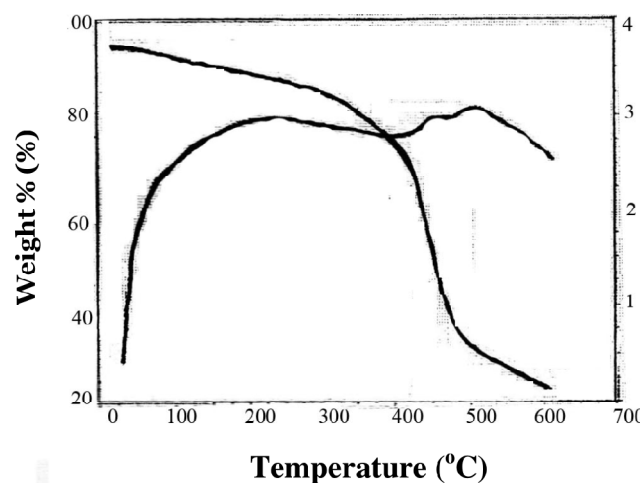**Figure 4(a):** TGA/DTA curve of LT1

Figure 4(b): TGA/DTA curve of LT2

Differential thermal Analysis (DTA)

DTA curves are recorded simultaneously with TGA curves (fig. 4a and 4b). DTA curves shows first order transistion namely crystallization and melting appears as peaks in the exothermic and endothermic directions respectively. After melting the material may undergo decomposition reactions at higher temperature which give broad peaks; these may be generally exothermic but are sometimes more complex in nature. DTA analysis (Table 3) shows two isotherms, a weak one around

452°C-455°C and a strong one above ranging from 472°C-511°C.The differential thermal analysis clearly indicates the thermal stability of the polymer sample at higher Temperature.

Table 3
Differential thermal Analysis of the Polymer Sample

Sample	1st exotherm	2nd exotherm
LTILT2	452455	472511

BIODEGRADATION STUDIES

Hydrolytic Studies

Hydrolytic stability test was carried out according to ASTMD 3137. Weight loss of polymer samples in media like water, ethanol and brine solution (IN Nacl) was estimated. The degree of biodegradation was estimated from the weight loss analysis of samples[27].

Weight loss $\% = \{(W_o - W_1)\} \times 100$

$W_o \rightarrow$ Weight of the original polymer.

$W_1 \rightarrow$ Weight of the residual film after degradation at each designated days.

Hydrolytic degradation was a slow process and negligible weight loss was observed from short interval. Degradation of polymer was studied and weight loss was estimated. Weight loss % are given in Table 4.

Table 4
Weight loss in Hydrolytic Stability Test

Sample	Weight loss%		
	Water	Ethanol	Salt Solution
LT1 AELO50T50	0.06	0	1.06
LT1AELO75T25	0.06	0	1.05
LT1AELO25T75	0.07	0	1.05
LT2AELO50V50	1.02	0	1.12
LT2AELO75V25	1.03	0	1.12
LT2AELO25V75	1.02	0	1.13

Chemical Resistance Test

Chemical resistance test was carried out according to ASTM D267. Degradation of polymer in dil.Hcl(IN) NaOH (IN) and 30%H_2O_2 was studied and weight loss was estimated. Weight loss % are given in Table 5. In chemical resistance test the weight loss of all samples was faster at high P^H greater than 10. It is because base promotes

hydrolysis by providing the strong nucleophilic reagent OH⁻.The degradation was faster with increase in P^H. [28]. After the chemical resistance test film surface becomes large number of pits, granular formation. cracks appeared. The cracks were more Pronounced and fragmentation of film occured. It indicaties the bio-degradability of polymer film.

Table 5
Weight loss in Chemical resistance test

Sample	Weight loss%		
	Acid (1N)HCl	Base (1N) NaOH	Oxidant 30%H_2O_2
LT1AELO50T50	0.99	42.61	3.42
LT1AELO75T25	1.13	43.21	3.61
LT1AELO25T75	2.72	78.02	5.23
LT2AELO50V50	2.96	79.04	5.81
LT2AELO75V25	1.82	82.46	5.51
LT2AELO25V75	1.18	54.32	4.23

CONCLUSION

Now biobased polymeric materials have been developed from plant oils as renewable resources. Waste plastic materials are the major concerns of environmentalists. Thus, renewable resources are now greatly favoured for the production of polymers. The wide range of mechanical properties like stress-strain behavior, tensile strength, tough ness they used as wide consumer applications. The vegetable oils provide a large variety of options for the preparation of polymers. Linseed oils are triglycerides of fattyacids and most contain unsaturated groups are also used in the preparation of epoxides and polymers. The incorporation of linseed oil in the preparation of polymers provides a great opportunity to the properties of commercial available rubbery materials and plastics.

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